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Investigations into the synthesis, characterisation and properties of some conjugated organic polymers

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Investigations into the Synthesis, Characterisation and Properties of Some Conjugated Organic Polymers

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Abstract

Investigations into the Synthesis, Characterisation and Properties of Some Conjugated Organic Polymers

This thesis describes some work directed to the synthesis and attempted synthesis of some conjugated organic polymers.

Chapter 1 provides a general review of the field of conjugated polymers, including their synthesis and interesting physical properties.

Chapter 2 gives an overview of the field of poly(arylene vinylene)s, including their physical properties, their electroluminescence and potential application in polymer light emitting devices and a review of the McMurry reaction. The synthesis of poly(4,4′-diphenylene diphenylvinylene) via the reductive coupling of 4,4′-dibenzoyldiphenyl is described along with work aimed at optimising this polymerisation. Characterisation details of poly(4,4′-diphenylene diphenylvinylene) are given and results from an investigation into the electroluminescence of the polymer are recorded. The extension of this type of polymerisation reaction to include other diketone monomers is described along with the characterisation of the materials produced.

Chapter 3 describes the proposed ring opening metathesis polymerisation of some quinone substituted norbornadiene monomers in an attempt to synthesise a conjugated redox polymer system. The attempted ROMP of the monomers using either $Mo(N-2,6-i-Pr_2-C_6H_3)(CHR)(OCMe_3)$ or $Ru((C_6H_{12})_3P)_2Cl_2(CH=CH=CPh_2)$ is reported.

Chapter 4 reports on the attempted development of a novel synthetic route to polyaniline via an triphenylarsine imine intermediate. Work concerning a model reaction and the spectral identification of the intermediate and results from the attempted synthesis of a polyaniline related polymer are reported.

Acknowledgments

The work outlined in this thesis would not have been completed without the help and encouragement of a great number of people. Thanks (in no particular order) are due to:

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Steve and Dan for domestic bliss (almost),

and finally to Susie for being there and believing,

Splendid.

Memorandum

The work reported in this thesis was carried out at the Interdisciplinary Research Centre in Polymer Science and Technology at the University of Durham between October 1992 and October 1995. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Statement of Copyright

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Chapter 4: An Investigation of a Potential Synthesis of Polyaniline and Polyaniline Related Polymers via a Novel Triphenylarsine Oxide Catalysed Process

Appendices

One morning after breakfast Tom was fooling around
with his chemistry set and he invented anti-sticky.

<u>If only it was that easy.....!</u>

R.Hoban and Q. Blake in 'A Near Thing For Captain Najork', Random House, 1973.

CHAPTER 1

Conjugated Polymers.

A General Introduction.

1.1 Introduction

Organic polymers are becoming more and more ubiquitous, both in technological and everyday applications, where their low cost, low weight and mechanical properties give them advantages over natural and inorganic materials. One area of polymer science where great scientific interest has been generated is the field of conjugated polymers, initial interest arising from their potential as electric conductors followed, more recently, by interest in their potential optoelectronic properties.

A vast array of literature concerning the subject of conjugated polymers is available and books and reviews are plentiful.[1-8] In many of the earlier papers the two expressions 'Conjugated Polymers' and 'Conducting Polymers' seem to have been used indiscriminately but more recently, with the discovery of applications other than as conductors, these two terms have been differentiated. For further information the reader is directed to the literature detailed at the end of this chapter and the references contained therein.

The feature common to conjugated polymers is that they posses a delocalised π-electron backbone. Take, for example, the simplest conjugated linear polyene, 1,3-butadiene. The carbon atoms are all sp^2 hybridised, with three electrons in σ-bonds (from the hybridisation of one 2s and two 2p orbitals) and one electron in a perpendicular 2p orbital. Electrons in adjacent p orbitals can interact to form a π-bond. For short

$$H_2C=CH\text{——}CH=CH_2$$

$a > b$
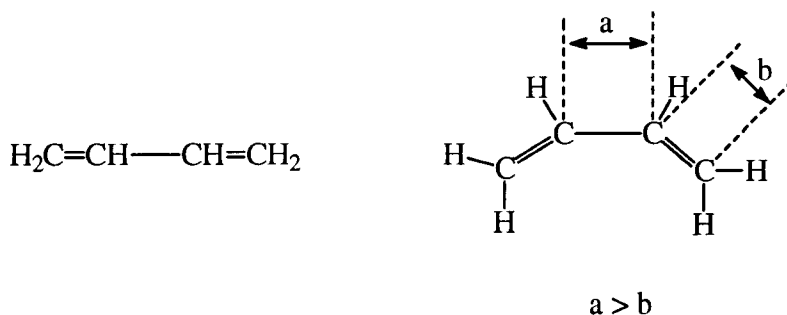
Figure 1.1 Structural representations of 1,3-butadiene

polyenes the π-bonds are more or less localised between alternate pairs of carbon atoms and bond alternation occurs, the carbon carbon double bond lengths are shorter than the

carbon carbon single bond lengths. For example, in 1,3-butadiene the carbon carbon double bonds are predominantly localised between carbons 1 and 2 and 3 and 4 (see Figure 1.1). This situation can be contrasted with the delocalised system of benzene where all the carbon carbon bonds are of the same length.

The energy of the π-electrons in polyenes is defined by a set of π-molecular orbitals and their associated antibonding orbitals.[7] Increasing the length of the linear polyene increases the number of both the bonding and antibonding energy levels found in the molecules and decreases the band gap between the highest occupied bonding orbital and the lowest antibonding orbital (see Figure 1.2). Additionally, as the π system increases in size the bonding orbitals become essentially degenerate and can be thought of as having a band structure rather than being a set of many discrete energy levels. An infinite polyene structure gives rise to two possibilities.[4,7] Do the valence and conduction bands meet
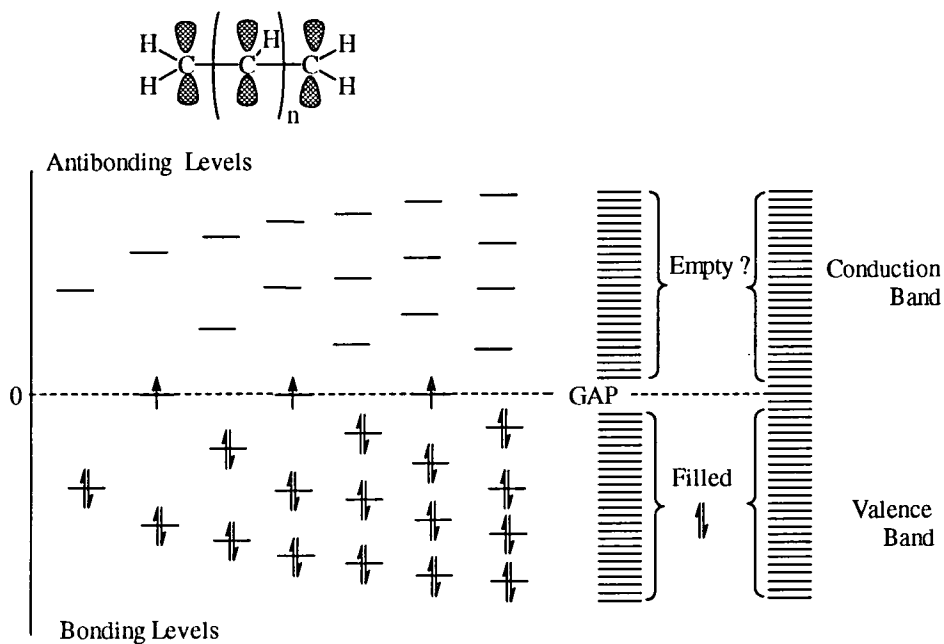
Figure 1.2 Energy diagram for the bonding and antibonding orbitals of polyenes

and result in the formation of a continuous half filled band, similar to that found in metals, or does a band gap still exist, the size of which would determine whether the material was a semiconductor or an insulator? The former situation would be characterised by all the bond lengths becoming equal, whilst in the latter the

carbon carbon bond lengths would alternate. Early theories predicted that the former situation would prevail and the π electron system could thus provide the basis for metallic behavior in organic polymers. In reality polyacetylene (an 'infinite' polyene) shows bond alternation and there is a 1.5 eV band gap associated with the material. The band gap (Eg in Figure 1.3) in conjugated polymers is found to be much smaller than the band gap of non conjugated polymers and as conjugation lengths increase the band gap narrows further. Smaller band gaps allow easier introduction of electrons into non bonding or antibonding orbitals via reductive doping or photoexcitation or the creation of mobile holes (radical cations) at the top of the valence band via oxidative doping. Once these mobile charge carrying species are created electrical conductivity becomes a possibility.
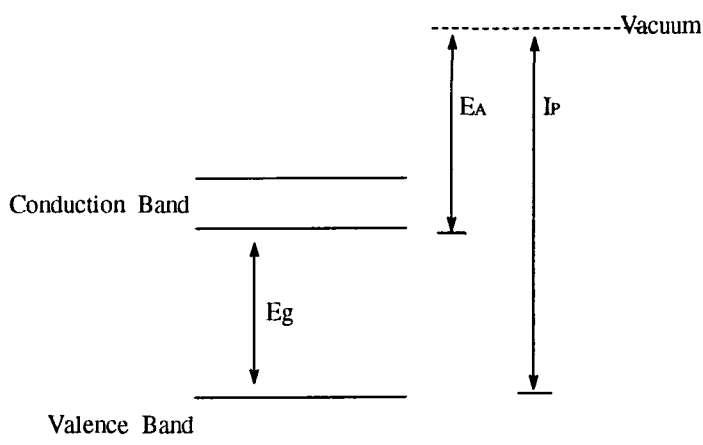
Figure 1.3 Schematic representation of the band model for conjugated polymers showing the band gap (Eg), electron affinity (E_A) and ionisation potential (I_P)

On a general note, polyenes have two drawbacks that have slowed the exploitation of their properties. Firstly is their inherent reactivity which leads to environmental instability and arises from the weakly bound π electron system, the feature that made them attractive for electronic applications in the first place and secondly many are insoluble and infusible, making processing difficult or impossible. Various methods have been developed to overcome these two problems and are outlined below.

1.2 Materials - Synthesis and Processing

Conjugated polymers are prepared either directly or via precursor routes. Precursor

polymers, once synthesised, under go one of two processes in order to form the required product polymer. These are elimination, for example of methanol in the synthesis of PPV and isomerisation, for example the cyclopropyl-allyl rearrangement. Generally precursor polymers are soluble and stable enough to allow processing and polymer characterisation. Several examples are included in the section below.

Polyacetylene

Polyacteylene (PA) is the simplest conjugated polymer and has been extensively studied.[4] It was first polymerised by bubbling acetylene gas through a solution of a Ziegler-Natta type catalyst resulting in a black powdery precipitate. Shirakawa used a modified process, where acetylene gas was passed over the surface of a solution of the catalyst, and was able to synthesise free standing films of PA. At low temperature all cis PA is formed which on heating is converted to the all trans form. This Shirakawa PA was shown to have high conductivities on oxidative doping. Precursor routes to PA have
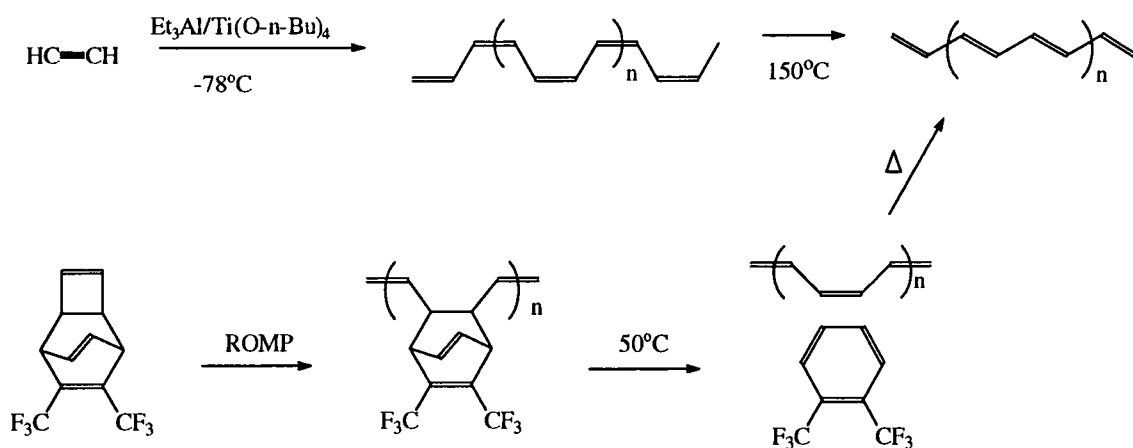
Figure 1.4 Synthesis and conversion of PA

been developed in which a soluble, processable precursor polymer, produced by ROMP, when heated undergoes a retro Diels Alder reaction, eliminating hexafluoroxylene, producing PA[5,8] (see Figure 1.4). PA synthesised by this route, Durham PA, has different properties to Shirakawa PA and allows more thorough removal of catalyst residues than PA synthesised by other routes. PA is stable to UV radiation and is (once converted to the trans form) thermally stable in an inert atmosphere. However the

polymer is very sensitive to oxygen, contact with which results in an overall decrease in the conductivity of the polymer.

Poly(p-phenylene)

Poly(p-phenylene) PPP and its related polymers are chains of phenylene rings, with or without hetroatoms incorporated between the rings, which show moderate conductivity when doped. Like PA they are insoluble and infusible and to obtain high molecular weight materials precursor routes are used. An advantage of PPP over polyacetylene is that it is stable to atmospheric oxygen and moisture. One way to overcome the insolubility of PPP is via the use of long alkyl chain substituents attached to the phenylene rings but these polymers still have low degrees of polymerisation (~30). Coupling reactions used include the Ni catalysed coupling of Grignard reagents and the reaction of an aryl boronic acid with an aryl bromide in the presence of palladium[1] (Figure 1.5).
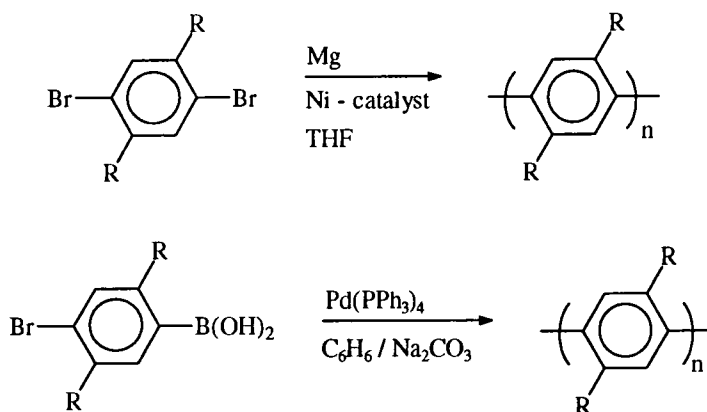
Figure 1.5 Synthesis of substituted PPPs

Precursor routes to PPP are more common. Early examples used dehydrogenation, which required high temperatures for conversion, and often did not go to completion. The use of different leaving groups (see Figure 1.6) gives precursor polymer that eliminates at lower temperature.[8] Whichever route is used the presence of 1,2 substituted rings cannot, so far, be prevented.
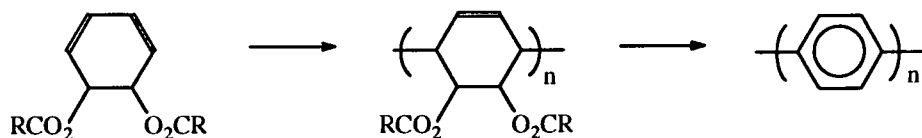
Figure 1.6 Precursor route to poly(p-phenylene)

Poly(phenylene sulphide) has a sulphur atom in the polymer chain between the phenylene rings. Although of low molecular weight the polymer has a doped conductivity of 80 Scm^{-1}, is soluble in high boiling solvents in its pristine form and is easily processed.[1] Figure 1.7 shows a commercially used synthetic route to poly(phenylene sulphide)
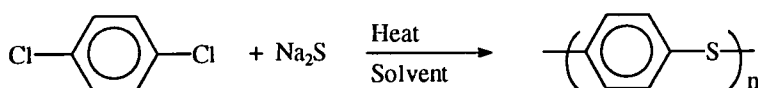
Figure 1.7 Synthesis of poly(phenylene sulphide) - trade name 'Ryton'

Polypyrrole, polythiophene and poly(isothionaphthalene)

Pyrrole and thiophene both can be synthesised electrochemically,[1,8] resulting in the formation of a film of polymer at the anode. Polymer is then removed and used. Synthesis via this method results in the oxidised form of the polymer which is the conducting form. Polypyrrole (Figure 1.8) can be reduced by reversing the potential and shows good stability for repeated doping and undoping, making it suitable for application as an electrode material. Another advantage of polypyrrole is that it has excellent stability under normal atmospheric conditions and at temperatures up to 600K. The linkages in polypyrrole are expected to be all 2,5 but in reality many conjugation lowering 2,3 links occur.
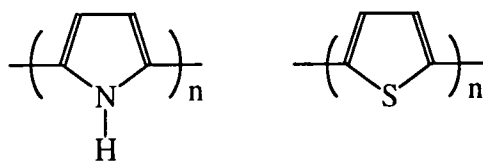
Figure 1.8 Polypyrrole (left) and polythiophene (right)

Polythiophene, and polypyrrole, can be synthesised chemically as well as electrochemically.[1,8] The synthesis of substituted polythiophenes via chemical routes allows more structural control over the polymer, including the nature of head tail type configuration and ensuring 2,5 linkages. Substitution allows the formation of soluble, processable materials but tends to limit conductivity.

Bond alternation in conjugated polymers can be drawn in two ways, for example the benzenoid and quinonoid forms of PPP. However, in polymers other than linear polyenes these two forms are non degenerate and one will be favoured over the other, an effect that increases the band gap of the material. A clever way to minimise this effect was proposed by Wudl who synthesised a polythiophene derivative where bond alternation was reduced by having aromatic stabilisation in both forms.[1] This polymer, poly(isothionaphthalene) (Figure 1.10) has a very small band gap, approximately 1eV.
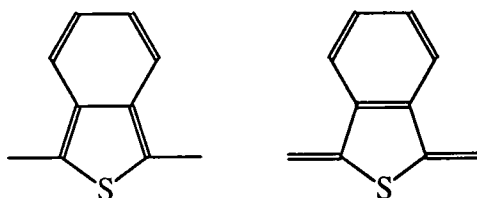
Figure 1.10 The bond alternate structures of poly(isothionaphthalene)

Polyaniline

The polyanilines are a series of polymers which are interconvertable via oxidation and reduction and can be represented by the form shown in Figure 1.11 where (1-y) varies from 1, fully oxidised polymer, to 0, fully reduced polymer.[1,2] All forms are stable and
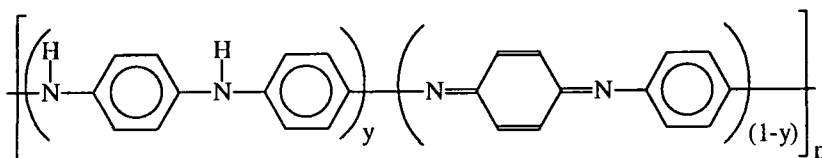
Figure 1.11 Generalised structure of polyaniline

conductivities, after doping, of up to 10^2 Scm^{-1} are possible. Protonic acid doping of the emeraldine form (y=0.5) results in conducting polymer without altering the number of

Chapter One

electrons on the polymer chains and is unique, within conjugated polymers, to polyaniline. Due to its stability and simple synthesis there has been great interest in polyaniline and its conducting forms. A more detailed review of polyaniline is given in Chapter 4.

Poly(p-phenylene vinylene)

Poly(p-phenylene vinylene) is an insoluble infusible material which when doped, even with strong oxidants such as AsF_5, has a low conductivity, ~10 Scm^{-1}. Principle interest in this polymer and its related structures arises from its electroluminescence and potential application as the emitting layer in polymer light emitting devices. Synthesis is generally via soluble, processable high molecular weight precursor polymers which then undergo thermal elimination to give PPV. Substituted PPVs can also be synthesised via similar precursor routes or via condensation polymerisations and allow variation of the electroluminescence colour. Poly(p-phenylene vinylene) and the related poly(arylene vinylene)s are discussed more thoroughly in Chapter 2.

Other polymers

Many other types of conjugated polymers are known. Of particular interest are the polydiacetylenes.[1,5] Single crystals of certain diacetylene monomers can be polymerised in the solid state, using light or gamma irradiation, to give polymer in which the order of the monomer crystal is not lost (see Figure 1.12). These materials do not have high conductivity but have been shown to be sensitive to environmental changes such as solvent, temperature and mechanical stress, leading to striking changes in colour.
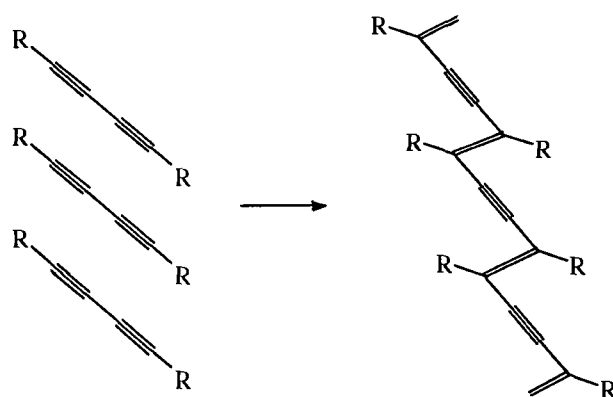
Figure 1.12 Generalised scheme for the polymerisation of diacetylenes

Ladder polymers have also been synthesised in an effort to generate an intrinsic conductor similar to graphite.[1] The simplest example, polyacene, would be expected to have a completely delocalised structure. However synthesis of this material results in the formation of a powder which becomes more insoluble and more air sensitive as the number of fused benzene rings increases. Ladder polymers can be synthesised with solublising substituents and with hetro atoms within the rings.

X = O, S, NH
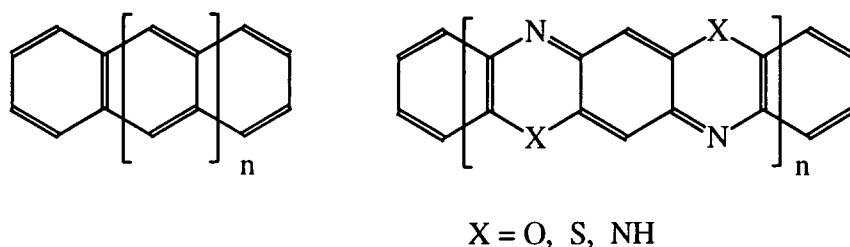
Figure 1.13 Polyacene and a generalised ladder polymer

1.3 Electronic properties

Since the report that oxidative doping of polyacetylene increases the conductivity of the polymer by six orders of magnitude from 10^{-5} Scm^{-1} to 38 Scm^{-1} much research effort has been directed towards the synthesis of and the optimisation the properties of conducting polymers.[1-3]

Most conjugated polymers are insulators in their 'pristine' form and need doping before they show conducting behaviour. The best conductivity results are remarkable and metallic conductivity close to the value for copper (10^{6} Scm^{-1}) has been claimed for oriented, iodine doped polyacetylene($>10^{5}$ Scm^{-1}). Doping can be either chemical or electrochemical and is oxidative (p-type) or reductive (n-type).[2] This is illustrated in Figure 1.14. It is worth pointing out that the term 'doping' has been borrowed from inorganic semiconductor technology and is not strictly correct. Instead of low level substitutive doping of inorganic semi-conductor technologies doping of conjugated polymers involves, comparatively, large scale redox modification of the polymer.

Chemical Doping

(a) p-type; for example
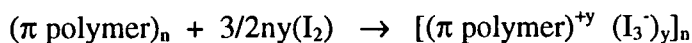
$$(\pi \text{ polymer})_n + 3/2ny(I_2) \rightarrow [(\pi \text{ polymer})^{+y} (I_3^-)_y]_n$$

(b) n-type; for example

$$(\pi \text{ polymer})_n + [Na^+(Naphthalide)^-] \rightarrow [(Na^+) (\pi \text{ polymer})^{-y}]_n + (Napth)^0$$

Electrochemical Doping

(a) p-type; for example

$$(\pi \text{ polymer})_n + [Li^+(BF_4^-)]_{soln} \rightarrow [(\pi \text{ polymer})^{+y} (BF_4^-)_y]_n + Li(electrode)$$

(b) n-type; for example

$$(\pi \text{ polymer})_n + Li(electrode) \rightarrow [(Li^+)_y (\pi \text{ polymer})^{-y}]_n + [Li^+(BF_4^-)]_{soln}$$
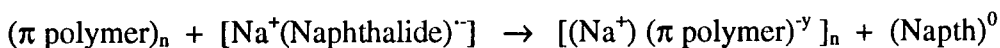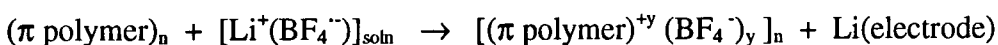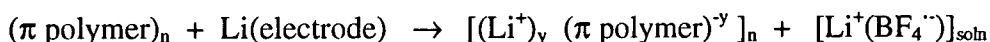
Figure 1.14 Doping of conjugated polymers

Stronger doping materials, for example AsF_5, may even result in bond formation and cleavage within the polymer structure, for example the formation of phenanthrene type units in the doping of poly(arylene vinylene)s (see Figure 1.15).
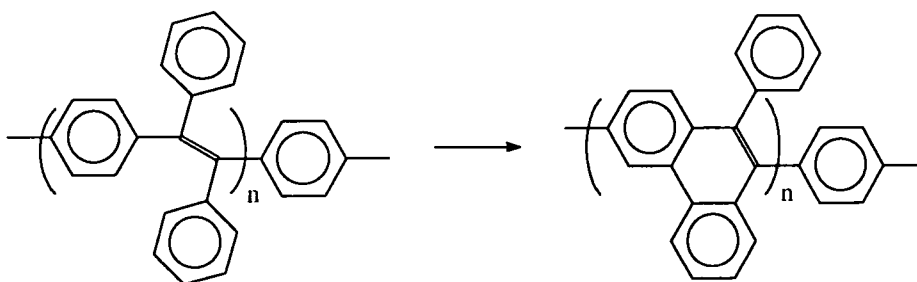
Figure 1.15 Possible formation of phenanthrene structures after doping of vinylene substituted poly(arylene vinylenes)

Other methods to obtain conductivity in conjugated polymers include photoexcitation where electrons are promoted from bonding orbitals (within the valence band) into antibonding orbitals (within the conduction band) and charge injection at a metal-insulator-semiconductor interface.

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Another physical property that is of interest is the electroluminescence of some conjugated polymers. The major advances in this field have been made using PPV and poly(arylene vinylene) polymers (see Chapter 2) but electroluminescence has been demonstrated for PPP, polythiophenes and polypyrroles. Charges injected from either side of a thin film of the polymer migrate through the polymer and if a positive hole and an electron combine they form an excited state species. This can decay radiatively emitting light, the colour of which depends on the band gap of the polymer. Different polymers and different substituents on a polymer allow the emission colour to be tuned. Optimised efficiencies for polymeric LEDs are the order of a few %, which is similar to existing inorganic technology, and the potential processing advantages associated with polymers makes their commercial application in display screens and devices a possibility.

Conjugated polymers also exhibit non-linear optical properties,[9] that is, when light is directed at a material the electric field of the electromagnetic radiation interacts with the charge distribution within the material. This induces a polarisation within the material which is related to the energy of the radiation. Most optical properties of materials can be explained using just the first order term of the relationship between energy and polarisation. The second and third order terms have only small effect at low electric field strengths. However, at high field strengths these effects can be detected experimentally. One commonly observed effect is that when monochromatic light, typically from a laser, is passed through or reflected from an active non linear material some of the light emerges as frequency doubled or frequency tripled radiation, a phenomenon which may eventually have applications in optical processing.

The brief summary above gives an insight into the range of known conjugated polymers and synthetic methods used in obtaining them. Additionally some potential applications of their physical properties are described by way of an explanation of the large amount of research interest in these materials. No doubt during the next few years commercial applications will become reality and the current limits of their physical properties will be greatly extended.

1.4 References

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CHAPTER 2

Poly(arylene vinylene)s via Reductive Coupling of Aromatic Diketones.
Synthesis and Characterisation.

2.1 Introduction

2.1.1 Poly(arylene vinylene)s

Poly(p-phenylene vinylene) (PPV) is simplest poly(arylene vinylene) (PAV) and is essentially an alternating co-polymer of acetylene and a p-phenylene unit. Modification of PPV to include different arylene units or substituents on the vinylene allows the

Ar = aromatic
R = R' = H, aryl, alkyl

PPV
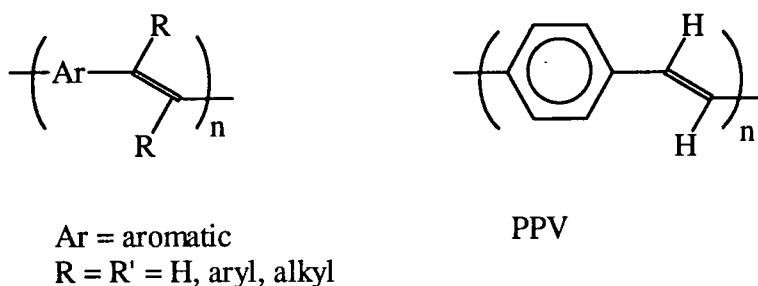
Figure 2.1 The general structure of poly(arylene vinylene)s and PPV

properties of these polymers, particularly the optoelectronic properties, to be varied and controlled. Attachment of side chains to the arylene part, usually to improve solubility, is also possible.

Synthesis

Most synthetic routes to PPV are via condensation polymerisations. Polymerisation of an α,α'-disubstituted xylene, where the substituents (X) are good leaving groups, results in the formation of PPV (Scheme 2.1).

R = H or aryl
X = halogen, -S$^+$R$_2$, etc.
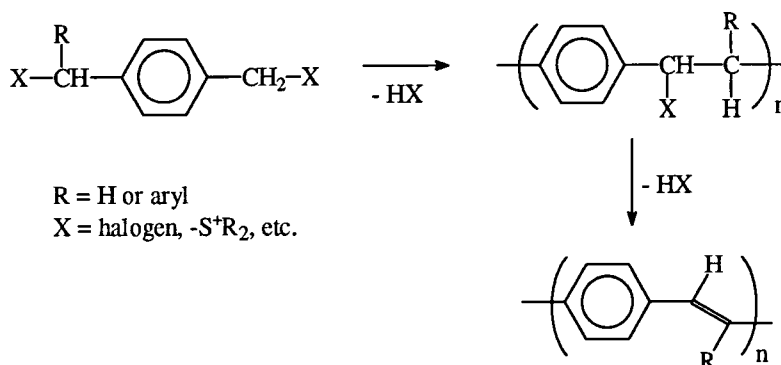
Scheme 2.1

Dehydrohalogenation of a α,α'-dichloro-p-xylene to give PPV was reported in 1965 by Hoeg.[1] Both dehydrohalogenation and dehalogenation have been used extensively by Horhold to synthesise a wide range of PAVs and substituted PPVs.[2,3-6] Many of the PAVs synthesised by Horhold have pendant phenyls attached to the vinylene part of the polymer and some examples are shown in Figure 2.2. Substitution generally makes the polymers more soluble and this allows the synthesis of higher molecular weight materials in contrast to the use of unsubstituted monomers which results in the formation of insoluble oligomers.
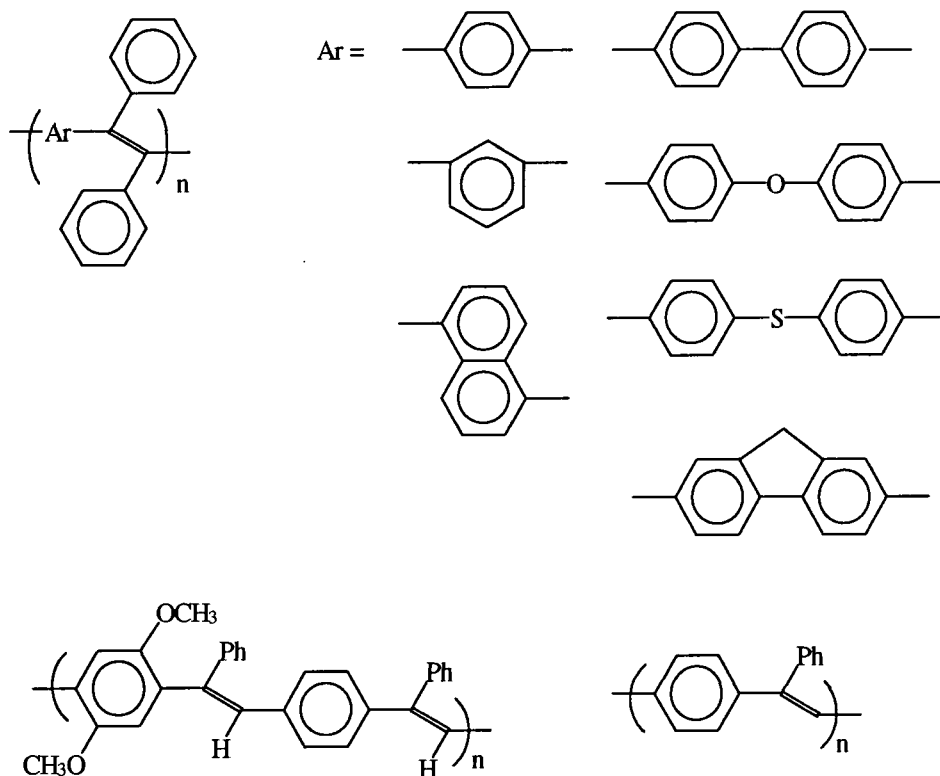
Figure 2.2 Examples of polymers synthesised via dehalogenation

Application of the Wittig reaction to the synthesis of PAVs has also been successful. In 1960 McDonald reported the synthesis of PPV from p-xylene-bis-(triphenylphosphonium chloride) and terephthaldehyde.[7] Similar work was reported by Kossmehl in 1970 who extended the reaction to include 1,2 and 1,3 substituted dialdehydes and thiophene rings[8] (see Scheme 2.3).

Ph₃P⁺CH₂—Ar—CH₂P⁺Ph₃ + OCH—Ar'—CHO ⟶

$$Ph_3\overset{+}{P}CH_2-Ar-CH_2\overset{+}{P}Ph_3 \quad + \quad OCH-Ar'-CHO \longrightarrow$$

Cl⁻   Cl⁻
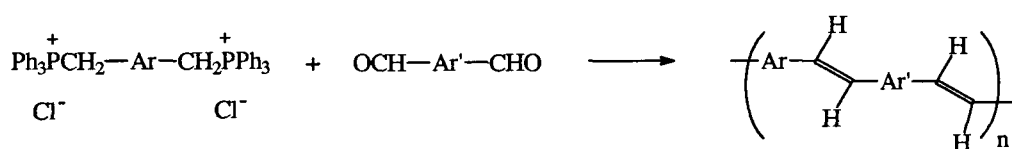
Figure 2.3 Formation of PAVs via the Wittig reaction

Although not now widely used to synthesise PPV or PAVs, the Wittig method is still used to synthesise PPV and PAV oligomers via controlled stepgrowth reactions.[9]

Another reaction that has found use in the synthesis of soluble PAVs is the Knoevenagel condensation of aldehydes with activated methylenes. Holmes and co-workers have used this reaction in the synthesis of a series of polymers with the electron withdrawing cyano group attached to the olefinic part of the molecule.[10,11]

R = CH₃, CH(CH₃)₂, C₆H₁₅

$R = CH_3, \ CH(CH_3)_2, \ C_6H_{15}$
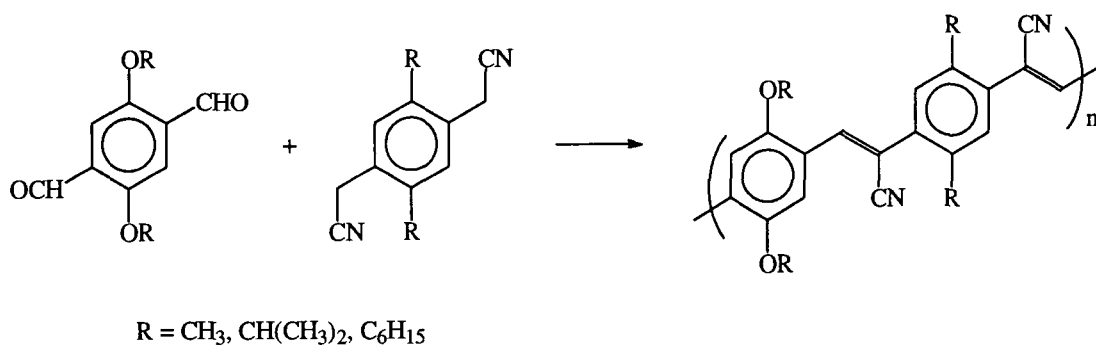
Scheme 2.2

One problem in the synthesis of PPV is that the polymer is insoluble. Many of the early attempts resulted in the formation of short oligomers rather than high polymer and the application of precursor routes to the synthesis of this polymer eventually gave satisfactory results. The most commonly used routes to PPV, and many PAVs, are based on the method of Westling and Zimmerman.[12,13] This synthesis involves the production of a water soluble, high molecular weight polyelectrolyte intermediate which when treated with excess base or exposed, as a solid, to elevated temperatures undergoes elimination to produce PPV as film, fibres or coatings (see Scheme 2.3).
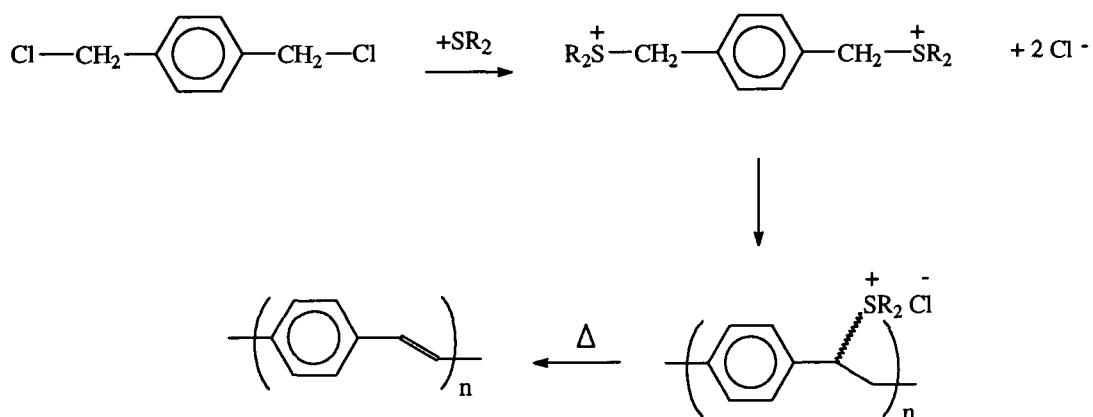
Scheme 2.3

More recently Gagnon,[14] Murase[15] and the Cambridge group[16-18], amongst others, have all successfully used this route to produce high molecular weight films of PPV. Once the intermediate polyelectrolyte has been synthesised it can be characterised and processed. To obtain high polymer molecular weights the precursor polymer is dialysed against water for extended periods of time to remove oligomers. Heating the sample under vacuum at temperatures in the region of 300°C for several hours produces the required PPV. The leaving group of the precursor polymer can be varied and widely used examples are shown in Figure 2.4.
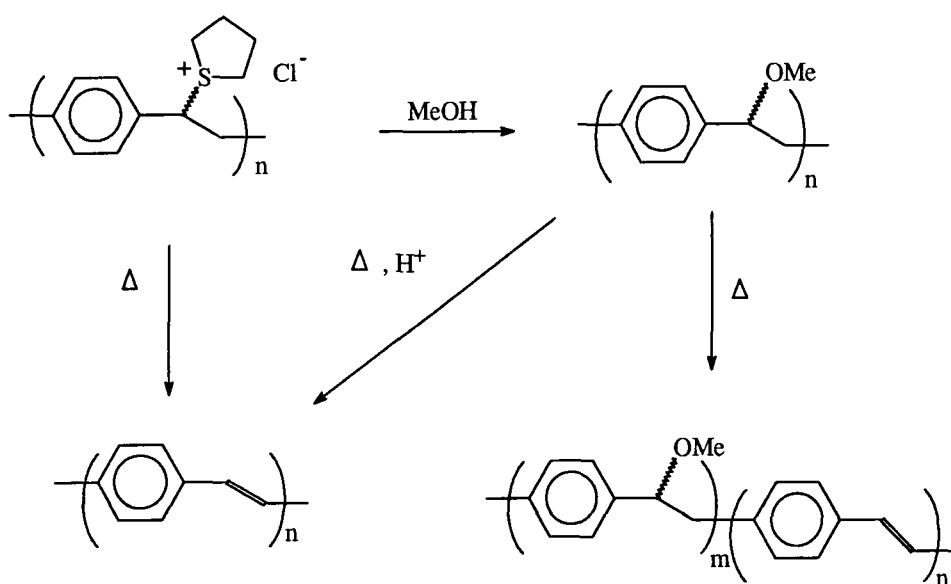
Figure 2.4 Modified Westling route to PAVs

Replacing the sulphonium ion with OMe gives methoxy leaving group precursor polymer which, unlike the sulphonium precursor polymer, is soluble in aprotic organic solvents, such as chloroform, dichloromethane and THF, which conveys some processing advantage. Although the sulphonium leaving group polymer requires a temperature of approximately 300°C to fully complete elimination the polymer is slightly unstable at room temperature and some spontaneous elimination may occur, giving segments of conjugated polymer which are insoluble and non processable. One advantage of the methoxy leaving group polymer is that it is much more stable and no elimination at room temperature occurs, however more severe elimination conditions, heat and treatment with acid, are required to fully remove the OMe group. These different properties of the precursor polymers allow selective elimination. If complete elimination is required fresh sulphonium precursor is used.[16] However if partial elimination is required, for example in the synthesis of a polymer with breaks in the conjugation,[17,19] methoxy polymer is synthesised and then partial elimination can be effected by heating without acid.

Both the sulphonium ion and methoxy leaving group precursor polymers can be used to synthesise substituted and soluble PAVs if suitably substituted monomers are used.[20] Some of the examples are shown in Figure 2.5.
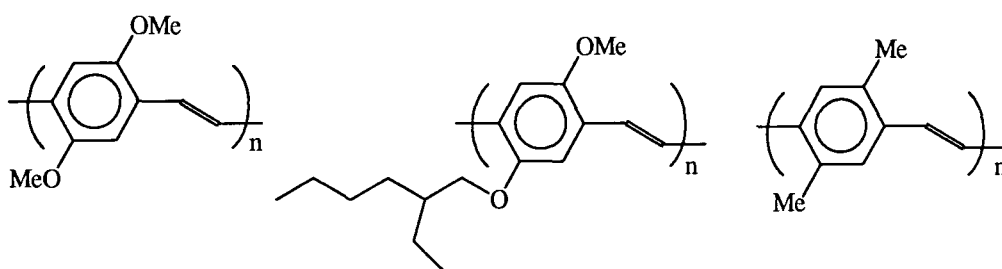
Figure 2.5 Substituted polymers synthesised via precursor routes

Reductive coupling has been shown to be suitable for the synthesis of soluble PAVs. An initial report in 1980 demonstrated that the reductive coupling of terephthaldehyde using a low valent titanium species generated by the reaction of titanium trichloride and lithium aluminium hydride produce an insoluble yellow solid identified as oligomeric PPV.[21]
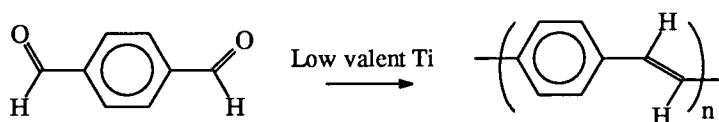
Scheme 2.4

Others repeated this experiment using low valent titanium generated from titanium trichloride and zinc and obtained results similar to those obtained 10 years previously.[22-24] However, soluble high molecular weight poly(4,4'-diphenylene diphenylvinylene) has been obtained via reductive coupling.[25] The application of reductive coupling in the synthesis of poly(arylene vinylene)s is the theme of this work and will be discussed in detail below.

Metathesis has also been shown to be suitable for the synthesis of PPV and PAVs. Thorn-Csanyi has synthesised PPV via ROMP of an olefinic p-cyclophane derivative[26] (Scheme 2.5) and has used ADMET to synthesise substituted PPV oligomers (Scheme 2.6).[27]
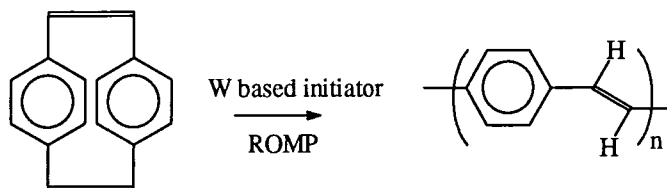
Scheme 2.5
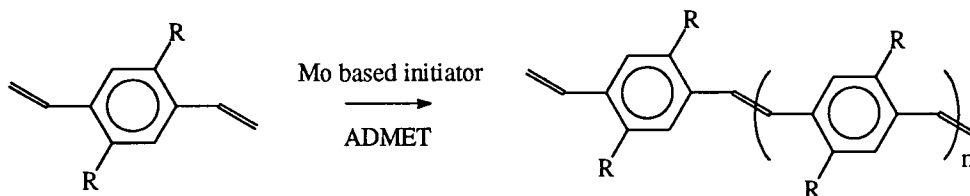
Scheme 2.6

Grubbs has devised a route using the ROMP of a substituted bicyclooctadiene (Scheme 2.7) to generate a precursor polymer which gives PPV on thermal elimination.[28] This synthesis allows good control of molecular weight and molecular weight distribution

(determined from the precursor) and has a lower elimination temperature than the Westling route.
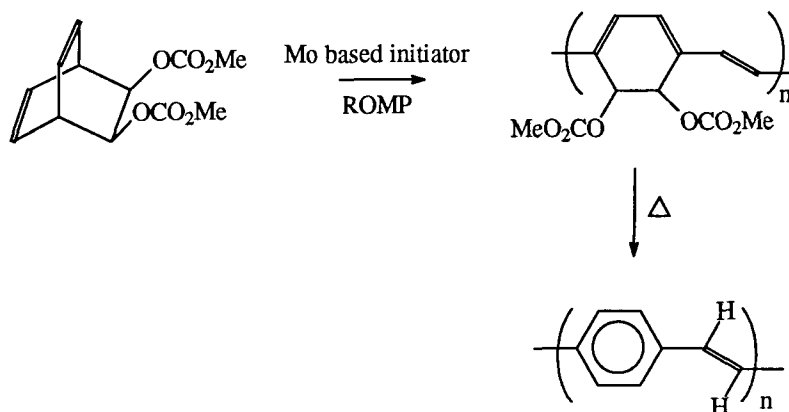
Scheme 2.7

Another application of ROMP is in the synthesis of side chain PPVs. Monodisperse PPV oligomers are synthesised and incorporated onto a norbornene monomer which can be ROM polymerised to generate polymer.[29] These polymers are soluble and all the conjugation lengths in the side chain oligomers are identical which allows more control of and reduces the emission peak width of the electroluminescence spectrum (see below).

Of the methods detailed above, most of the PPV and PAVs reported in the literature are currently synthesised via the Westling precursor route. A brief but informative review of some more unusual synthetic routes to PPV and PAVs is available.[30]

Physical and Chemical Properties

PPV itself is a bright yellow solid, insoluble, infusible and intractable.[21] Non-precursor routes to PPV, dechlorination, Wittig reaction and reductive coupling, result in the formation of PPV oligomers, with degrees of polymerisations of about 10. The development of the sulphonium ion and methoxy precursor polymers has allowed polymers with molecular weights of between 10,000 and 500,000(gpc, $CHCl_3$ on precursor) to be obtained.[19,20] Substituted PPVs and PAVs also show high molecular weights. The Knoevenagel type condensation gives PAVs with molecular weights of Mn 4,000-15,000 and Mw 11,000-17,000,[11] reductive coupling gives

poly(4,4'-diphenylene diphenylvinylene) with molecular weight values of Mn 36,000 and Mw 120,000[25] and dechlorination gives PAVs with Mn of 9,000-25,000.[5]

As made PPV is an insulator whose conductivity, in the region 10^{-8}-10^{-14} Scm^{-1}, depends on the synthetic route used. Doping of PPV with I_2, SO_3 or AsF_5 causes the conductivity of the material to increase dramatically. Oligomeric PPV, prepared via Wittig or dechlorination routes, shows a conductivity of 10^{-1}-10^{-3} Scm^{-1} after exposure to AsF_5,[9,31] whereas higher molecular weight material, produced by the sulphonium salt route, shows a conductivity of the order 10-10^2 Scm^{-1} after exposure to AsF_5 or SO_3.[14,15] Substituted PPVs also show conductivity in the semiconducting region when treated with I_2, SO_3 or AsF_5. These values are not exceptional , compared to the values obtainable with polyacetylene or polyaniline, and interest in the conductivity of PPV is not particularly marked.

One of the more interesting properties of PPV and PAVs is that they are photoluminescent (PL). When irradiated with long wavelength uv light the polymers show bright PL emission, PPV emits a yellow/green light and the colour of other PAVs varies from red,[11] cyano substituted PPV, to yellow-blue, partially converted methoxy precursor polymer.[19] Solid state PL efficiencies can be reasonably high, PPV has an efficiency of up to 25%,[32] cyano substituted PPV an efficiency of up to 45% and poly(4,4'-diphenylene diphenylvinylene) an efficiency of 50%. The solid state PL efficiency has been cited as currently being the only guide, however inaccurate, of potential electroluminescent efficiency.[33]

Currently the driving force behind the interest in PPV and PAVs is that they are electroluminescent (EL), that is, when a thin film of polymer is sandwiched between two electrodes and a voltage is applied across the film light, with a wavelength similar to that of the polymer's PL, is emitted. The discovery of this phenomenon in PPV was made by the Cambridge group in 1990 and has initiated a large amount of research into PPV and PAVs.[16] PPV emits a bright yellow/green light and for PAVs to be useful in commercial applications for full colour display screens red, green and blue emitters are required with device efficiency better than existing technology (see below).

The mechanism of EL can be described as follows. Applying a voltage across a sample of polymer results in the injection of electrons from the cathode and positive holes from the anode. These migrate through the material, under the influence of the applied electric field, and if they combine an excited state species is formed. This excited state can then relax back to the ground state radiatively, emitting light, or non radiatively. The excited state species that emits in EL is considered to be the same species that emits in PL. To obtain useful levels of emitted light emission must occur at a wavelength which the polymer does not absorb. Since in PL the emitted light is shifted to longer wavelength than the absorbed light, a Stokes shift, and the emitting species in PL and EL are similar this is negligible problem.

Colour of emission depends on the band gap of the molecule which is in turn affected by the nature of the repeat unit and the extent of conjugation of the polymer. Materials with short conjugation lengths have a larger band gap and show a blue shift in their EL with respect to materials with longer conjugation lengths.[17] Some examples of colours that can be obtained are shown in Figure 2.6.

Synthesis of polymers with blue EL emission is currently a major aim of this research community. So far no PPVs or PAV have been reported that have blue emission. The 'best' blue shift obtained for a PAV was for partially eliminated methoxy precursor which emitted at 508nm, green/yellow.[17] However combinations of PPV with other materials can result in blue emission, for example blends of PPV with poly(N-vinylcarbazole) emit at 495nm,[34] short PPV oligomer chains as a copolymer with a solublising flexible polyether emit at 465nm[35] and side chain PPV oligomers attached to poly(norbornene) emit at 450nm.[29] These materials have shown blue shifts in EL colour and improvements in device efficiency compared to the original blue emitter, poly(p-phenylene) which emits at 470nm.[36]

QR CN

OR

CN OR

OR

R = C₆H₁₃ → R = C6H13

red (710nm)

yellow (552nm)

OMe

blue shifted (c.f. PPV) (508nm)

OR CN

CN OR

R = C6H13

green (510nm)
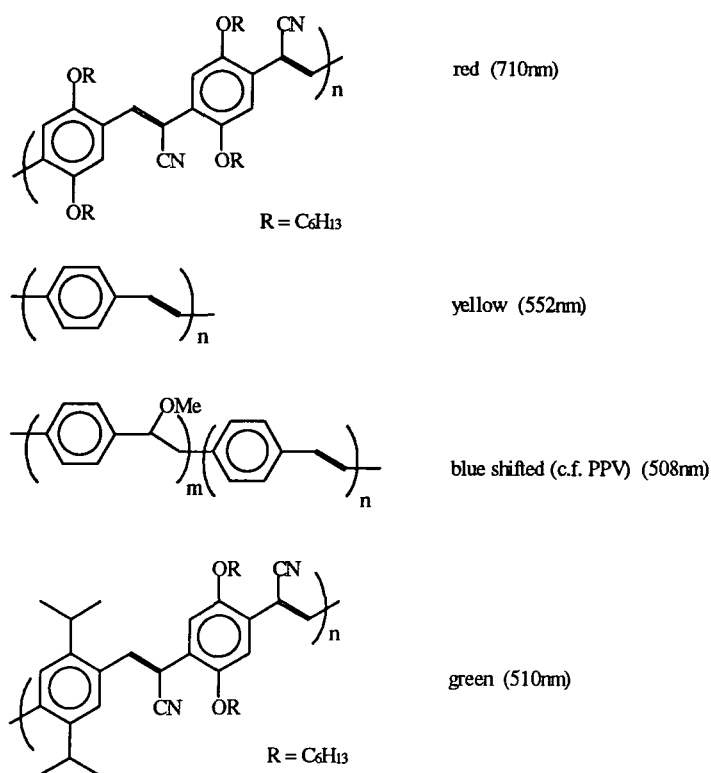
Figure 2.6 Electroluminescence emission colour (emission peak)

The EL quantum efficiencies (the ratio of emitted photons per electron injected) of devices based on PAVs have improved greatly from 0.05% in 1990[16] to 4% in 1993.[11] Control of the rates of charge injection, careful choice of electrode material and confinement of the excited state to a small part of the polymer molecule have been shown to affect the efficiency of EL devices.[11] Injection of electrons and positive holes into the emissive layer needs to be balanced to increase efficiency. Studies of devices based on PPV have shown that positive hole migration is relatively unrestricted and that the majority of the positive hole pass through the device to the cathode without becoming involved in the radiative decay process. To overcome this problem attempts to minimise the barriers to electron injection and transport and to confine the positive holes within the emissive layer have been made. The interfaces between the electrodes and polymer layers act as barriers to charge injection so if the polymer and electrode material can be matched these barriers can be reduced. For PPV, using Ca rather than Al as a cathode increased the device efficiency from 10^{-3} to 10^{-1}.[37] Additionally a hole blocking, electron transporting layer can be included in the device between the emissive layer and the cathode which causes the positive holes to accumulate within the emissive layer

rather than passing straight through and increases the electric field between the emissive layer and the cathode, stimulating increased electron flow. This increases the chances of a positive hole and an electron combining and therefore increases device efficiency. Electron transporting layers include polymer blends containing 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) which increase efficiency by up to eight times,[37]
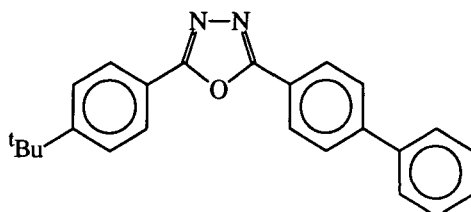
Figure 2.7 2-(4-Biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD)

while PPV is used as a hole transporting layer. It has also been determined that confining the excited state to a specific part of the polymer chain also increases device efficiency. This can be achieved by either introducing breaks in the conjugation, use of a multilayer device, the interfaces between layers preventing migration of the excited state,[38] or by the addition of an electron withdrawing group onto the polymer chain backbone.[11]

Applications

The use of PPV and PAVs as the emitting layer in organic LEDs shows great potential for commercial application. A schematic representation of a polymer LED is shown in Figure 2.8.

CATHODE - Al, Ca, Mg, etc

ANODE - ITO

GLASS

ELECTRON TRANSPORTING LAYER

POLYMER

HOLE TRANSPORTING LAYER
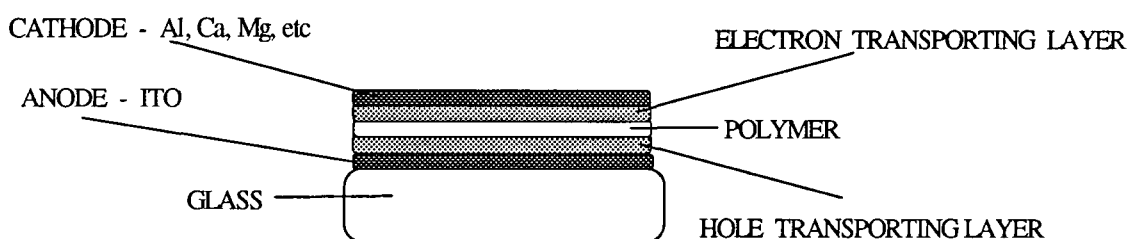
Figure 2.8 Schematic diagram of a polymer LED

Existing LED technology falls into four categories:[39] (i) inorganic semiconductor LEDs, (ii) fluorescent ion doped inorganic semiconductor devices, (iii) inorganic semiconductor powder devices and (iv) sublimed molecular dye devices. Categories (i) to (iii) are commercially available but have limitations when it comes to large area applications. Inorganic semiconductor LEDs are currently used in small display devices but fabrication of samples with sufficiently few non-radiative centres for large area devices is difficult and expensive. Commercially available devices with suitable efficiencies (above 1%) are limited to green and longer wavelength colours. Fluorescent ion doped inorganic semiconductor devices operate by accelerating electrons or holes to high enough energies to ionise or excite fluorescent ion centres, e.g. Mn or Eu. The high fields required for these devices requires high operating voltages which increases the cost of the technology and limits the stability of the emitting films. Inorganic semiconductor powder devices are most efficient (~3%) but suffer from the need for high operating voltages, poor stability and poor colour tunability. The sublimed molecular dye devices comprise an emissive electron transporting layer and a hole transporting layer sandwiched between two electrodes and show reasonable efficiencies (~1%) at low operating voltages. Additionally red, green and blue emission has been demonstrated.

Polymeric LEDs are similar to this final category of device but have been shown to be capable of operation without the electron or hole transporting layer and offer certain advantages.

LEDs based on PPV and PAVs have emission colours which cover the full spectrum from red to blue, the polymers are soluble or can be synthesised via soluble precursor polymers, the efficiencies of the devices can be improved by several orders of magnitude by careful choice of electrode material and through the use of positive hole and electron transporting layers, the materials are mechanically robust and relatively air stable. It is for these reasons that PPV and PAVs have been investigated so thoroughly during the past five years.

Two recent literature reports that illustrate the potential of these polymer based EL devices includes the fabrication of a flexible LED based on a polyethylene terephthalate

substrate using a substituted PPV as the emissive layer[40] and the fabrication of a device in which the emission colour varies as a function of the applied voltage. This system uses submicometer-sized domains of phase separated substituted polythiophenes as the emissive components.[41]

2.1.2 Reductive Coupling

During the early 1970's, three research groups independently and more or less simultaneously discovered that carbonyl compounds could be reductively dimerised to produce olefins in the presence of a low valent titanium species.[42-44]

R = R' = H, aryl and alkyl
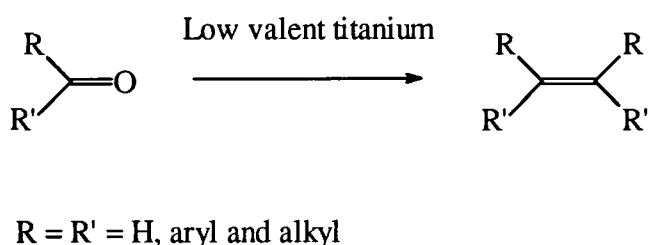
Figure 2.9 Reductive dimerisation of a carbonyl compound

Mukaiyama reported a titanium tetrachloride/zinc system[43] and Tyrlik reported a titanium trichloride/magnesium system[44] both of which reduced aromatic aldehydes and ketones to pinacols (1,2-diols) and olefins in high yields. Shortly afterwards McMurry reported a titanium trichloride/lithium aluminium hydride system[42] that reduced both aromatic and aliphatic aldehydes and ketones to olefins in high yields. Early work showed that the yield of olefin was dependent upon which reducing agent was used. This reductive coupling of carbonyl compounds to olefins has become known as the McMurry Reaction.

Reagents and conditions used for reductive coupling

Shortly before the publications reporting the titanium systems a similar reaction was reported that used a low valent tungsten species.[45] The yields of olefins using these tungsten systems were much lower than the yields obtained for the titanium systems. McMurry reports in a later review that only low valent titanium and low valent tungsten are capable of deoxygenating the intermediate diol to give olefin. Some systems based

on other transition metals have been shown to be capable of reducing carbonyls to the intermediate pinacol[46] and many others, for example Co, Ni, Fe, Sn and Cr[47] or Al, Fe, V, Cr and Zn[48] have been shown to be ineffective altogether.

The original reducing system reported by McMurry was generated from the reaction of titanium trichloride and lithium aluminium hydride in the ratio 2:1. This ratio of reagents would be expected to generate Ti(I) species as the reducing agent. Further investigation showed that the reaction mixture contained a number of titanium species including Ti(0) and Ti(II) and concluded that the active species was probably Ti(0).[47] One drawback of the $TiCl_3$/LiAlH$_4$ system was that it was said to give 'capricious results' depending on the quality of the reagents used.[48] Although individual experiments were occasionally unproductive the $TiCl_3$/LiAlH$_4$ system was found on the whole to give reproducible reductions. To overcome these minor vagaries other reducing systems were developed. Examples include titanium trichloride/potassium, titanium trichloride/lithium and titanium trichloride/copper-zinc systems. In each case the active species was shown to be Ti(0). Whichever system is used care in the preparation of the reducing species is required to give reproducible results. McMurry has reported that a $TiCl_3$/Zn-Cu system in which the $TiCl_3$ is refluxed for 3 days in dimethoxyethane before addition of the Zn-Cu couple seems to be much less affected by variation in the quality of the $TiCl_3$ than other reagents.[46]

Solvent also has an effect on the yield of olefin. For systems using sodium or magnesium to reduce $TiCl_3$, THF was found to be the only solvent in which coupling took place, while systems using lithium, potassium and lithium aluminium hydride produced olefin when glyme, diglyme, diethyl ether, dimethoxyethane or THF were used. However the best results were recorded for THF and this is the solvent of choice.[47,48]

Temperature effects have also been shown to affect the products of the coupling reaction. Lower temperatures result in the formation of pinacol only, whilst elevated temperatures, usually the reflux temperature of the solvent, are used in the synthesis of olefins.[45]

Reaction mechanism

The reaction mechanism proposed by Dams[47] for the reductive coupling of two carbonyl compounds to an olefin is shown in Figure 2.10. Using different reducing agents does not affect the reaction mechanism other than the oxidation state of the bulk titanium particles. When Mg or K are used the bulk oxidation state is close to zero but if $LiAlH_4$ is used the bulk oxidation state is approximately +1.

Various studies have shown that the reaction does not involve a five membered ring intermediate consisting of two carbon, two oxygen and a titanium atom, the cleavage of the carbon oxygen bonds is not concerted and that the reaction occurs at the surface of a titanium particle and not between two separate particles.[47,48] All these observations are in agreement with the mechanism shown below.
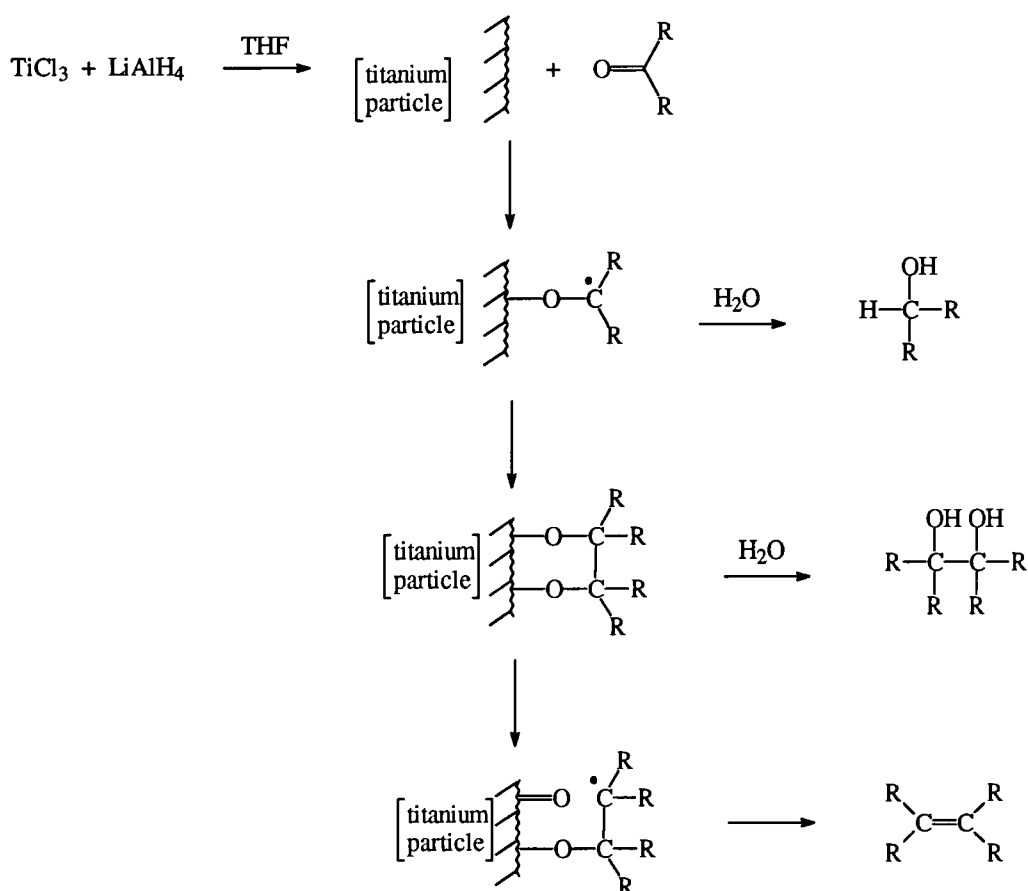
Figure 2.10 Schematic reaction mechanism for the McMurry reaction

The initial step of the reaction is the transfer of an electron from titanium to the carbonyl generating a radical anion. A pair of these radicals, on the same particle of titanium but probably bonded to different Ti atoms, combine to produce a pinacolate. Stepwise cleavage of the carbon oxygen bonds results in the formation of an olefin and an oxide coated titanium particle.

Two potential side reactions that are of relevance are also shown in Figure 2.10. Both involve the reaction of a hydrogen, often from water, with the species bonded to the titanium particle. Reaction with the radical anion results in the formation of an alcohol, which if the carbonyl is a ketone generates a secondary alcohol, and reaction of the pinacolate results in the formation of the pinacol dimer of the carbonyl compound.

Applications

Due to its simplicity and the fact that it involves the formation of a new carbon carbon bond, the McMurry reaction has been used extensively in organic synthesis. Several types of reaction are listed below. The synthesis of strained olefins is possible because the thermodynamic driving force provided by the formation of the titanium oxygen bonds allows the generation of olefins containing a large amount of steric hindrance. For example the dimerisation of a diisopropyl ketone is possible[46] (see Scheme 2.8).
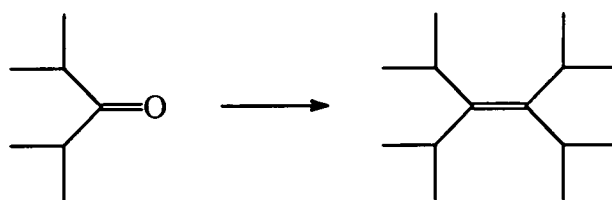
Scheme 2.8 Formation of strained olefins

Another application of the McMurry reaction is in the intramolecular cyclisation of diketones. Rings of three to twenty carbon atoms have been synthesised in yields that in many cases are greater than those for ring closure via other methods[46] (see Scheme 2.9).
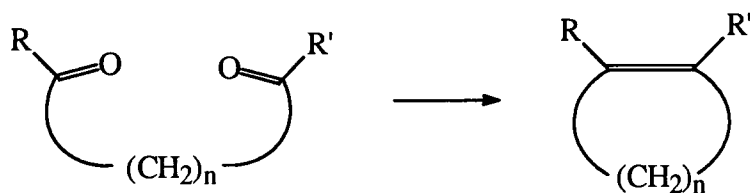
Scheme 2.9

Usually McMurry reactions are the reductive dimerisation of a symmetrical carbonyl compound and consequently will result in only one product. Reaction using asymmetrical carbonyls gives a mix of cis and trans products, literature reports indicate that the trans products tend to be predominant. Mixed couplings are also possible when two different carbonyls are used and the mixture of products usually contains all of the possible olefins.[46,49]

As would be expected given the strong reducing conditions of the reaction certain functional groups are reduced. Some functionalities are partly tolerated, usually for limited reaction time, and some are tolerated whatever reducing system is used. Examples given by McMurry[46] are shown in Table 2.1.

Compatible	Semicompatible	Incompatible
acetal	alkyne	allylic alcohol
alcohol	amide	1,2-diol
alkene	ester	epoxide
amine	ketone	quinone
ether	toluenesulphonate	α-halo ketone
halide		nitro
sulphide		sulphoxide

Table 2.1 Tolerance of functionality to McMurry reaction

Given the high yields of olefin, the McMurry reaction has potential as the coupling reaction in step growth polymerisations to give high molecular weight polymer. In 1979 Rajaraman reported the synthesis of PPV from terephthaldehyde using $TiCl_3/LiAlH_4$ to give a bright yellow sparingly soluble product (Scheme 2.10). No molecular weight

values were obtained due to the insolubility of the polymer and it was assumed that this insolubility prevented the synthesis of high molecular weight material.[21]
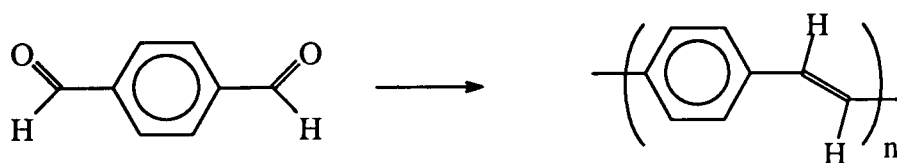
Scheme 2.10

Ten years later in 1989 and then 1991 Wagener reported the same polymerisation of terephthaldehyde but using a $TiCl_3/Zn$ system.[22,23] Again a bright yellow sparingly soluble product was formed with a molecular weight value (nmr end group analysis) of approximately 1000. Insoluble higher molecular weight material was isolated but was contaminated with inorganic residues and could not be fully characterised. Wagener also reported the synthesis of poly(phenylene ethylenediol), the intermediate pinacol, which was of higher molecular weight, this increase being attributed to the solublising effect of the hydroxyls. Also in 1991 an Italian group reported the synthesis of PPV and poly(m-phenylene vinylene) from terephthaldehyde and isophthaldehyde, respectively, giving sparingly soluble brown solids.[24] In 1983 Millichamp reported the reductive coupling of 4,4'-dibenzoyldiphenyl using $TiCl_3/LiAlH_4$ to give poly(4,4'-diphenylene diphenylvinylene)[25] (Scheme 2.11). The inclusion of the phenyl group
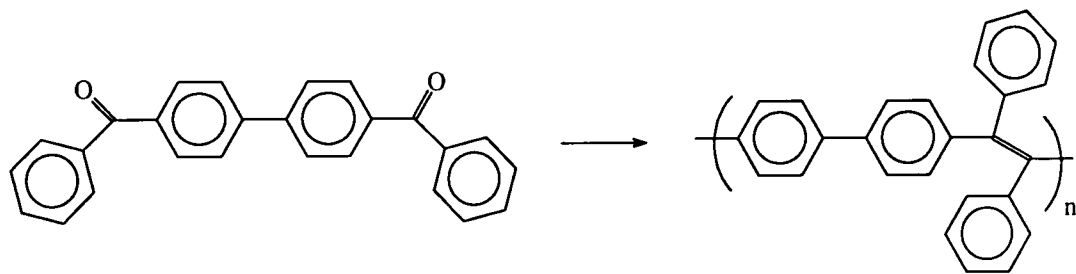
Scheme 2.11

on the monomer produced a polymer which was soluble in THF and chloroform and allowed the synthesis of high molecular weight polymer. This synthesis showed that

when applied to soluble polymers the McMurry reaction could be successfully used to generate high molecular weight materials.

Reductive coupling as a method of producing soluble PAVs has several advantages over the conventional dehalogenation or precursor routes:

(i) the product polymers are soluble and can be purified to remove any inorganic residues from the polymerisation reaction,

(ii) no sulphur or chlorine, which may act as quenching sites for PL or EL and/or create device problems because of ionic migration, are present,

(iii) no heat treatment of the polymer is required. In device preparation using precursor polymers the precursor polymer is heated to form PPV/PAV after being cast onto the ITO substrate. This heating may release HCl which can contaminate the ITO and degrade the polymer ITO interface, and

(iv) a wide range of monomers are available, allowing control of substituents on both the aromatic part and vinylene part of the polymer chain.

However reductive coupling is only suitable for the synthesis of soluble PAVs and gives poor control over the molecular weight and molecular weight distribution.

2.1.3 Project Aims

Since the work of Millichamp[25] in 1983 the electroluminescence of PPV and related polymers was discovered[18] and developed. Conventional synthetic routes to PPV and PAVs, dehalogenation or sulphonium ion and/or methoxy leaving group precursor polymers, have several drawbacks including the possibility of inorganic residues in the product polymers. Reductive coupling as a synthetic route to soluble poly(arylene vinylene)s should allow the synthesis of polymers that are free from inorganic impurities and, without the need for precursor polymers, allows spin coating from solution which is a processing technique familiar to potential users.

This project aimed to develop the reductive coupling method outlined by Millichamp and to optimise the reaction conditions of the polymerisation of 4,4′-dibenzoyldiphenyl in an attempt to minimise the occasional irreproducibility of the $TiCl_3$/$LiAlH_4$ reducing system

used. Additionally the possibility that poly(4,4'-diphenylene diphenylvinylene) was electroluminescent needed to be investigated in light of the discovery of the electroluminescence of PPV. It was also planned to extend the scope of this polymerisation reaction to include other aromatic diketones in an effort to obtain an insight into how to 'tune' the electroluminescent colour of related polymers.

Initially the TiCl$_3$/LiAlH$_4$ reducing system was chosen for two reasons; firstly the reaction had been shown to work and provided a suitable starting point for the project and secondly literature reports indicated that in the dimerisation of benzophenone (the model reaction used for the polymerisation of 4,4'-dibenzoyldiphenyl) the TiCl$_3$/LiAlH$_4$ system gave the highest yield and should therefore give the highest extent of conversion when applied to this monomer.

2.2 RESULTS AND DISCUSSION

2.2.1 Introduction

In 1983 Millichamp reported the synthesis of poly(4,4'-diphenylene diphenylvinylene) via the reductive coupling of dibenzoyldiphenyl using a low valent titanium species generated from $TiCl_3$ and $LiAlH_4$ in THF.[25,50] Also reported was the application of this
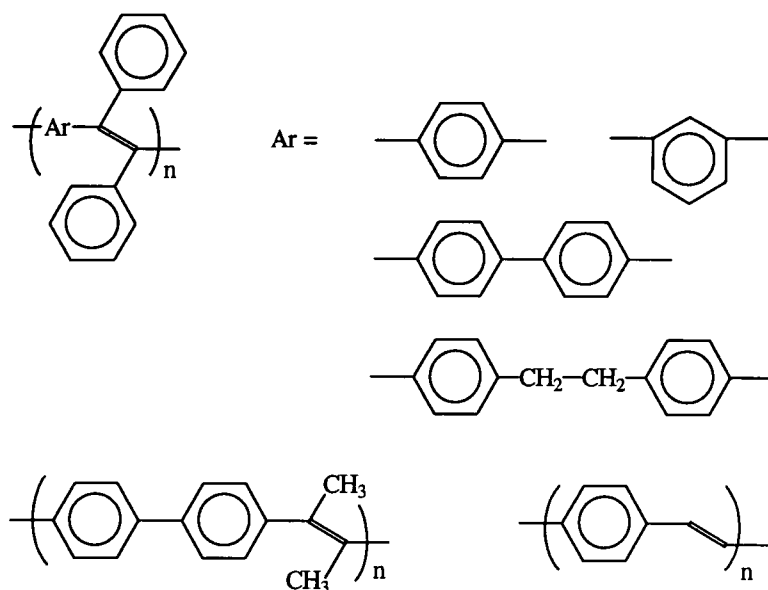
Figure 2.11 Poly(arylene vinylene) polymers synthesised by Millichamp

method to other aromatic diketone monomers to produce the polymers shown in Figure 2.11.

The results presented in this chapter continue that work, investigating more fully the optimal conditions for the reductive coupling of 4,4'-dibenzoyldiphenyl and extending the range of monomers polymerised.

2.2.2 Monomer Synthesis

Monomers I-VI shown in Figure 2.12 were all known compounds. Monomers I, II, IV and V were prepared following literature methods,[50-52] stocks of pure monomer III were available from previous workers and monomer VI was obtained from Aldrich.

The synthesis of monomers I and IV was by Friedel-Crafts benzoylation of diphenyl and p-terphenyl respectively and monomer II by the Friedel-Crafts reaction of terphthaloyl chloride with benzene. Synthesis of IV gave an insoluble white solid which was not
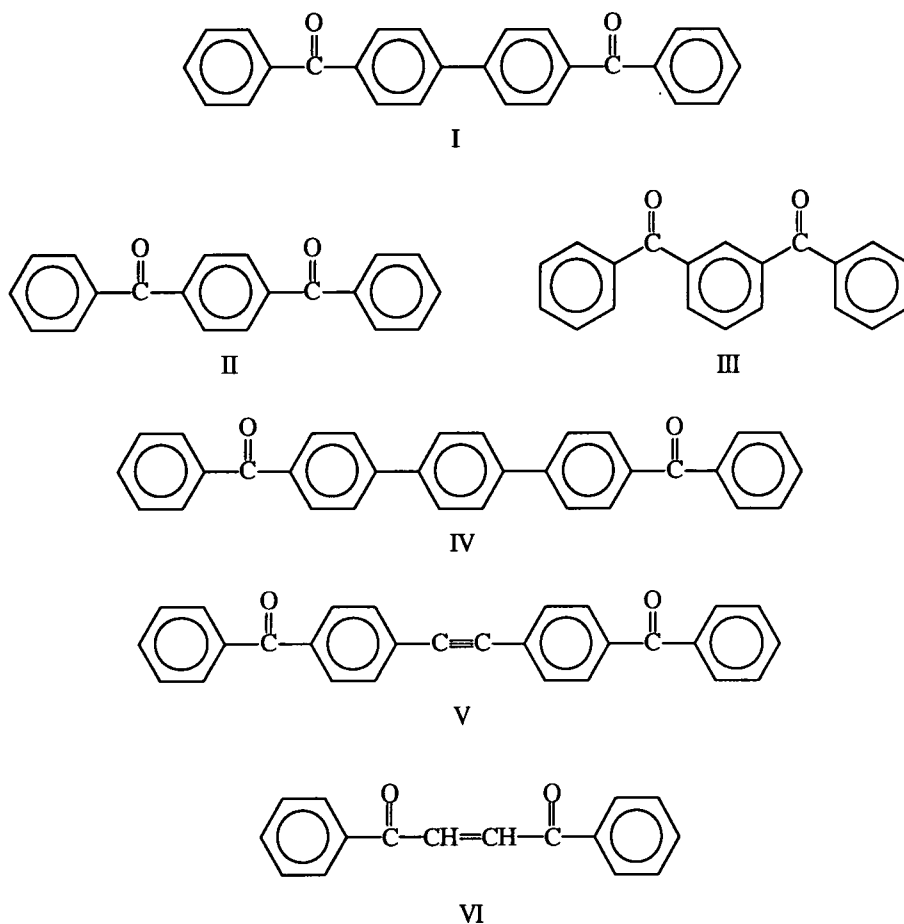
Figure 2.12 Diketone monomers

recrystallised before use. Literature reported recrystallisation from nitrobenzene[52] but this was considered unsuitable for several reasons. Firstly with a boiling point of 210°C removal of the solvent before polymerisation would be very difficult and secondly any residual nitrobenzene would interfere with the polymerisation reaction, since nitrogroups are reduced by the LiAlH$_4$/TiCl$_3$ system. This insolubility meant that high resolution ^{1}H and ^{13}C nmr spectra could not be obtained. IR spectroscopy did not show the presence of either a benzoic acid carbonyl or hydroxyl peak so the impure mixture was assumed to contain product, p-terphenyl and perhaps some residual aluminium salts. These side products were expected to be inert to the coupling conditions of the polymerisation reaction and therefore could be left in the monomer mixture. However the presence of

the mono substituted compound, 4-benzoyl-p-terphenyl, could not be excluded and if present it would be chain terminating, restricting the molecular weight the product polymer.

Initial attempts to directly benzoylate diphenylacetylene were unsuccessful. A literature report[51] attributed this lack of reaction to the reactivity of the carbon-carbon triple bond. To prevent this the acetylene group of diphenylacetylene was protected with dicobaltoctacarbonyl, the resulting dicobalthexacarbonyl complex was then benzoylated followed by deprotection to give monomer V (Scheme 2.12).
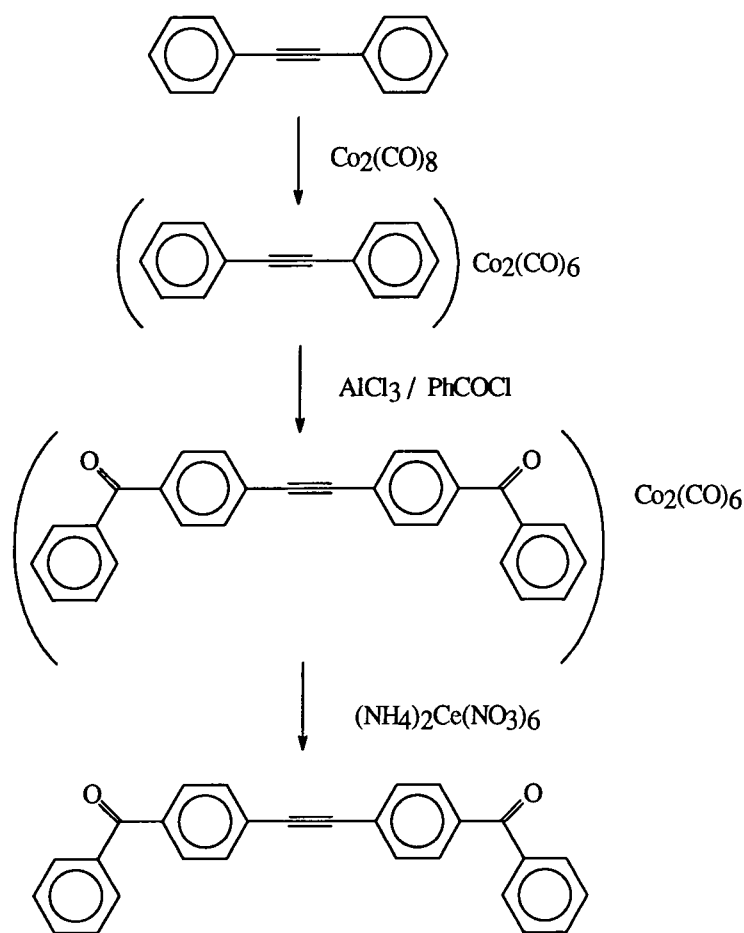
Scheme 2.12

2.2.3 Polymer Synthesis

Introduction and general methods

The general method established by Millichamp,[25,50] polymerisation via the reductive coupling of diketone monomers with $TiCl_3/LiAlH_4$, was followed. Millichamp reported that the polymerisations were sometimes irreproducible and attributed this in part to the

quality of the titanium trichloride. The variable quality of titanium trichloride was commented on by McMurry both in the initial report of reductive coupling and in a later review paper.[42,46] In the author's experience only low molecular weight polymer could be synthesised initially and after much work it was found that even under apparently well controlled reaction conditions, although synthesis of high molecular weight polymers was possible, the sytem retained an element of unpredictability. The experimental parameters required for success were:

(i) a titanium trichloride to lithium aluminium hydride molar ratio of 1.00 : 2.00. Any deviation from this resulted in a significant lowering of the molecular weight of the product polymer.

(ii) titanium trichloride and lithium aluminium hydride needed to be weighed out in a moisture free environment. Titanium trichloride fumes on contact with moisture and Millichamp reported that if a sample was seen to fume when opened in a glove box it was unsuitable for use in polymerisation reactions.

(iii) monomers were recrystallised to constant, sharp melting points and were dried thoroughly by continuous pumping on the vacuum line (ca. 10^{-2} mbar) for a minimum of 20 hours before use.

Throughout this section, where results are reported for polymerisation reactions without details, the conditions were standard; a molar ratio of $TiCl_3$: $LiAlH_4$: diketone monomer of 2.00 : 1.00 : 0.50 ($\pm$ 0.02), a monomer concentration of 10% w/v in THF and a reaction time of 18-20 hours. Each sample prepared was assigned a unique reference number.

Polymer molecular weight measurements were made using gel permeation chromatography (gpc) using chloroform as solvent, PL-gel columns and polystyrene calibration standards. Where polymer samples produced by different methods were to be compared, the samples were run consecutively to minimise any variation in the calibration of the instrument between runs. Additionally during attempts to optimise reaction conditions the polymer samples that were analysed were the total recovered 'crude' polymer from the reaction and were not purified by reprecipitation before analysis. This was done to prevent any form of fractionation, that may have occurred

during reprecipitation, biasing the results. The samples were, however, filtered before analysis to prevent insoluble solids entering the instrument. This may have had two effects; firstly it will have removed any residual titanium or aluminium salts from the sample and secondly it would have removed any insoluble very high molecular weight polymer. This second effect is acceptable because all subsequent characterisation of the polymer was made on samples which had been filtered, reprecipitated and/or had been processed from solution.

Poly(diphenylene diphenylvinylene)

Poly(diphenylene diphenylvinylene) (PDDV) was synthesised from 4,4'-dibenzoyldiphenyl. The general reaction procedure and reaction conditions used in

PDDV
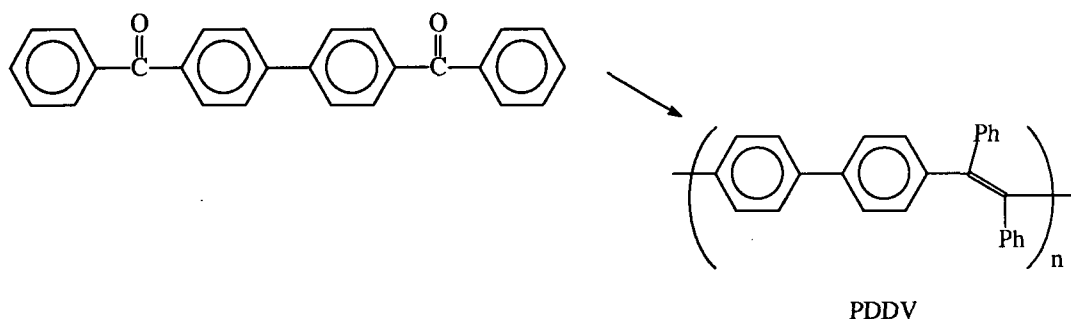
Scheme 2.13

all subsequent polymerisations, including those involving other monomers, were investigated and optimised using this polymerisation.

Molecular Weight Measurements

The observed molecular weight distributions for all of the samples of PDDV prepared in this work were found have a characteristic form. The polymers exhibited a large, broad peak at short retention time, corresponding to the bulk of the material, followed by two or three smaller and sharper peaks at longer retention times, corresponding to low molecular weight material (see Figure 2.13). Enrichment of a sample with monomer resulted in the formation of a new peak at still lower molecular weight indicating that the lower molecular weight peaks were not monomer and probably corresponded to oligomers.
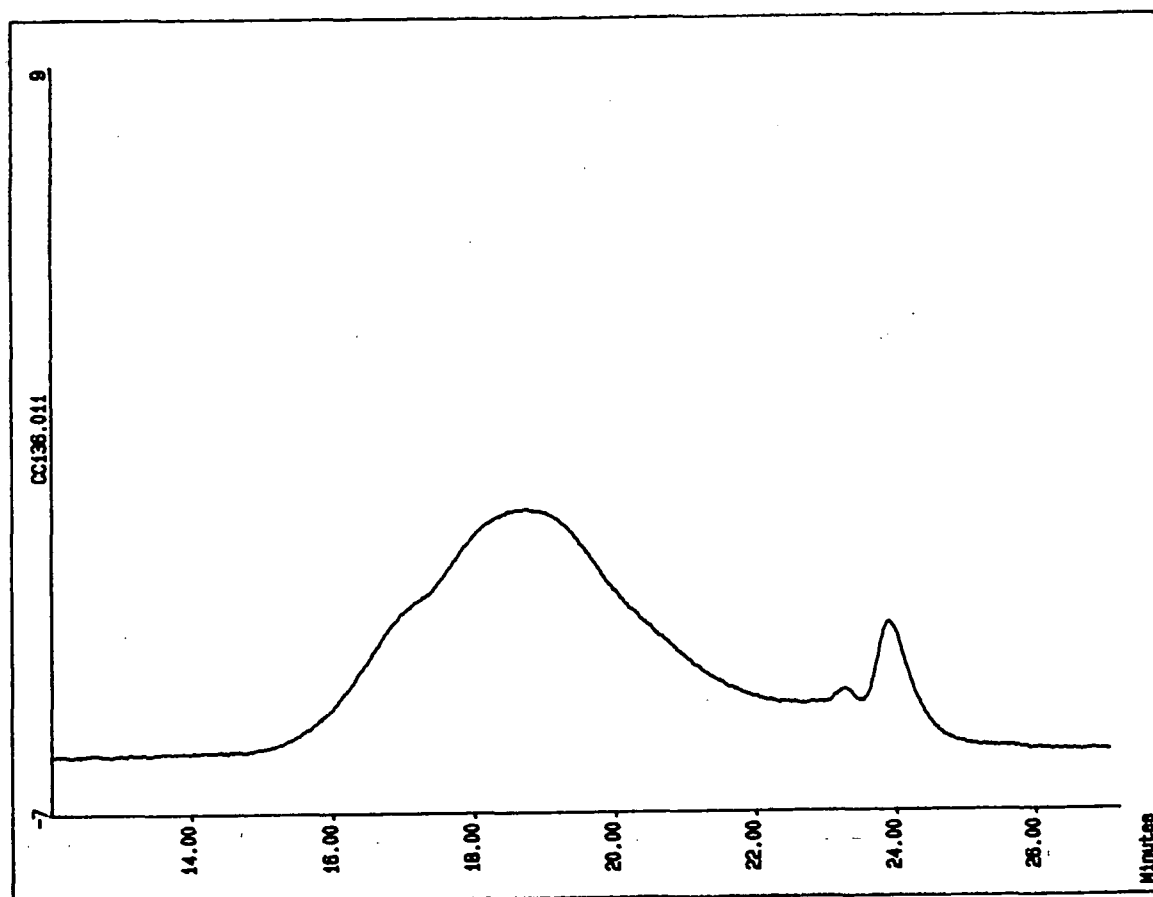
Figure 2.13 A typical gpc trace of poly(diphenylene diphenylvinylene)

Reprecipitation and attempted fractionation of polymer samples did not result in the removal of these low molecular weight peaks. The molecular weight values reported by Millichamp were manually calculated results and did not include these low molecular weight peaks[25,50] These values are referred to as the 'extrapolated' values and were calculated by drawing a curve that assumed a monomodal molecular weight distribution of polymer and therefore included all the high molecular weight material but excluded most of the area covered by the peaks corresponding to oligomers (hatched area in Figure 2.14). This 'extrapolation' of the molecular weight distribution curve was then analysed by dividing the area under the curve into i vertical columns of equal width, each of which corresponded to a given molecular weight. Using the formulae

Chapter Two

$$\overline{Mn} = \frac{\sum NiMi}{\sum Ni} \qquad \text{(Equation 2.1)},$$

$$\overline{Mw} = \frac{\sum NiMi^2}{\sum NiMi} \qquad \text{(Equation 2.2) and}$$

$$PDI = \frac{\overline{Mw}}{\overline{Mn}} \qquad \text{(Equation 2.3)}$$

the values of Mn, Mw and the polydispersity index (PDI) could then be calculated. This technique was adopted to allow comparison of the best sample obtained in this work with the results of Millichamp (labeled IM). These are shown in Table 2.2.
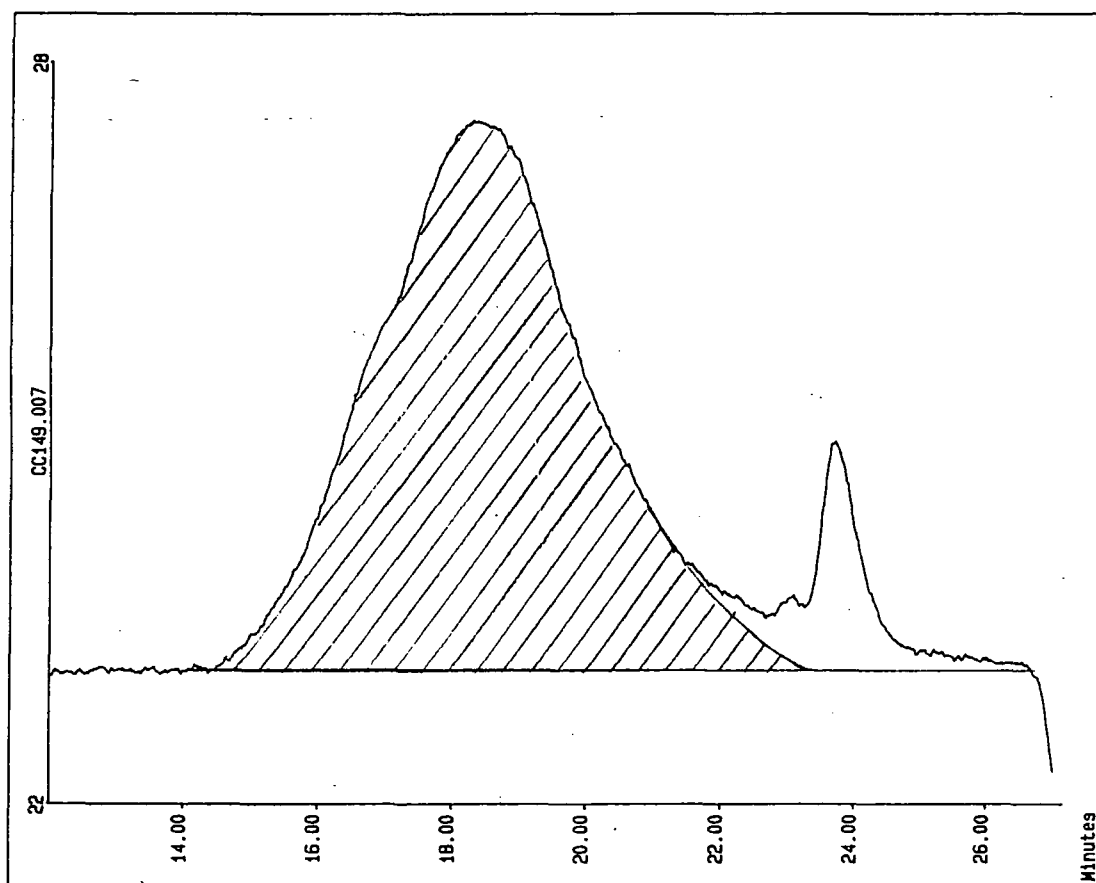
Figure 2.14 A gpc trace for poly(diphenylene diphenylvinylene) showing the extrapolation curve

PDDV Sample	Molecular Weight Determination Method	Molecular Weight		
		Mn	Mw	PDI
IM	Analysis of extrapolated major peak	37,000	74,000	2.0
This work 1	Total distribution, instrument analysis	4,500	54,000	11.9
This work 1	Analysis of extrapolated major peak	64,000	195,000	3.0
This work 2	Total distribution, instrument analysis	5,600	51,000	9.0
This work 2	Analysis of extrapolated major peak	57,000	151,000	2.7

Table 2.2 Comparison of polymer molecular weights from literature[50] and this work

The sample IM was from a 16 hour polymerisation reaction and was reprecipitated twice from chloroform into methanol. Samples 1 and 2 are the same sample of polymer, except that sample 1 was the total polymer product and sample 2 was reprecipitated four times from chloroform into methanol. The IM molecular weight distributions were recorded on a different instrument (THF as solvent) to that used in this work so the two sets of data are not directly comparable but are included as evidence that reproduction of and improvement on previous work was possible. It should also be noted that the reprecipitation procedure adopted for PDDV had no beneficial fractionating effect.

Reaction Stiochiometry

Dams reports that for the reductive coupling of benzophenone the optimum yield of tetraphenylethylene was achieved using a molar ration of 2.00:1.00 for titanium trichloride to lithium aluminium hydride.[47] In the early stages of the study, when this exact ratio of reagents was not used, the molecular weights of the polymers produced were low compared to samples produced using this exact ratio (Table 2.3).

Sample	Ratio TiCl$_3$:LiAlH$_4$	Reaction Time (hrs)	Reaction Concentration (w/v)	Molecular Weight		
				Mn	Mw	PDI
3	1.82 : 1.00	20	10.0	2,200	6,300	2.8
4	2.00 : 1.00	20	10.0	4,700	38,000	8.0
1	1.98 : 1.00	20	10.9	4,500	54,000	11.9

Table 2.3 Variation in the molecular weight of poly(diphenylene diphenylvinylene) with reaction stoichiometry

These results appear to be sensible given the relationship between molecular weight in stepgrowth polycondensation and the extent of conversion expressed in the Carothers' Equation. The influence of reagent stoichiometry on the yield of tetraphenylethylene in the coupling of benzophenone is shown in Table 2.4 along with the calculated DP, assuming that the polymerisation of 4,4'-dibenzoyldiphenyl proceeds with the same

Ratio TiCl$_3$:LiAlH$_4$	Reported Yield	Theoretical DP
2.00 : 1.00	99%	100
1.82 : 1.00	93%	14

Table 2.4 Yields for the model coupling reaction reported by Dams[47]

extent of conversion as the coupling of the model compound. The highest whole product, gpc derived number average PD obtained for the synthesis of PDDV was 16 (Mn 5,300, sample 11). Allowing for the uncertainty in this value it is disappointingly low and may indicate some deviation from an ideal stepgrowth polymerisation, due perhaps to premature termination, via loss of chain end functionality, cyclisation or side reactions, leading to low molecular weight products. However it is clear that the bulk of the sample has a relatively high DP and that to obtain high molecular weight polymer via reductive coupling the reaction stoichiometry has to be carefully controlled.

Reaction Times

Millichamp reported reaction times of 16 hours for most polymerisations although McMurry and Dams, respectively, reported reaction times of between 4 and 6 hours for the dimerisation of benzophenone.[42,47] In order to verify the work of Millichamp a series of polymerisations were carried out which were identical, within the limits of

experimental control, in every respect except reaction time. The results of these reactions are shown in Table 2.5 and the gpc traces in Figure 2.15.
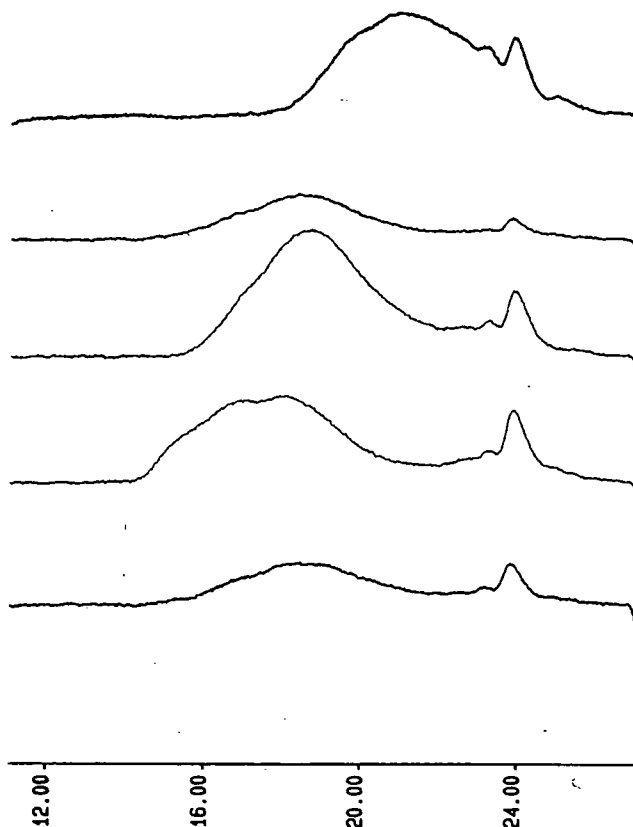
Figure 2.15 Offset gpc traces for the polymerisation of poly(diphenylene diphenylvinylene) using different reaction times. The horizontal axis represents retention time - increasing left to right.

From top to bottom: sample 8 (40hrs), sample 1 (20hrs), sample 7 (15hrs), sample 6 (10 hrs) and sample 5 (5hrs).

Sample	Polymerisation Time (hrs)	Ratio TiCl₃:LiAlH₄	Molecular Weight		
			Mn	Mw	PDI
5	5	1.99 : 1.00	2,900	46,000	15.5
6	10	2.01 : 1.00	3,300	96,000	29.1
7	15	1.99 : 1.00	3,600	32,000	8.7
1	20	1.98 : 1.00	4,500	54,000	1̇1.9
8	40	1.99 : 1.00	2,000	6,000	2.9

Table 2.5 Variation of polymer molecular weight with polymerisation time for the synthesis of poly(diphenylene diphenylvinylene)

These results illustrate the difficulty of carrying out precisely reproducible reactions using the $TiCl_3$/$LiAlH_4$ system. Mass recovery for the polymers was never the expected 100%, i.e. assuming all monomer was converted into polymer and was extracted from the reaction mixture (allowing for the loss of oxygen) but was generally greater than 85%. In the reaction with a polymerisation time of 40 hours the recovered mass of polymer after repeated extractions with chloroform was only 60%, indicating that polymer was still contained in the reaction mixture, a view supported by the observation of photoluminescence from the residual reaction mixture. It is possible that high molecular weight and cross linked material had been produced.

Given these results and Millichamp's earlier observations all subsequent polymerisations, including those using other monomers, were carried out at reflux for between 18 and 20 hours. Although an initially arbitary decision this reaction time has given satisfactory results.

Reaction Concentration

Initial reactions were carried out using a monomer to solvent weight to volume (w/v) ratio of 10% (i.e. 10g of monomer was polymerised in 100ml of THF). One disadvantage of using this concentration was that occasionally when adding the $LiAlH_4$ to the stirred $TiCl_3$/THF slurry the slurry solidified after addition of approximately 10% of the $LiAlH_4$. No explanation could be found for this observation and warming the mixture resulted in the solid becoming a stirrable slurry once more. The rate at which the $LiAlH_4$ was added seemed to play some part in the formation of this solid and slower addition (2g per hour) lessened the frequency of this solidification. In some instances extra solvent (5-10ml) had to be added to return the reaction mixture to a slurry. The yields and molecular weights of the polymers produced from these batches of reducing agent were unaffected. It was proposed that a more dilute reaction solution would prevent this solidification from taking place. However dilute reaction conditions are not expected to promote the synthesis of high molecular weight polymer so a series of polymerisations at different concentrations was carried out. These results are shown in Table 2.6 and the gpc traces in Figure 2.16.
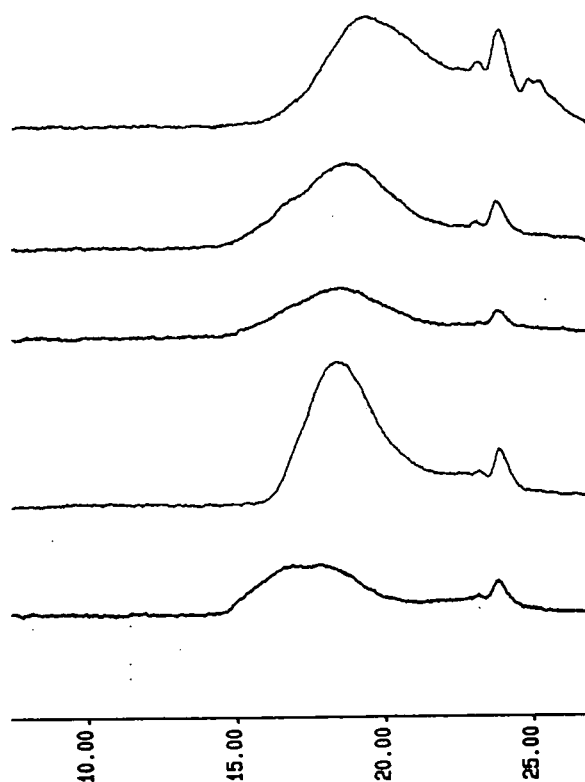
Figure 2.16 Offset gpc traces showing the variation of polymer molecular weight with monomer concentration for the synthesis of poly(diphenylene diphenylvinylene).

Horizontal axis shows retention time - increasing left to right.

From top to bottom: sample 12 (19.4%), sample 11 (14.7%), sample 1 (10.9%), sample 10 (5.9%) and sample 9 (5.5%).

| Sample | Polymerisation Concentration (w/v) | Ratio TiCl$_3$:LiAlH$_4$ | Molecular Weight | | |
			Mn	Mw	PDI
9	5.5	1.99 : 1.00	4,200	88,000	20.6
10	5.9	1.98 : 1.00	5,400	33,000	6.1
1	10.9	1.98 : 1.00	4,500	54,000	11.9
11	14.7	1.99 : 1.00	5,300	51,000	9.5
12	19.4	2.01 : 1.00	1,600	13,000	8.0

Table 2.6 Variation of polymer molecular weight with polymerisation concentration for the synthesis of poly(diphenylene diphenylvinylene)

These results do not show any easily identified correlation between polymerisation concentration and polymer molecular weight. Both the polymerisation mixtures using high concentrations, samples 11 and 12, became solid during the addition of LiAlH$_4$ to the TiCl$_3$/THF slurry and when quenched with hydrochloric acid had solid lumps in the reaction mixture from which polymer was difficult to extract. The author has no explanation for the low molecular weight values recorded for sample 12. Again these results show the unpredictable nature of the coupling reaction. It was decided that polymerisation using a 10% w/v ratio of monomer to solvent provided an acceptable balance between polymer molecular weight, ease of reaction and extraction of products. Careful addition of LiAlH$_4$ to the reaction mixture generally prevented the solidification of the TiCl$_3$/LiAlH$_4$/THF slurry.

Recoupling of Polymer

Early attempts to produce poly(4,4'-diphenylene diphenylvinylene) resulted in polymers with IR spectra that indicated the presence of carbonyl groups. These peaks appeared at wavenumbers similar to those of the monomer. It was found with these samples that the polymer could be reacted with a fresh quantity of reducing agent to produce higher molecular weight material in which this carbonyl peak could not be detected. Table 2.7 summarises these results.

Sample	Ratio TiCl$_3$:LiAlH$_4$	Reaction Time (hrs)	Carbonyl peak in IR	Molecular Weight		
				Mn	Mw	PDI
13	2.05 : 1.00	4	yes @ 1658cm^{-1}	1,500	4,700	3.0
14	1.37 : 1.00	18	no	3,000	11,000	3.6

Table 2.7 Effect of recoupling on polymer molecular weight for PDDV synthesised using non-optimised reaction conditions

Sample 13 is the initially produced polymer and sample 14 the same material after reaction with a fresh quantity of reducing agent. Given the incorrect ratio of titanium trichloride to lithium aluminium hydride the doubling of molecular weight values was surprising but showed that recoupling of material that still contained carbonyl functionality was possible and effective.

In later experiments using optimised reaction conditions, which allowed higher molecular weight polymer to be synthesised, the carbonyl peak was not detected. Recoupling of the polymer sample produced by these optimised conditions was attempted to see if it was possible to increase the molecular weights of a given sample. The results of this experiment are shown in Table 2.8.

| Sample | Ratio TiCl₃:LiAlH₄ | Reaction Time (hrs) | Carbonyl peak in IR | Molecular Weight | | |
				Mn	Mw	PDI
15	2.00 : 1.00	18	no	2,600	38,000	14.8
16	2.00 : 1.00	18	no	1,500	70,000	45

Table 2.8 Effect of recoupling on polymer molecular weight for polymer synthesised using optimised reaction conditions

The results shown above were somewhat unexpected. The initial polymer produced (sample 15) was very difficult to extract from the reaction mixture and full extraction was not possible, even after repeated washings with solvent. Because of this the molecular weight values were found to be, as expected, lower than those normally observed (e.g. sample 1). IR spectroscopy did not show the presence of a carbonyl peak and recoupling was not expected to result in a change in molecular weight. Analysis after recoupling (sample 16) showed an increase in molecular weight and a very large broadening in molecular weight distribution. Again the polymer produced was difficult to extract from the reaction mixture and complete extraction was not achieved.

The continued presence of the low molecular weight peaks in the gpc traces of PDDV after recoupling could be explained if any low molecular weight material was present as either cyclic oligomers or linear oligomers with non-carbonyl end groups. Linear oligomers with carbonyl end groups would be expected to react to give higher molecular weight products during the recoupling process. The nature of non-carbonyl end groups is uncertain although Millichamp proposed that they could be secondary alcohols, produced by side reactions of the intermediate species in the McMurry coupling.[50] No direct evidence to confirm this view was observed in this work. However some spectral

observations were made which supports the proposal. IR spectroscopy (see below) indicated an OH stretching peak in the spectrum of PDDV at ~3440cm^{-1} which could be attributed to either OH from methanol, pinacol OH from incomplete reduction of carbonyl or from a secondary alcohol end group. ^{1}H and ^{13}C nmr spectroscopy did not indicate residual methanol and repeated reprecipitation from chloroform into petroleum ether followed by extended pumping on the vacuum line did not alter the intensity of this peak in the IR spectrum, indicating that it was not due to methanol. Reaction of a polymer sample with sodium metaperiodate (a standard test for 1,2-diols) showed no variation in the molecular weight or molecular weight distribution of the polymer indicating that a 1,2-diol unit (pinacol group) was not present. Finally a nmr deuterium exchange experiment showed the presence of a labile proton which could be assigned as secondary alcohol but, without any corroborating evidence, a definite assignment of end group as a secondary alcohol was not possible. Isolation of the low molecular weight components from the bulk polymer sample, for example by fractionation, would make their positive identification and determination of the nature of the end groups simpler. However neither fractionation of polymer or isolation of these components was satisfactorily achieved during the course of this work and the nature of end group remains unresolved.

The results of recoupling for poly(4,4'-diphenylene diphenylvinylene) show that if a carbonyl peak is observed in the IR spectra of the polymer recoupling to give polymer of higher molecular weight is possible. However if no carbonyl peak is seen although recoupling does increase polymer molecular weight it also increases molecular weight distribution and generates insoluble polymer. For 4,4'-dibenzoyldiphenyl it appears that a single polymerisation reaction, using the correct reaction conditions, can give reasonably high molecular weight material in good yield.

IR and ^{1}H and ^{13}C nmr spectroscopy

A typical IR spectrum of PDDV is shown in Appendix 1.11. The peak assignments are shown in Table 2.9

Peak (cm^{-1})	Assignment
3439	O-H from either methanol or secondary alcohol end group (see above)
3053, 3023	aromatic C-H stretch
1947, 1908, 1800, 1743	overtone bands - characteristic of ring substitution
1596, 1492	aromatic ring C-C breathing mode
767, 745, 698	mono substituted aromatic C-H out of plane vibration
808	1,4 substituted aromatic C-H out of plane vibration

Table 2.9 IR assignments for poly(4,4'-diphenylene diphenylvinylene)

The small peaks seen in the region 2000 - 1650cm^{-1} are characteristic of the type of ring substitution present in the polymer.[53] A group of four bands whose intensity decreases towards lower wave number is typical of a mono substituted phenyl ring. 1,4-substitution is characterised by two bands, the one at higher wavenumber being of greater intensity. The band pattern seen for poly(4,4'-diphenylene diphenylvinylene) is similar to that expected for mono substitution but the pattern for 1,4-substitution is not clearly seen, the higher wavenumber peak (more intense) could be incorporated in the slightly broader peak at 1906cm^{-1} with the lower wavenumber peak (less intense) not being observed. No peak corresponding to monomer carbonyl at 1649cm^{-1} was present.

The ^{1}H and ^{13}C nmr spectra are shown in Appendix 1.12 and Figure 2.17 respectively and ^{13}C peak assignments are recorded in Table 2.10. In the ^{1}H nmr spectrum peaks at $\delta 0.88$ and $\delta 1.26$ are impurities originating from the nmr tube caps and the peak at $\delta 2.16$ is from acetone (used to clean the nmr tube). The small broad peaks at $\delta 4.0$ and $\delta 5.3$ appeared in all the ^{1}H nmr spectra of poly(4,4'-diphenylene diphenylvinylene), they were not assigned but may have been due to defects or end groups. No specific assignments of the aromatic region signals were possible.

Peak assignments of the ^{13}C nmr spectra of PDDV, PPTDV, PPDV and PMDV were made by comparison with the literature,[50,54] model compounds and by comparisons between related polymer structures. Peak assignments for all the polymers were made using all the available information but are certainly not unequivocal.
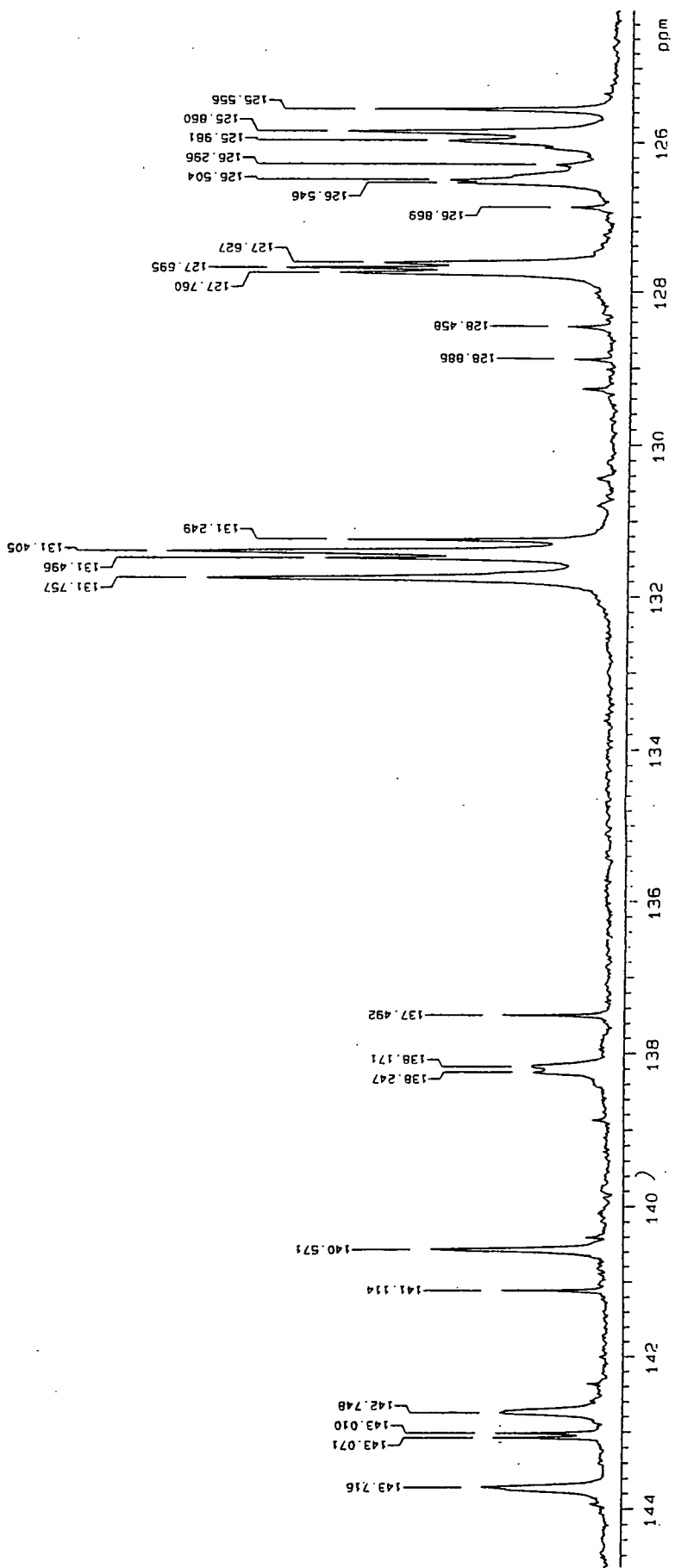
Figure 2.17 ^{13}C nmr spectrum of poly(4,4′-diphenylene diphenylvinylene)
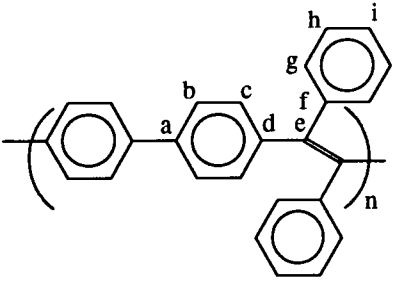
carbon	^{13}C (δ)	carbon	^{13}C (δ)
			poly(4,4′-diphenylene diphenylvinylene)
a	138.24 and 138.17	f	142.75
b	125.98 and 125.86	g	131.75 or 131.41
c	131.75 or 131.41	h	127.76
d	143.72	i	126.50
e	140.57	-	-

Table 2.10 ^{13}C nmr assignments of poly(4,4′-diphenyl diphenylvinylene)

Peaks that were not assigned to PDDV could be assigned to an end group. Nine peaks remained which consisted of four in quaternary carbon (δ143.07, 143.01, 141.11 and 137.49) and five in aromatic or olefinic carbon environments (δ131.50, 131.25, 127.70, 126.55 and 125.56). These corresponded exactly with the number and type of peaks expected for an end group consisting of secondary alcohol or unreacted carbonyl(see Figure 2.18). Other ^{13}C nmr spectra of higher molecular weight samples of PDDV also showed these nine peaks but at a lower intensity (relative to the peaks of PDDV) than in Figure 2.18, this observation supporting their assignment to an end group.
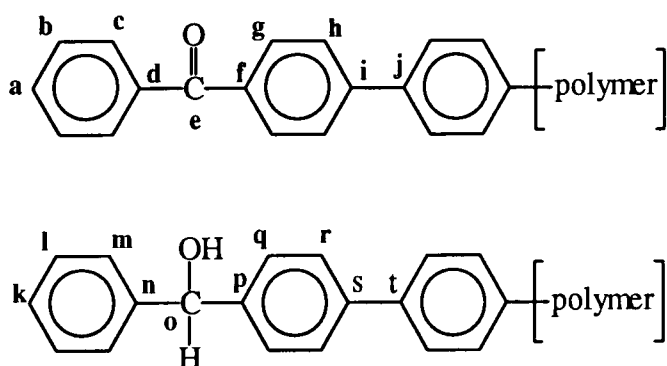
Figure 2.18 Potential PDDV end groups - carbonyl (top) and secondary alcohol (bottom)

The two potential end groups (shown in Figure 2.18) posess similar structures and their ^{13}C nmr spectra were expected to be similar. Without knowing the exact chemical shifts of any of the aromatic carbons of the two structures, differentiation between them soley on the basis of the five aromatic carbon peaks detailed above was not possible. However the expected chemical shifts of carbons e and o were expected to be markedly different, carbon e was expected in the region δ196 and carbon o in the region δ76 and identification of a peak in either/both of these regions would be strong evidence that either/both structures were present. However no peaks in either of these regions were detected due to the intensity of the peak/peaks being below the detection limit of the instrument or that neither of the structures were present. The presence of an OH stretching peak and the absence of a carbonyl absorption in the IR specrum of PDDV favours secondary alcohols as the predominant chain ends.

The question remains as to whether the vinylene carbon units are cis or trans in the polymer chain. Peaks in Table 2.10 assigned to carbons a and b are both split in a roughly 1:2 intensity ratio, suggesting that both cis and trans vinylenes may be present but not indicating which is predominant.

The three peaks between δ129.6 and δ128.4 were unassigned.

Poly(1,4-phenylene diphenylvinylene)

Poly(1,4-phenylene diphenylvinylene) (PPPDV) was synthesised from 1,4-dibenzoylbenzene (Scheme 2.14).

PPPDV
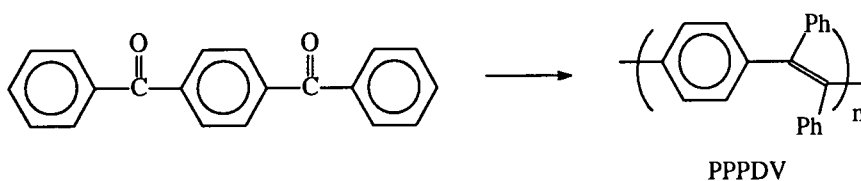
Scheme 2.14

In all of several polymerisation attempts low molecular weight material was obtained (see Table 2.11) which showed a strong residual carbonyl peak (1652cm^{-1}) in the IR

spectrum. These results were in agreement with those of Millichamp[50]. Horhold reported[55] that dechlorination polymerisation of 1,4-bis(phenyldichloromethylbenzene) gives soluble PPPDV with Mn 22,000 (vpo) so the molecular weight values obtained were lower than expected and disappointing.

Sample	Polymerisation run	Ratio TiCl$_3$:LiAlH$_4$	Reaction Time (hrs)	Molecular Weight		
				Mn	Mw	PDI
17	-	1.99 : 1.00	18	330	1,100	3.4
18	-	2.01 : 1.00	18	320	1,100	3.5
19	-	1.97 : 1.00	18	360	1,200	3.4
20	-	2.00 : 1.00	18	580	1,900	3.3

Table 2.11 Molecular weight values for different samples of PPPDV

The values above show that the reductive coupling reaction used was not an effective synthetic route to PPPDV, producing only dimers, trimers and unreacted monomer. Because Horhold reports that PPPDV is soluble, lack of solubility cannot be the reason for lack of polymerisation in this case. No attempt to recouple the initial product was made for two reasons; firstly the molecular weights were very low so even if they could be doubled or tripled the recoupled values would still be much lower that those obtained by other synthetic routes and secondly PPPDV had been extensively studied by other workers, so was not a particularly important target in this work.

The IR spectrum is shown in Appendix 1.13 and peak assignments in Table 2.12.

Peak (cm^{-1})	Assignment
3443	O-H from either 1,2-diol or secondary alcohol end group
3056, 3024	aromatic C-H stretch
1950, 1907 1812, 1771	overtone bands - characteristic of ring substitution
1652	carbonyl C=O
1597, 1492	aromatic ring C-C breathing mode
739, 699	mono substituted aromatic C-H out of plane vibration
785	1,4 substituted aromatic C-H out of plane vibration

Table 2.12 IR assignments for poly(1,4-phenylene diphenylvinylene)

The OH peak could not be from methanol because methanol had not been used in the polymerisation reaction nor had the polymer been reprecipitated into methanol before the spectrum was obtained. However the OH peak could have been due to either end group or pinacol arrising from incomplete coupling. Four overtone bands between 2000 and 1650cm^{-1} are present. 1,4 substituted phenylenes give two peaks, the one at higher wavenumber approximately double the intensity of the one at lower wavenumber.[53] This pattern combined with the four peak pattern for mono substituted phenyl should give a large peak at high wave number and two or three much smaller peaks at lower wavenumber. This is what is observed. Residual carbonyl is detected which is attributed to unreacted monomer and dimer end group.

The ^{1}H and ^{13}C nmr spectra are shown in Appendix 1.14 and 1.15 respectively and assignments are recorded in Table 2.13.

The ^{1}H nmr spectrum showed the presence of monomer and a broad set of aromatic peaks assigned to oligomers. [13]C nmr confirmed the presence of monomer and showed the presence of other aromatic carbons. These peaks were assigned to dimer but closer inspection of the ^{13}C spectrum showed that there was a peak at δ75.8 which was unaccounted for and one too few quaternary peaks. Additionally a peak at δ5.9 in the ^{1}H spectrum which disappeared after a deuterium exchange nmr experiment (indicating that it was due to an OH hydrogen) was unassigned. If the partially reduced intermediate 1,2-diol compound (VII) was present, rather than the fully reduced dimer, these two extra peaks could be accounted for. The presence of the 1,2-diol would also account for the large OH peak seen in the IR spectrum.

Peak assignments were made with the aid of values calculated from tables of ^{13}C nmr shifts, where more than one peak is given the assignment was ambiguous.
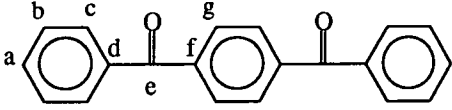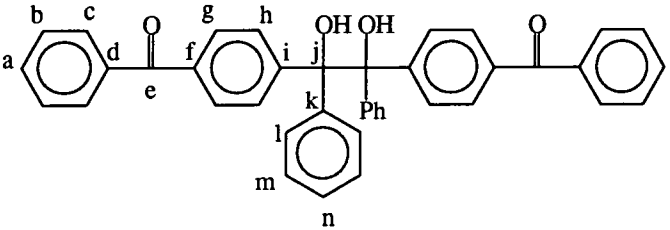
		1,4-dibenzoylbenzene

carbon	^{13}C (δ)	carbon	^{13}C (δ)
a	132.87	e	196.29 or 195.95
b	130.03 or 128.37	f	140.52
c	130.03 or 128.37	g	129.63
d	136.81	-	-

	1,2-diol containing dimer (VII)

carbon	^{13}C (δ)	carbon	^{13}C (δ)
a	132.30	h	130.24, 129.90, 128.60, 128.14, 126.54 or 126.12
b	130.24, 129.90, 128.60 or 128.14	i	148.12
c	130.24, 129.90, 128.60 or 128.14	j	75.81
d	137.44 or 136.52	k	143.15
e	196.29 or 195.95	l	126.54 or 126.12
f	137.44 or 136.52	m	130.24, 129.90, 128.60 or 128.14
g	130.24, 129.90, 128.60, 128.14, 126.54 or 126.12	n	127.87

Table 2.13 ^{13}C nmr peak assignments of the products from the attempted synthesis of poly(1,4-phenylene diphenylvinylene)

The IR and nmr spectra of the product of this attempted polymerisation together with the gpc data are consistent with the proposal that product only contained a mixture of unreacted monomer and partially reduced dimer (VII) containing 1,2-diol units and was not high molecular weight polymer.

Poly(1,3-phenylene diphenylvinylene)

Poly(1,3-phenylene diphenylvinylene) (PMPDV) was synthesised from
1,3-dibenzoylbenzene (Scheme 2.15).

PMPDV
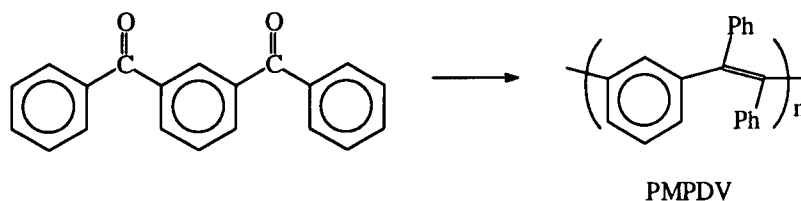
Scheme 2.15

In marked contrast to PPPDV the 1,3 substitution pattern in the arylene part of the
monomer resulted in the formation of polymers of reasonable molecular weights which
were readily soluble in chloroform. The molecular weight values for the product
polymer after one, two and three coupling reactions are recorded in Table 2.14.

Sample	Polymerisation run	Ratio TiCl$_3$:LiAlH$_4$	Reaction Time (hrs)	Molecular Weight		
				Mn	Mw	PDI
21	-	2.00 : 1.00	18	3,300	17,000	5.0
22	-	2.00 : 1.00	18	3,200	12,000	3.7
23	first	2.01 : 1.00	18	2,400	13,400	5.5
24	second	2.01 : 1.00	18	5,700	29,000	5.1
25	third	2.01 : 1.00	18	5,700	32,000	5.6

Table 2.14 Polymer molecular weights of various samples of poly(1,3-phenylene
diphenylvinylene)

Samples 21, 22 and 23 are the products from single polymerisation reactions and samples
24 and 25 are sample 23 recoupled once and twice respectively. It can be seen that the
first polymerisation of monomer to give PMPDV (samples 21, 22 and 23) produce
material of reasonable molecular weight (DP 10-13, derived from gpc data,
corresponding to a reaction conversion of >92%) and that a single recoupling of this
polymer allows higher molecular weight material to be produced (sample 24 and 25, DP
23, overall conversion >95%). The shape of the gpc traces was similar to those of
PDDV with a large broad peak at low retention volume corresponding to high molecular

weight material and a single small peak at high retention volume corresponding to low molecular weight material. After recoupling the intensity of the small peak, compared to the larger one, diminished. It also can be seen that a third recoupling reaction does not significantly affect polymer molecular weight.

Sample 23 did not display a carbonyl peak in its IR spectrum, unlike sample 13 in the recoupling of PDDV, and the recoupling experiment was not expected to be effective. However recoupling was effective and molecular weight values were doubled. One explanation might be that, in this case, there was on average only one carbonyl group on each polymer chain after the initial polymerisation. If this were so, any residual carbonyl group would only be a very small proportion of the material present and the intensity of the carbonyl peak in the IR would be very low and perhaps undetectable. Whatever the reason, it can be concluded that for PMPDV a second recoupling experiment is effective and significantly improves polymer molecular weight.

Samples of PMPDV produced after 2 and 3 recoupling experiments formed films, the quality of which was not sufficiently good to allow electroluminescent testing (see below). These samples were photoluminescent, emitting a pale green/yellow light when irradiated with long wavelength uv light. This blue shift in the perceived colour of the photoluminesce emission with respect to PDDV is attributed to a disruption of the conjugation length of the polymer caused by the 1,3-substituted phenylene ring in the polymer back bone. Reprecipitation of PMPDV from chloroform into non-solvent (either methanol or petroleum ether) increased Mw (but not Mn) and PDI.

The IR spectrum of PMPDV is shown in Appendix 1.16 and the assignments recorded in Table 2.15.

The observed OH peak could be due to either methanol or a secondary alcohol end group. As for PDDV methanol was not detected in ^{1}H nmr spectroscopy so this peak is tentatively assigned to an end group. PMPDV contains both mono and 1,3 substituted phenylene rings so the overtone bands between 2000 and 1650 cm^{-1} are expected to be a combination of the two patterns. 1,3 substitution gives three peaks of similar intensity

Peak (cm^{-1})	Assignment
3455	O-H from either methanol or secondary alcohol end group
3050, 3017	aromatic C-H stretch
1942, 1876, 1803, 1750	overtone bands - characteristic of ring substitution
1595, 1490	aromatic ring C-C breathing mode
756, 698	mono substituted aromatic C-H out of plane vibration
756	1,3 substituted aromatic C-H out of plane vibration

Table 2.15 IR assignments of poly(1,3-phenylene diphenylvinylene)

(the middle one being slightly larger) with the peak at lower wavenumber being slightly broader than the other two.[53] In the spectrum of PMPDV four peaks are seen, the three at higher wavenumber of similar intensity and larger than the fourth peak. This pattern can be explained if it is assumed that the peak pattern of the two phenyl rings obscures the peak pattern of the one 1,3 substituted phenylene ring. These two substitution patterns are confirmed by the peaks at low wavenumbers, with two characteristic peaks for mono substituted phenyl and one peak for 1,3 substituted phenylene (756cm^{-1}) which is superimposed over one of the phenyl peaks (expected between 770-730cm^{-1}). The peak for the isolated H of the 1,3 substituted phenylene was expected to be weak and was not identified.

The ^{1}H and ^{13}C nmr spectra of PMPDV are shown in Appendix 1.17 and Figure 2.19 respectively and the peak assignments recorded in Table 2.16. The ^{1}H nmr spectrum shows only two broad aromatic peaks which cannot be assigned further. Peaks at δ1.25, δ0.83 are impurity (from the nmr tube caps), δ1.58 is water and δ3.74 and δ1.85 are from THF.

The ^{13}C nmr spectrum of PMPDV was relatively simple but the peaks were broad and unresolved. Comparison with related polymers allowed relatively unambigioius identification of the phenyl carbons of the diphenylenevinylene part of the polymer. No peaks that could be identified as end groups were detected. The peak at δ143.47 was
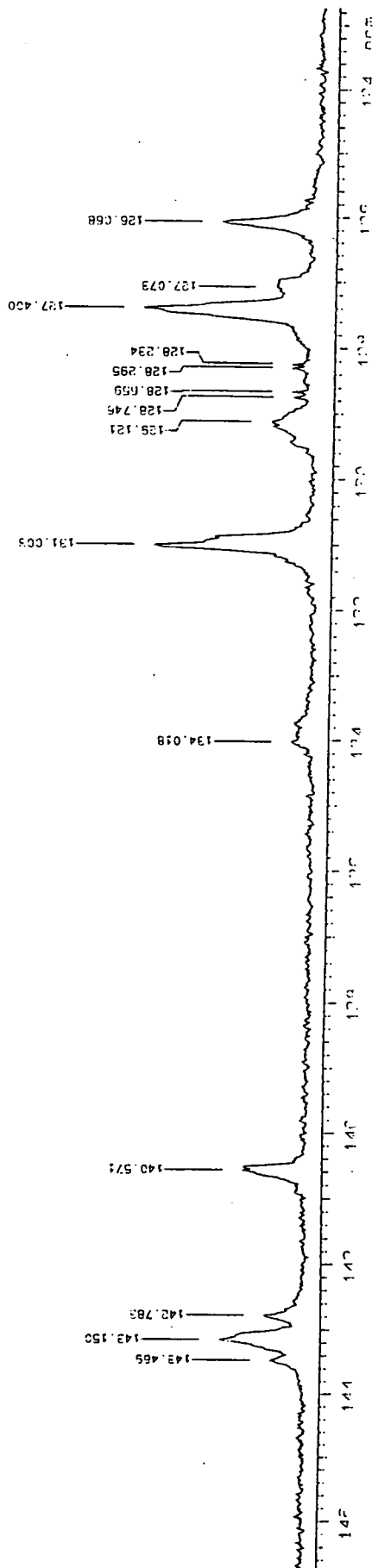
Figure 2.19 ^{13}C nmr spectrum of poly(1,3-phenylene diphenylvinylene)
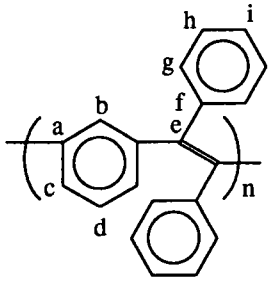
carbon	^{13}C (δ)	carbon	^{13}C (δ)
a	143.15	f	142.78
b	134.02	g	131.00
c	129.12	h	127.40
d	127.07	i	126.07
e	140.57	-	-

Table 2.16 ^{13}C nmr peak assignments of poly(1,3-phenylene diphenylvinylene)

unassigned in this anaylsis but along with the peaks at δ143.15 and δ142.78 was at a chemical shift value corresponding to a quaternary carbon adjacent to a vinylene unit. Because only two peaks were expected and three peaks were observed, one of which was broad, this may indicate cis/trans vinylene effects.

Poly(4,4″-terphenylene diphenylvinylene)

Poly(4,4″-terphenylene diphenylvinylene) (PPTDV) was synthesised from 4,4′-dibenzoyl-p-terphenyl (Scheme 2.16).

PPTDV
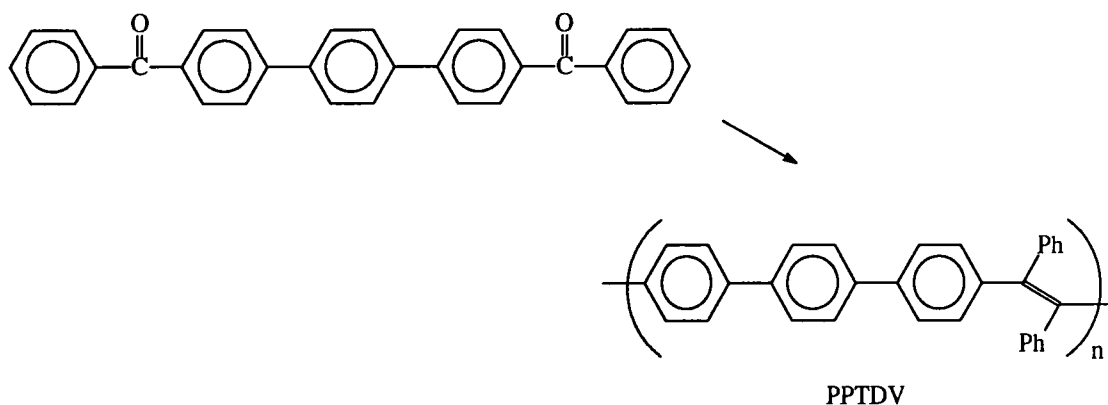
Scheme 2.16

4,4′-Dibenzoyl-p-terphenyl was an insoluble white powder which was polymerised without prior purification. Reductive coupling yielded a pale yellow solid which was soluble in large volumes of chloroform allowing separation of the polymer from the reaction mixture and polymer characterisation (gpc and nmr). PPTDV could be cast into thin films (not free standing) but they were not of sufficiently good quality for EL testing. When irradiated with long wavelength uv light samples of PPTDV emitted yellow light which was visually 'less blue' shifted than the emission from PMPDV and appeared similar to the PL of PDDV. This was unexpected as poly(p-phenylene) (PPP) has a large band gap and displays blue electroluminescence and photoluminescence. Because PPTDV has more PPP character than PMPDV it was expected that PPTDV would show a more blue shifted emission. This observation can be rationalisied if the emitting feature of the polymer structure was based on the diphenylvinylene part rather than the arylene part of the molecule. However if this were the case all the polymers synthesised would have very similar PL emissions as all the polymers synthesised contain the same vinylene structure (diphenylvinylene) but this is not the case so the lack of a blue shift in the observed PL of PPTDV with respect to PDDV was puzzling.

Polymer molecular weights are shown in Table 2.17.

Sample	Polymerisation run	Ratio TiCl$_3$:LiAlH$_4$	Reaction Time (hrs)	Molecular Weight		
				Mn	Mw	PDI
26	first	2.00 : 1.00	18	2,700	6,900	2.5
27	second	2.00 : 1.00	18	2,300	6,400	2.8
28	third	2.00 : 1.00	18	2,200	6,300	2.8

Table 2.17 Polymer molecular weight values for poly(4,4″-terphenylene diphenylvinylene)

Sample 26 is polymer produced after one polymerisation reaction, sample 27 is sample 26 recoupled and sample 28 is sample 26 recoupled twice. Unlike the other polymers the effect of recoupling is negligible. One problem encountered with the polymerisation reaction was that product polymer was only sparingly soluble in chloroform and the extraction of polymer from the reaction mixture was consequently

difficult. Extraction was continued until the wash layers were no longer coloured but at this point PL of the residual reaction mixture was still observed, indicating that some PPTDV remained unrecovered. Any insoluble polymer was probably high molecular weight material and if it remained in the residual reaction mixture would account for the relatively low polymer molecular weight values obtained. Another explanation for the low observed molecular weight values could be that the monomer contianed some mono substituted 4-benzoyl-p-terphenyl. The presence of this mono functional ketone would be chain growth terminating and would explain the lack of an increase in product molecular weight after recoupling.

The IR spectrum of PPTDV is shown in Appendix 1.18 and peak assignments recorded in Table 2.18.

Peak (cm^{-1})	Assignment
3465	O-H from either methanol or secondary alcohol end group
3052, 3024	aromatic C-H stretch
1945, 1910	overtone bands - characteristic of ring substitution
1597, 1489	aromatic ring C-C breathing mode
750, 699	mono substituted aromatic C-H out of plane vibration
808	1,4 substituted aromatic C-H out of plane vibration

Table 2.18 IR assignments of poly(4,4″-terphenylene diphenylvinylene)

Methanol was not detected in the ^{1}H nmr spectrum so the weak OH peak was probably due to alcoholic end group. The overtone bands[53] were expected to be similar to those of PDDV involving only mono and 1,4 substituted phenylene rings. However only two of the expected four peaks were resolved, the lack of the other two cannot be accounted for but may be due to the poor quality of the spectrum. The peaks at low wavenumbers are consistent with the presence of both phenyl and 1,4 substituted phenylene rings.

The ^{1}H and ^{13}C nmr spectra are shown in Figures 2.20 and 2.21 and the ^{13}C nmr peak assignments recorded in Table 2.19.
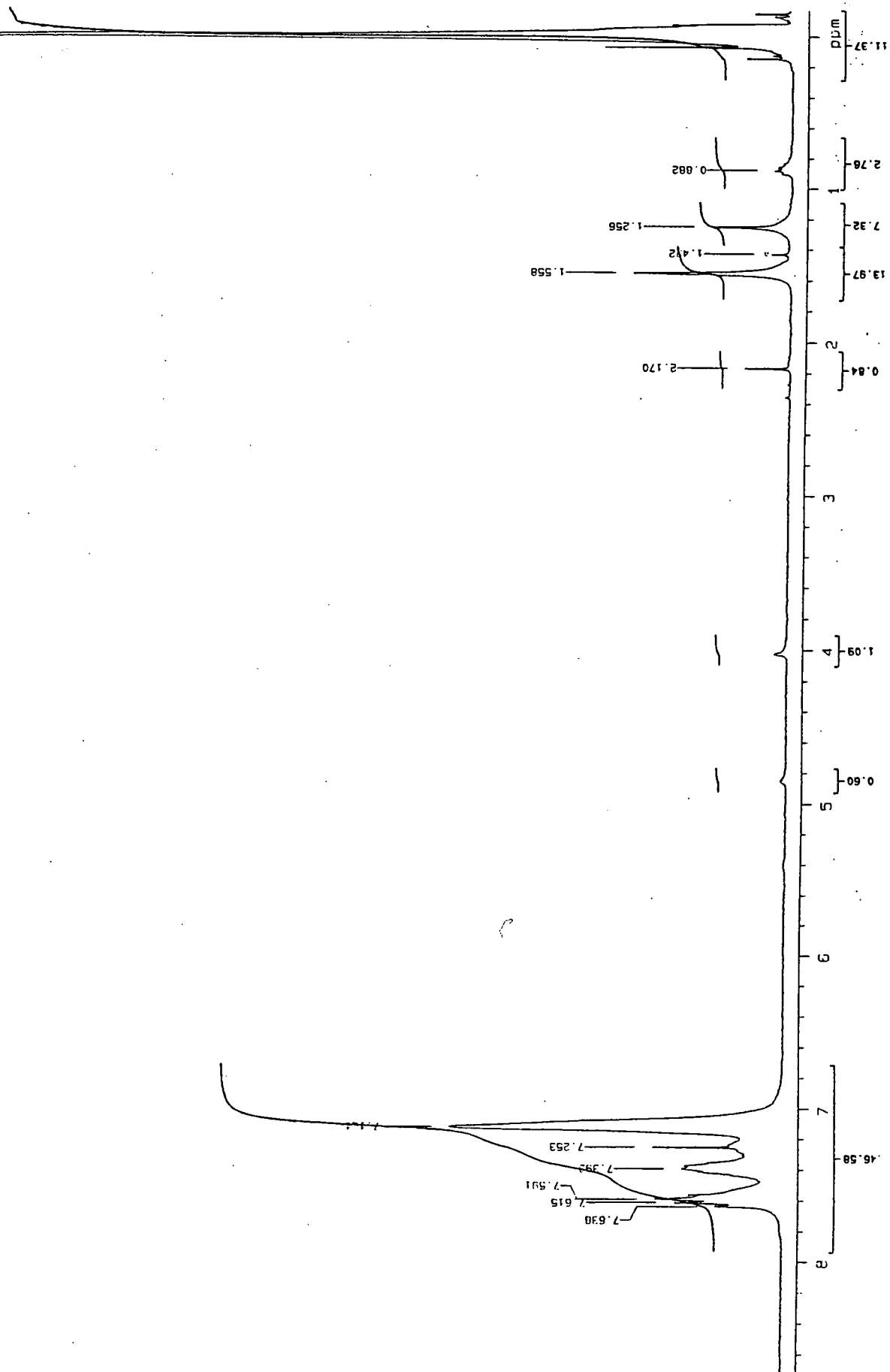
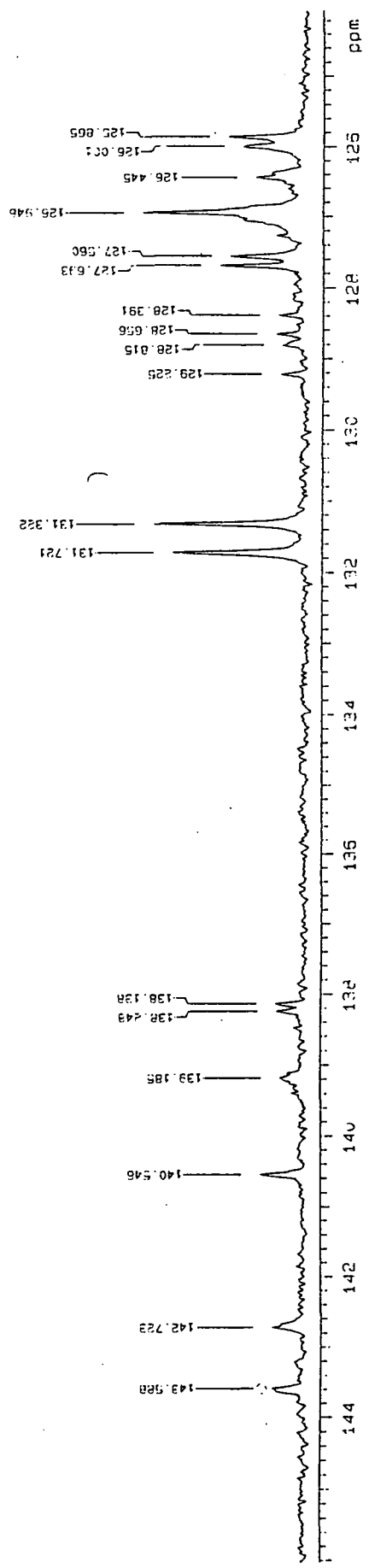**Figure 2.20** ¹H nmr spectrum of poly(4,4″-terphenylene diphenylvinylene)

Figure 2.21 ^{13}C nmr spectrum of poly(4,4″-terphenylene diphenylvinylene)

The ^{1}H spectrum showed a set of broad aromatic peaks assigned to polymer. Comparison with monomer was not possible because the monomer was insoluble and no nmr spectra were obtained. The upfield peaks were identified (as before) as impurities, water and acetone whilst the two small peaks between δ5 and δ4 were unassigned but may have been due to end groups.
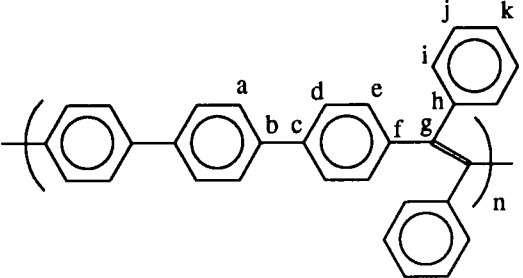
carbon	^{13}C (δ)	carbon	^{13}C (δ)
a	126.95	g	140.55
b	139.19 or 138.24 and 138.14	h	142.72
c	139.19 or 138.24 and 138.14	i	131.72 or 131.32
d	126.00 and 125.87	j	127.69 and 127.56
e	131.72 or 131.32	k	126.45
f	143.59	-	-

The structure shown in the table is poly(4,4″-terphenylene diphenylvinylene), with carbons labelled a, b, c, d, e, f, g, h, i, j, k and repeat unit n.

Table 2.19 ^{13}C nmr peak assignments of poly(4,4″-terphenylene diphenylvinylene)

Peak assignments follow from comparison with related polymer structures. Like PDDV and PMPDV the peaks are often broad and sometimes split, indicating the possibility of cis/trans vinylene effects. The peaks between δ129.3 and δ128.3 were unassigned but may have been due to end groups but without a spectrum of monomer to estimate the peak positions of potential end groups assignment was not attempted.

Poly(4,4'-diphenylacetylene diphenylvinylene)

The synthesis of poly(4,4'-diphenylacetylene diphenylvinylene) (PDADV) from 4,4'-dibenzoyldiphenylacetylene (Scheme 2.17) was attempted and the molecular weights of the products recorded in Table 2.20.

PDADV
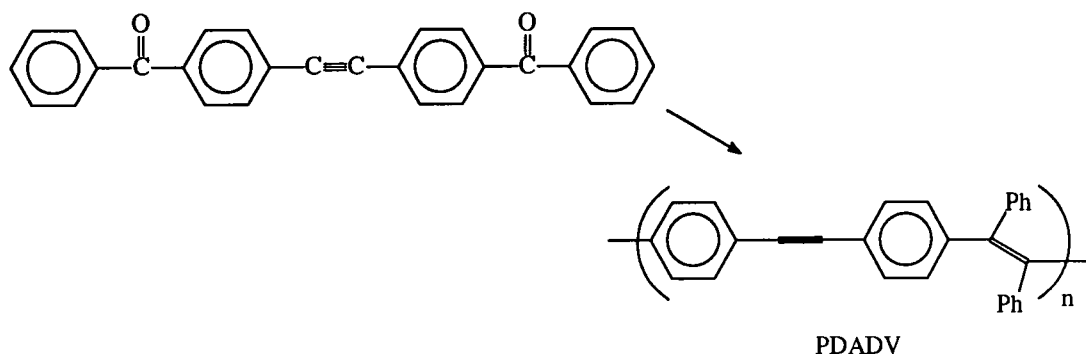
Scheme 2.17

Sample	Polymerisation run	Ratio TiCl₃:LiAlH₄	Reaction Time (hrs)	Molecular Weight		
				Mn	Mw	PDI
32	-	2.00 : 1.00	18	890	1300	1.5

Table 2.20 Polymer molecular weight values for poly(4,4'-diphenylacetylene diphenylvinylene)

It can be seen that the molecular weight of this product is very low. The gpc trace showed two distinct peaks, the one at higher retention volume (lower molecular weight) corresponded to unreacted monomer. The product was relatively insoluble in chloroform which made extraction of PDADV from the reaction mixture difficult and did not allow high resolution nmr spectra to be obtained. Lack of polymerisation was surprising and might be attributed to preferential reaction with the acetylene group leading to an imbalance in the stoichiometry of the reducing agents or perhaps the insolubility of the initial product preventing further reaction. This system was not intensively investigated.

The IR spectrum is shown in Appendix 1.19 and peak assignments are recorded in Table 2.21.

| Peak (cm^{-1})	Assignment
3440	O-H from either 1,2-diol or secondary alcohol end group
3042, 3022	aromatic C-H stretch
2922, 2852	aliphatic C-H stretch
1645	carbonyl C=O
1601, 1508	aromatic ring C-C breathing mode
740, 694	mono substituted aromatic C-H out of plane vibration
804	1,4 substituted aromatic C-H out of plane vibration

Table 2.21 IR assignments of poly(4,4″-terphenyl diphenylvinylene)

The OH was assigned to end group or pinacol (not methanol as polymer had not been reprecipitated). Aliphatic C-H peaks seen at ~2900cm^{-1} could have been from either solvent (chloroform or THF) or from reduced acetylene. Neither THF nor chloroform (except the trace amount seen in deuterochloroform used as solvent to obtain nmr spectra) was detected in the ^{1}H nmr spectrum so this peak could be reduced acetylene. A peak corresponding to acetylene was not observed in either monomer or polymer, which is as expected because both the monomer and polymer repeat unit are symmetrical and only asymmetrically substituted acetylenes are sensitive to IR spectroscopy. Poor resolution in the spectrum did not allow the overtone peaks between 2000 and 1650cm^{-1} to be clearly identified. A carbonyl absorbtion was observed, consistent with the presence of residual monomer.

The ^{1}H nmr spectrum is shown in Appendix 1.20 and by comparison with reference spectra showed the presence of monomer in low concentration and broad aromatic peak assigned to oligomer at δ7.10-6.48, peaks at high field corresponding to impurity and water in the solvent. Due to the low solubility of the product neither ^{13}C nmr or good quality ^{1}H nmr spectra could be obtained, although no peaks corresponding to reduced acetylene (either olefinic or aliphatic hydrogen) were observed the possible occurrence of this side reaction could not be ruled out.

Poly(1,2-ethylene diphenylvinylene)

The synthesis of poly(1,2-ethylene diphenylvinylene) (PEDV) from trans-1,2-dibenzoylethylene (Scheme 2.18) was attempted.
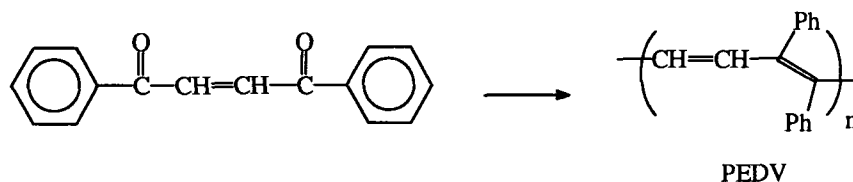
Scheme 2.18

This polymer, PEDV, is a form of poly(phenylacetylene) with an exclusively head-head tail-tail configuration of repeat units which should be contrasted with conventional poly(phenylacetylene) which is believed to have an all head-tail head-tail configuration.[56] If this synthesis could be achieved the product would provide a useful reference point for establishing the structures of poly(phenylacetylene).
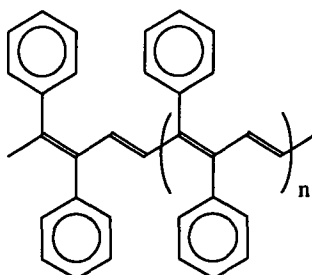
Figure 2.22 The head-head tail-tail configuration of poly(1,2-ethylene diphenylvinylene)

The molecular weights for the products of this synthesis are shown in Table 2.22 and correspond to dimer, trimer and perhaps tetramer.

Sample	Polymerisation run	Ratio TiCl$_3$:LiAlH$_4$	Reaction Time (hrs)	Molecular Weight		
				Mn	Mw	PDI
33	first	2.00 : 1.00	18	300	430	1.4
34	second	2.00 : 1.00	18	610	810	1.3
35	third	2.00 : 1.00	18	630	850	1.4

Table 2.22 Polymer molecular weight values for poly(1,2-ethylene diphenylvinylene)

The IR spectrum of PEDV is shown in Appendix 1.21 and peak assignments in
Table 2.23.

Peak (cm^{-1})	Assignment
3445	O-H from either secondary alcohol end group or methanol
3055, 3023	aromatic C-H stretch
2925	aliphatic C-H stretch
1945, 1873, 1800, 1717	overtone bands - characteristic of ring substitution
1598, 1492	aromatic ring C-C breathing mode
758, 698	mono substituted aromatic C-H out of plane vibration

Table 2.23 IR assignments of poly(1,2-ethylene diphenylvinylene)

Traces of methanol were detected in the ^{1}H nmr spectrum of PEDV so the OH peak was
due probably to both methanol and end group. An aliphatic C-H peak was observed
which may have been due to reduced ethylene but no clear corresponding aliphatic
hydrogen peaks were seen in the ^{1}H nmr spectrum. Also a peak at identical wavenumber
was observed in the IR spectra of all the other polymers synthesised and could not be
assigned for those samples so positive assignment of this peak to reduced ethylene in this
case is not possible. The overtone band pattern was expected to be that for mono
substituted phenyl but the peak at lowest wavenumber is of much greater intensity than
the other three (expected to be smaller than the other three) which is probably due to the
poor quality of the IR spectrum. No carbonyl corresponding to monomer (1649cm^{-1})
was observed.

The ^{1}H and ^{13}C nmr spectra of PEDV are shown in Appendix 1.22 and 1.23 respectively.
They are both of poor quality and provide little structural information about PEDV. The
^{1}H spectrum has a large broad peak assigned to aromatic and olefinic hydrogens and
does not show the presence of aliphatic hydrogens whose integration would be sufficient
to account for reduced ethylene. Other high field peaks identified were trace methanol
(δ3.48), water (δ1.56) and impurity (δ1.26, δ0.86). The ^{13}C spectrum shows a broad
peak at ~δ128 corresponding to aromatic and olefinic carbons, such broad peaks being
characteristic of poor quality samples of poly(phenylacetylene). A single peak at δ45.2

was recorded which could not be assigned and no corresponding hydrogen peak could be seen (the peak at δ29.5 is nmr tube cap impurity) and it could be possible that this peak is an instrument artifact. Overall the nmr peak positions of PEDV in both the ^{1}H and ^{13}C spectra were similar to those expected for poly(phenylacetylene) but the resolution of the spectra was very poor and confirmation of the head-head tail-tail structure of this oligomeric product was not possible.

2.2.4 Further Polymer Characterisation

Further characterisation of the polymers was carried out in order to investigate some of the physical properties of the materials.

Photoluminescence and Electroluminescence Studies

Photoluminescence (PL) and electroluminescence (EL) studies were carried out by Dr. Franco Cacialli at the Cavendish Laboratory at the University of Cambridge and the author is indebted to him for the results reported here. In order to study polymer samples by these methods the polymer under investigation needed to be available as stable films. Only PDDV formed films of suitable quality and the results given below are for this polymer. The PDDV analysed was from Sample 4 (see above) with Mn - 4,700, Mw - 37,000 and PDI - 8.0.

To obtain PL spectra, thin films of polymer were formed by spin casting or drop casting from solution onto a spectrosil substrate in an air and moisture free environment.

Sample	Solvent and Casting Method	Film Thickness (nm)	PL Efficiency
4a	Toluene - Spin	~ 80	~ 45%
4b	Toluene - Drop	~ 1630	~ 40%
4c	Chloroform - Spin	~ 70	~ 50%

Table 2.24 PL efficiencies of films of PDDV spun cast or drop cast from different solvents

Table 2.24 shows the solid state PL efficiencies of PDDV films of different thicknesses. Compared to other poly(arylene vinylene)s the solid state PL efficiency of PDDV is very encouraging, for example poly(p-phenylene vinylene) has a solid state PL efficiency of ~ 27%, methoxy-PPV ~ 22% and cyano substituted hexoxy-PPV ~ 45%. As expected the thinner films show a higher efficiency than the thicker one. This is attributed to the fact that while efficiency measures the light emitted from the sample, PL occurs throughout the film and some of the 'generated' light is internally reflected within the sample and is not emitted from the polymer layer. For thinner films this effect is less and the PL efficiency is higher.

The PL spectra for the three PDDV samples are shown in Figure 2.23 and were obtained by irradiating the samples at 354 and 365nm (Ar$^+$ laser, 3mW), all three samples gave similar spectra. Occasionally, other poly(arylene vinylene)s display some form of vibrational fine structure in the PL spectrum but this was not the case for PDDV and a single smooth emission peak was seen.
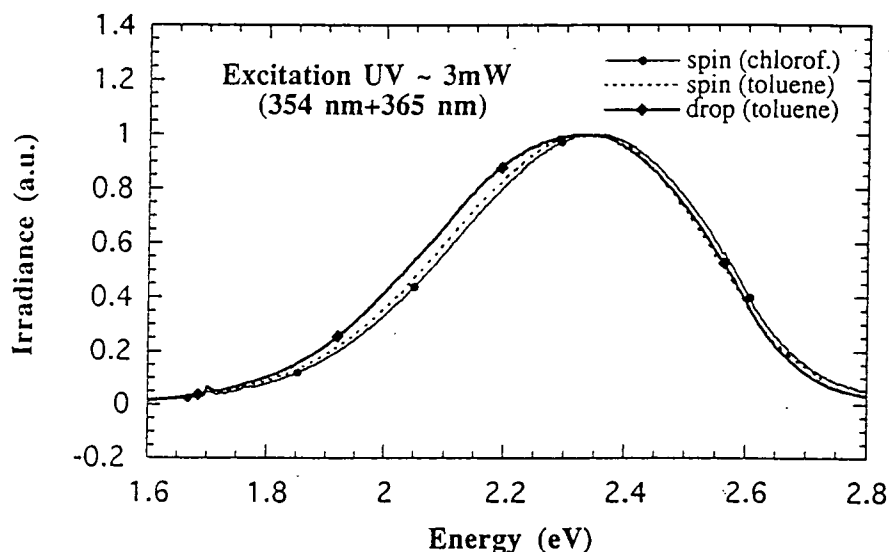

Figure 2.23 PL spectrum of poly(4,4'-diphenylene diphenylvinylene)

Sample	Solvent and Casting Method	Peak (nm)	Peak (eV)	Full Width at Half Maximum (eV)
4a	Toluene - Spin	526.5	2.35	2.567-2.059 = 0.509 (119.0 nm)
4b	Toluene - Drop	534.4	2.32	2.571-2.030 = 0.541 (128.2 nm)
4c	Chloroform - Spin	526.5	2.35	2.581-2.073 = 0.508 (117.4 nm)

Table 2.25 PL of poly(4,4'-diphenylene diphenylvinylene) films

These results are similar to those of Millichamp[50,57] who reported for solution spectra a PL peak at 2.4eV (515nm), (chloroform solution, irradiation at 360nm). He also reports that the shape of the emission spectrum was a broad structureless peak which is in agreement with the observations of this work. Friend reports[33] that solid state PL is currently the only (however inaccurate) guide to EL efficiency. This observation coupled with the fact that the aim of this work was to synthesise polymers with potential electroluminescent properties, led to the descision that studies of solution state PL spectra of all the polymers synthesised were unnecessary.

To obtain EL spectra an electronic device, comprising of a single layer of polymer sandwiched between ITO and calcium electrodes, was fabricated. The layer of PDDV was spun cast from toluene onto an ITO covered glass substrate in an air and moisture free environment. A calcium electrode was then added and the EL of this device under an applied voltage investigated.

The EL spectrum of PDDV is shown in Figure 2.24. The three separate spectra are from different areas of the same device and show that the EL observed does not vary across the surface of a cast film.
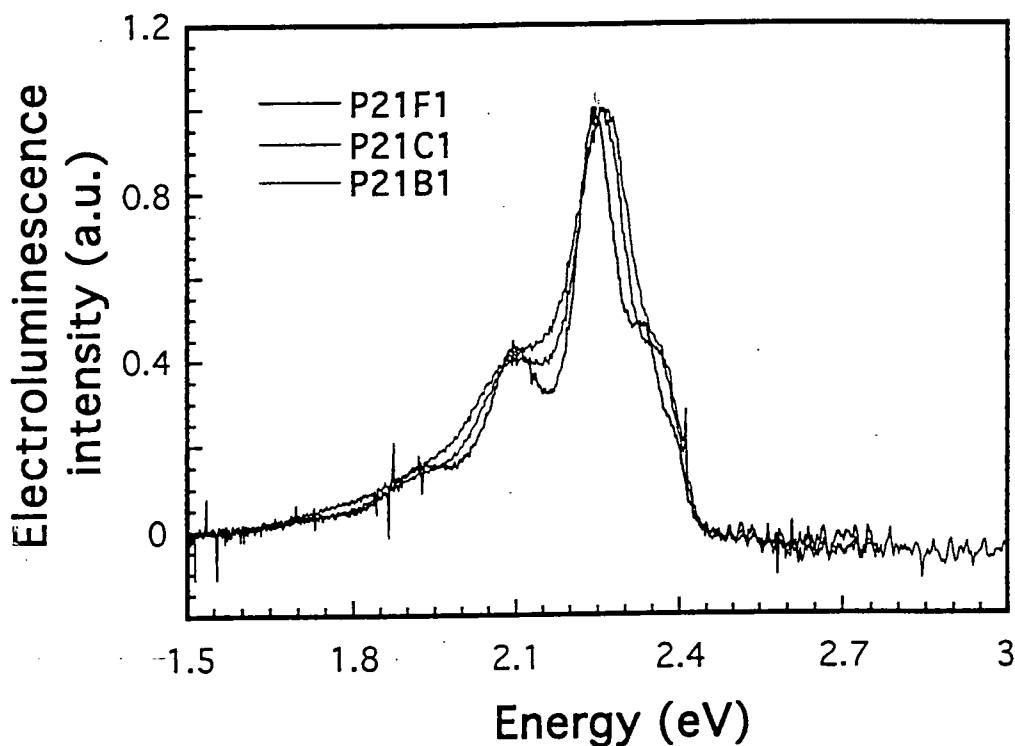
Figure 2.24 EL spectrum of a single layer device of poly(4,4'-diphenylene diphenylvinylene)

One interesting feature of the EL of PDDV is the observation that the EL spectrum of the polymer possesses some form of vibronic structure, identified by the underlying fine structure of the EL peak. This phenomenon has not been previously observed by the Cambridge workers in the EL spectra of other poly(arylene vinylene)s. At the moment this phenomenon remains an unexplained observation. If PL and EL emission are from the same excited state in the same material it would be expected that they would be the same. These observed differences, if and when they are understood, may give an insight into the device structure.

The maximum internal quantum yields (photons emitted per electrons injected) of the single layer PDDV device was ~ 0.035%. Optimisation of the device using a PPV and a poly(vinylcarbazole) layer has increased this value to 0.4 to 0.6%. These results are

summarised in Figure 2.25. This work is ongoing at the time of writing and depending on layer structure and history, yields of up to 1.2% have been recorded.
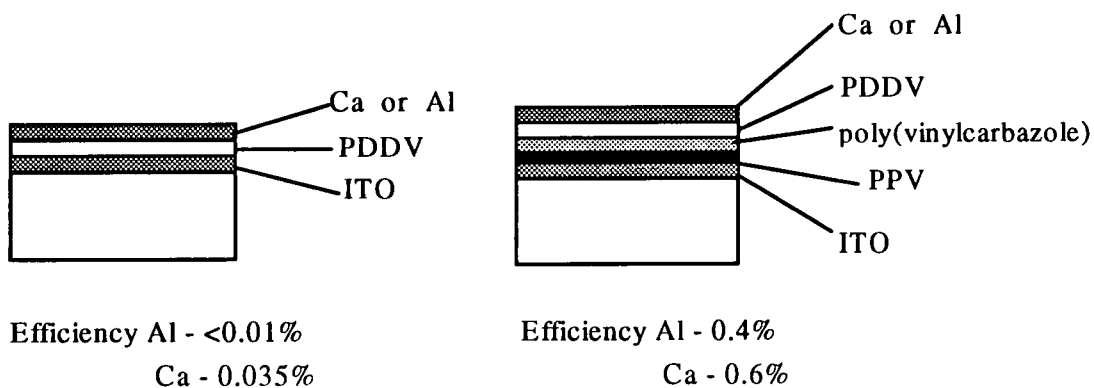

Efficiency Al - <0.01%
Ca - 0.035%

Efficiency Al - 0.4%
Ca - 0.6%

Figure 2.25 Structure and quantum efficiencies of poly(4,4′-diphenylene diphenylvinylene) EL devices

The positive holes are thought to be the majority charge carriers in PDDV and the addition of the poly(vinylcarbazole) and PPV layers are thought improve hole injection and thus increase efficiency. Compared to other PAV based systems these efficiencies are quite encouraging in view of their preliminary nature. Cyano substituted hexoxy-PPV has an EL efficiency of 4%. PPV shows an increase in efficiency of about 100 for devices fabricated with a Ca cathode rather than an Al electrode.[37] This difference is not observed for PDDV and currently no explanation for this phenomenon is available.

It is expected that the other polymers synthesised will also be electroluminescent but until stable films of the materials can be made the acquisition of EL spectra by the above technique will not be possible.

2.3 EXPERIMENTAL

2.3.1 Reagents and Apparatus

All organic reagents were purchased from Aldrich Chemical Co. and used as received unless indicated otherwise. Melting points were obtained on an Electrothermal digital melting point apparatus and are reported without correction. Infra-red spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. The ^{1}H and ^{13}C nmr spectra were recorded on either a Varian Gemini 200MHz or a Varian VXR 400MHz spectrometer. Chemical shifts are reported in parts per million (δ) and are referenced to internal TMS. Gel permeation chromatography was carried out using a Waters Model 590 (refractometer, column packing PL_{gel} 5μ mixed styrene-divinyl benzene beads, $CHCl_3$) using narrow molecular weight distribution polystyrene standards for calibration. The IR and nmr spectra for all compounds are recorded in Appendix 1.

Titanium trichloride and lithium aluminium hydride for the polymerisation reactions were weighed out in either a modified Miller Howe dry box under an inert atmosphere of oxygen-free nitrogen (working conditions 2-6 ppm oxygen 5-10 ppm H_2O) or an Atmosbag purged a minimum of five times with dry N_2 before use. The polymerisation reactions were carried out in oven dried glassware, flushed with dry nitrogen before use and throughout the reactions were kept under a positive pressure of dry nitrogen to exclude air and moisture.
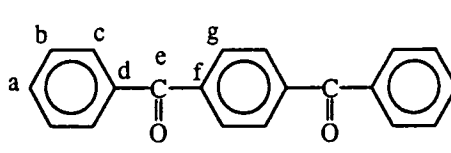
THF for the polymerisation reactions was obtained from the University of Durham Department of Chemistry and had been distilled from potassium and stored under dry nitrogen before use.

2.3.2 Preparation of monomers

trans-1,2-Dibenzoylethene (VI) was purchased from Aldrich and recrystallised twice from toluene before use. Stocks of pure m-dibenzoylbenzene (III) were available from previous workers in the IRC in Polymer Science and Technology and was recrystallised twice from toluene before use.

<u>Synthesis of 1,4-dibenzoylbenzene (II)</u>

The method of Millichamp[50] was used. Finely ground aluminium chloride (62.07, 0.465moles) was added portionwise over 60 minutes to a stirred slurry of terephthaloyl chloride (35.32g, 0.206moles) in benzene (280ml) keeping the reaction temperature below 10°C using an ice bath. Once the addition of aluminium chloride was complete the reaction mixture was refluxed for 3 hours, allowed to cool to room temperature and added to 10% aqueous hydrochloric acid solution (1200ml). The precipitated white solid was collected, successively washed with 5% potassium carbonate, 5% hydrochloric acid and water (2x200ml each) and then water until the washings were neutral. The white solid was dried overnight under vacuum (50°C, <1mbar) to give crude product (40.49g). Crude product was boiled in toluene with charcoal and recrystallised four times from toluene to give pure 1,4-dibenzoylbenzene (22.37g, 0.078moles, 38%, m.p.160.5-161.3°C, lit.[50]161°C). Found C,83.7; H,4.8; O,11.5% (calculated for $C_{20}H_{14}O_2$: C,83.9; H,4.9; O,11.2%). ^1H nmr (200MHz, $CDCl_3$), (Appendix 1.1) and ^{13}C nmr (50MHz, $CDCl_3$), (Appendix 1.2) assignments are recorded in Table 2.26. IR (KBr disc) 3083.4cm^{-1} (w, aryl C-H stretch), 1657.9cm^{-1} (s, diaryl ketone C=O), 1594.0, 1582.2, 1500.6cm^{-1} (s, aromatic C=C), (Appendix 1.3).
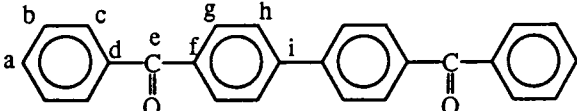

	^{13}C (δ)	^1H (multiplicity) (δ)	coupling (Hz)
a	132.93	7.64 (tt, 2H)	7.2, 1.5
b	130.09, 128.45*	7.51 (m, 4H)	-
c	130.09, 128.45*	7.84 (dd, 4H)	7.0, 1.5
d	136.92**	-	-
e	195.96	-	-
f	140.61**	-	-
g	129.69*	7.90 (s, 4H)	-

Note. the assignments marked with * or ** are interchangeable sets

Table 2.26 ^1H and ^{13}C nmr assignments of 1,4-dibenzoylbenzene (II)

Synthesis of 4,4'-dibenzoyldiphenyl (I)

The method of Millichamp was used.[50] Finely ground aluminium chloride (157.42g
1.18mol) was added portionwise over 90 minutes to a stirred slurry of diphenyl (16.91g,
0.11mol) and benzoyl chloride (179.00g, 1.27mol) in an ice bath. Once the addition was
complete the mixture was stirred at room temperature for 30 minutes and then at 80°C
for 4 hours during which time it formed into a brick red solid. Once cooled to room
temperature this solid was slowly added to ice water resulting in the precipitation of a
white solid. This solid was washed with 5% potassium hydroxide solution until the
washings were no longer acidic and then with water until the washings were neutral.
Crude product was dried overnight in a vacuum oven (50°C, >1mbar), boiled twice in
toluene with charcoal and then recrystallised five times from toluene to give pure
4,4'-dibenzoyldiphenyl product (15.99g, 40%, m.p.218.3-219.4°C, lit.[50,58] 213.5-
215.0°C, 214.5-215.5°C). Found C,86.0; H,4.8; O,9.2% (calculated for $C_{26}H_{18}O_2$:
C,86.1; H,5.0; O,8.9%). ^{1}H nmr (400MHz, CDCl₃), (Appendix 1.4) and ^{13}C (100MHz,
CDCl₃) (Appendix 1.5) assignments are recorded in Table 2.27. IR (KBr disc)
3045.1cm^{-1} (w, aryl C-H stretch), 1653.2, 1647.4, 1637.0cm^{-1} (s, ketone C=O),
1603.0cm^{-1} (m, aromatic C=C), (Appendix 1.6).

	^{13}C (δ)	^{1}H (multiplicity) (δ)	coupling (Hz)
a	132.53	7.62 (t, 2H)	7.2
b	130.00, 128.34**	7.52 (m, 4H)	-
c	130.00, 128.34**	7.85 (d, 4H)	7.6
d	137.01*	-	-
e	196.17	-	-
f	137.51*	-	-
g	130.77, 127.16**	7.93 (d, 4H)***	8.0
h	130.77, 127.16**	7.76 (d, 4H)***	8.0
i	143.83		

Note: the assignments marked with * or ** are interchangeable sets

Table 2.27 ^{1}H and ^{13}C nmr assignments of 4,4'-dibenzoyldiphenyl (I)

Synthesis of 4,4″-dibenzoyl-p-terphenyl (V)

The method of Muller was used.[52] Finely ground aluminium chloride (103.15g 0.77mol) was added portionwise over 120 minutes to a stirred slurry of p-terephenyl (38.11g, 0.17mol) and benzoyl chloride (129.01g, 0.92mol) in an ice bath. Once the addition was complete the mixture was stirred at room temperature for 120 minutes and then at 80°C for 2 hours during which time it became a brick red solid. Once cooled to room temperature this solid was slowly added to ice water (1500ml) resulting in the precipitation of a white solid. The solid was washed with 5% potassium hydroxide solution (3x300ml) until the washings were no longer acidic and then water (5x500ml) until the washings were neutral. Crude product was dried overnight in a vacuum oven (50°C, >1mbar) to give an insoluble white powder (85g). Due to this material's insolubility it was not recrystallised and was used in this unpurified state for subsequent polymerisation reactions. Found C,85.0; H,4.9; O,10.1% (calculated for $C_{32}H_{22}O_2$: C,87.6; H,5.1; O,7.3%). IR (KBr disc) 3049.9cm^{-1} (w, aryl C-H) 1644.4 cm^{-1} (s, diaryl ketone C=O), 1600.9, 1576.9cm^{-1} (m, aryl C=C), (Appendix 1.7).
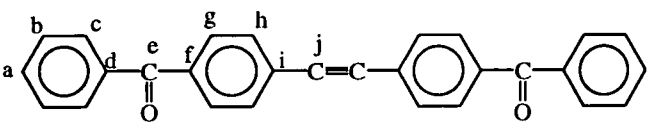
Synthesis of 4,4′-dibenzoyldiphenylacetylene (V)

The method of Seyferth was used.[51] The reaction was in three parts; (i) the formation of diphenylacetylene dicobalthexacarbonyl, (ii) the benzoylation of this complex and (iii) the release of the benzoylated compound from the cobalt complex.

(i) Diphenylacetylene (4.80g, 26.9mmol) was added over ten minutes to a stirred solution of dicobaltoctacarbonyl (9.76g 28.5mmol) in dry diethyl ether (50ml). The mixture was seen to effervesce as the diphenylacetylene was added. Once the addition was complete the mixture was stirred for 60 minutes after which time solvent was removed to give a dark purple solid, diphenylacetylene dicobalthexacarbonyl.

(ii) Benzoyl chloride (18.91g, 134mmol) was added over 10 minutes to a stirred slurry of finely ground aluminium chloride (19.72g, 148mmol) in dichloromethane (150ml) in an ice bath. Once this mixture had been stirred for 15 minutes at 0°C, diphenylacetylene dicobalthexacarbonyl (approx. 26.9mmol) in dichloromethane (50ml) was added

portionwise over 20 minutes. The mixture was stirred at room temperature for 3 hours and then poured into ice water (1000ml) and product extracted with dichloromethane (4x40ml) until the organic layers were colourless. Combined organic layers were dried (MgSO$_4$) and solvent removed to give a dark purple solid, crude 4,4′-dibenzoyldiphenylacetylene dicobalthexacarbonyl.

(iii) Ceric ammonium nitrate (29.50g, 53.8mmol) was added in spatula size portions to a stirred solution of 4,4′-dibenzoyldiphenylacetylene dicobalthexacarbonyl (approx. 26.9mmol) in acetone (150ml) allowing any effervescence to die down after each addition. The resulting slurry was stirred at room temperature for 2 hours after which time solvent was removed to give a dark blue solid. Water (80ml) was added to this solid resulting in the formation of a white precipitate. Dichloromethane (60ml) was added and product extracted with dichloromethane (9x40ml). Combined organic layers were dried (MgSO$_4$) and solvent removed to give a pale orange solid. This solid was refluxed in methanol (70ml) for 5 minutes and then cooled in a freezer to give crude off white product. Crude product was refluxed in toluene with charcoal and then recrystallised three times from toluene to give pure 4,4′-dibenzoyldiphenylacetylene (V) (1.80g, 32%, m.p.227.2-227.6°C, lit.[59] 226-227.5°C). Found C,87.2; H,4.6; O,8.2% (calculated for C$_{28}$H$_{18}$O$_2$: C,87.0; H,4.7; O,8.3%). ^{1}H nmr (400MHz, CDCl$_3$), (Appendix 1.8) and ^{13}C nmr (400MHz, CDCl$_3$), (Appendix 1.9) assignments are shown in Table 2.28. IR (KBr disc) 3050.3cm^{-1} (w, aryl C-H stretch), 1644.6cm^{-1} (s, diaryl ketone C=O), 1602.0, 1577.2cm^{-1} (m, aryl C=C), (Appendix 1.10).

	^{13}C (δ)	^1H (multiplicity) (δ)	coupling (Hz)
a	132.62	7.62 (tt, 2H)	7.2, 1.6
b	130.10, 128.38[*]	7.51 (t, 4H)	7.2
c	130.10, 128.38[*]	7.81 (dd, 4H)	7.2, 1.6
d	137.28, 137.21[**]	-	-
e	195.86	-	-
f	137.28, 137.21[**]	-	-
g	131.57, 129.97[*]	7.83 (d, 4H)[***]	8.4
h	131.57, 129.97[*]	7.67 (d, 4H)[***]	8.4
i	126.89	-	-
j	91.47	-	-

Note: the assignments marked with * or ** are interchangeable sets

Table 2.28 ^1H and ^{13}C nmr assignments of 4,4'-dibenzoyldiphenylacetylene (V)

The characterisation of the two intermediate compounds was in agreement with the literature.[51,59]

2.3.3 Preparation of polymers

All polymerisations were carried out using the same method regardless of which monomer or polymer was used.

In a typical polymerisation, lithium aluminium hydride (0.816g, 21.5 mmol) was slowly added, portionwise, over 30 minutes to a stirred slurry of titanium trichloride (6.56g, 42.5 mmol) and dry tetrahydrofuran (30ml) cooled in an ice bath, allowing any effervescence to subside after each addition. When the addition was complete the mixture was refluxed for 60 minutes. After cooling to room temperature 4,4'-dibenzoyldiphenyl (3.84g, 10.6 mmol) was added with stirring and further dry tetrahydrofuran (8ml) added. During the addition of reagents and reflux the reaction apparatus was kept under a slight positive pressure of dry nitrogen. The stirred mixture was refluxed for 18 hours, cooled to room temperature and poured into hydrochloric

acid (2M, 80ml). The reaction vessel was rinsed with HCl (2M, 20ml) and chloroform (3x30ml). Product was extracted using chloroform until the organic layers were no longer coloured (6x30ml). Combined organic layers were dried over magnesium sulphate and solvent removed to give crude polymer (2.36g). Crude material was reprecipitated from chloroform into methanol to give product polymer (2.14g, 56%).

Polymerisations of lower molecular weight polymer to higher molecular weight material were carried out using the method outlined above. The amount of polymer was estimated by assuming that after one polymerisation the material was present as 5mer and that after two polymerisations the material was present as 10mer. From these values and the assumption that polymer end groups were unreacted ketones the quantity of reducing agent could be calculated.

Experimental results are presented and discussed in Section 2.2.

2.4 CONCLUSIONS

Synthesis of poly(4,4'-diphenylene diphenylvinylene)

The results from the investigations into the synthesis of poly(4,4'-diphenylene diphenylvinylene) showed that reductive coupling of 4,4'-dibenzoyldiphenyl using TiCl₃/LiAlH₄/THF allowed high molecular weight polymer to be obtained. The effect of reaction concentration and reaction time were studied and, somewhat arbitrarily, set at 10%v/w monomer concentration and 20 hours reflux, for the majority of the polymerisations. These conditions gave satisfactory results. However, even after a large number of polymerisation reactions, spurious results were occasionally obtained for polymerisations which were performed under standard conditions. These unexplained results were attributed to the previously reported quality control problems in using the TiCl₃/LiAlH₄ system.

Characterisation of PDDV was possible and nmr spectra of reasonable resolution were obtained and tentatively assigned. These spectra seemed to indicate that cis/trans vinylene structures were present but the evidence is by no means conclusive. Samples of PDDV were found to be electroluminescent with quantum yields of 0.4-0.6% for multilayer devices using both Al and Ca as cathode materials.

Synthesis of other materials

Reductive coupling was also used in the synthesis of other polymers from diketone monomers. Poly(1,3-phenylene diphenylvinylene) and poly(4,4''-terphenylene diphenylvinylene) were both synthesised to reasonable molecular weights. Recoupling of the initially produced polymer to higher molecular weight material was possible for PMPDV but not PPTDV. This lack of reaction for PPTDV was attributed to either polymer insolubility or to the presence, in the impure monomer, of chain terminating mono benzoylated p-terphenyl. Purification of the monomer in future polymerisation reactions should be attempted. Thin films of PPTDV and PMPDV were obtained but were not of sufficiently high quality for EL testing, whilst the products from the attempted polymerisations of the other three monomers were not film forming at all. Given the EL of PDDV there is no reason why PMPDV and PPTDV should not be EL and EL testing of these material once they are available as good film forming samples

would be of interest as both polymers should have shorter conjugation lengths than PDDV and therefore should show a blue shift in their EL spectra.

Polymerisation of monomers 1,4-dibenzoylbenzene, 4,4'-dibenzoyldiphenylacetylene and trans-1,2-dibenzoylethylene were attempted using the TiCl₃/LiAlH₄ system but were, in each case, unsuccessful. In the attempted synthesis of poly(1,4-phenylene diphenylvinylene) monomer and pinacol dimer were formed, whilst the attempted synthesis of poly(4,4'-diphenylacetylene diphenylvinylene) and poly(1,2-ethylene diphenylvinylene) resulted in the formation of dimers, trimers and at best tetramers.

Suggestions for future work

Reductive coupling using TiCl₃/LiAlH₄ was found to be somewhat unpredictable. Although the yields for the model reaction, dimerisation of benzophenone, are reportedly lower using reducing systems other than TiCl₃/LiAlH₄ and would therefore be expected to produce polymer with a lower degree of polymerisation, the application of these other systems needs to be investigated especially as they are reported to give reproducible results and may produce materials with acceptable molecular weight. In particular, the reagent generated from TiCl₃ and a Zn-Cu couple in dimethoxyethane would be worth further study.

Recoupling of PDDV and PMPDV using fresh batches of reducing agent did result in an increase in polymer molecular weight. The possibility that end groups are secondary alcohols allows for their oxidation to generate carbonyl end groups which could be recoupled. Preliminary experiments, not reported in this work, involving oxidation and recoupling gave promising results.

More detailed investigation of the nature of the polymer end groups would also be beneficial. This would allow the chain termination steps to be determined and the experimental method modified to minimise their effect. For example if chain ends were found to be secondary alcohols arising from the reaction of water with intermediate species in the coupling reaction, polymerisation using even more rigorously dried reagents could be attempted.

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would be of interest as both polymers should have shorter conjugation lengths than PDDV and therefore should show a blue shift in their EL spectra.

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The range of monomers successfully polymerised in this work was disappointing. Those polymers which were synthesised all contained an arylene group in the polymer backbone and were all relatively soluble. Other polymers that might be of interest include:

(i) poly(p-quaterphenylene diphenylvinylene) which is expected to be only sparingly soluble but should give a polymer with a significant amount of PPP character,

(ii) polymers that are asymmetrically substituted about the vinylene which should allow further investigation into any cis/trans vinylene structures, and

(iii) polymers possessing electron withdrawing functionalities. These have been shown to alter EL emission colour and increase EL efficiency.

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CHAPTER 3

Investigations into the Attempted Ring Opening Metathesis Polymerisation of Quinone Substituted Norbornadiene Monomers

3.1 INTRODUCTION

3.1.1 Ring opening Metathesis Polymerisation

Ring opening metathesis polymerisation (ROMP) is the transition metal catalysed polymerisation of cyclic olefins to give linear unsaturated polymers and was developed
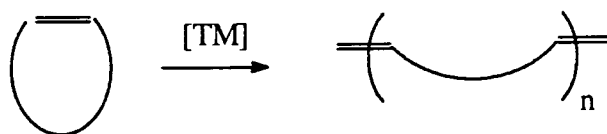
Figure 3.1 Schematic representation of ROMP

from the olefin metathesis reaction.[1] The first reported observation of ROMP was in 1955,[2] before the name ring opening metathesis polymerisation had been coined. Work by Calderon showed that transition metal catalysed alkene exchange and ring opening polymerisation were the same process and introduced the now accepted term 'olefin metathesis'.[3] A characteristic feature of this reaction is that the monomer carbon carbon double bond is preserved in the polymer and is not sacrificed in the polymerisation reaction. In addition, suitable monomers with additional carbon carbon double bonds retain this unsaturation in the polymer and bicyclic compounds retain a ring in the polymer repeat unit.
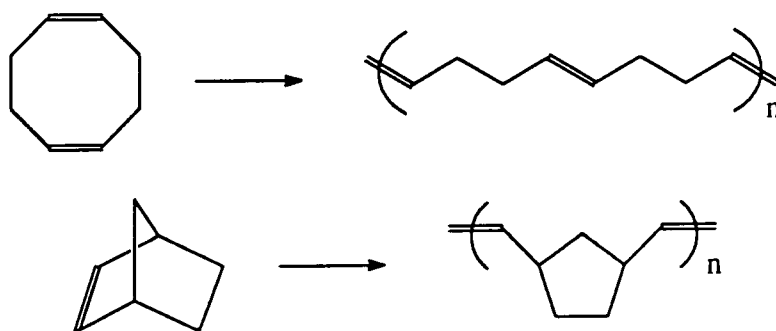
Figure 3.2 How monomer functionality can be retained after ROMP

The first generation of catalysts, known as the 'classical initiators', are transition metal halides usually activated by a co-catalyst (an organometallic compound or Lewis acid). Occasionally a third component (an alcohol or other oxygen containing compound) is added to the system to increase activity.

These classical initiators possess certain disadvantages that include (i) a limited tolerance to functional groups on the monomer, (ii) lack of control over the molecular weight and molecular weight distribution of the polymer (due to intermolecular reactions of the propagating species with double bonds already in the propagating chain), (iii) a complex reaction mechanism including the generation of many different species in the reaction mixture which are not easily characterised and (iv) an element of irreproducibility.

A second generation of initiators has been developed and these have been termed the 'well defined initiators' due to the fact that the initiators, initiating species and propagating species often can be fully characterised and a high degree of control over the polymerisation reaction is possible. These compounds are mainly based on organometallic compounds of the transition metals Ti, Mo, W and Ru. Early examples of well defined compounds that were capable of inducing metathesis were the Fisher and Casey carbenes[3,4] which were later shown to polymerise strained olefins.[5,6]

Figure 3.3 Fischer (left) and Casey (right) carbenes

Grubbs[7] reported titanium compounds which were able to ROM polymerise norbornene and are unique amongst the metathesis initiators in that they exist as metallocyclobutanes rather than as carbenes.
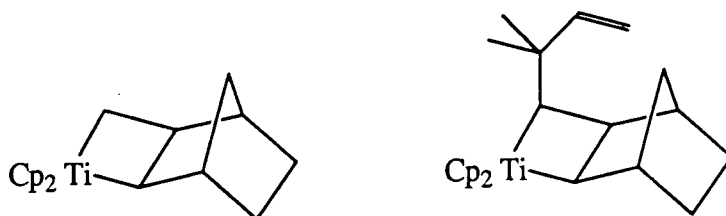
Figure 3.4 Grubbs titanacyclobutanes

The polymerisation reactions described later on in this chapter used either Schrock type molybdenum or Grubbs type ruthenium initiators and the next few pages of the introduction gives a brief overview of ROMP using these initiators.

Molybdenum and ruthenium based initiators

Schrock has reported a group of initiators based on Mo and W centred complexes surrounded by bulky ligands which have been shown to polymerise a wide range of monomers under various reaction conditions[8] and allow good control over the molecular weight of the polymer by varying the reaction stoichiometry, while giving a narrow molecular weight distribution.

M = Mo or W
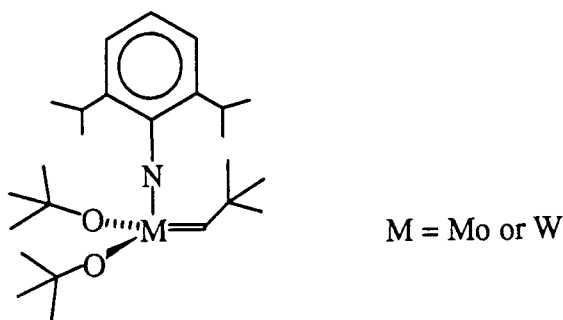
Figure 3.5 Schrock type initiators

The methyls of the t-butoxide groups can be replaced by trifluromethyl groups and this gives more active initiating systems.[9] Polymerisations using these initiators have been shown to be living, that is there is no spontaneous termination step. This allows control of molecular weight and the formation of block co-polymers. Termination of polymerisation reactions is generally via addition of an aldehyde (benzaldehyde) which 'caps' the end of the living chain.

One major disadvantage of these single component systems is that they are very sensitive to traces of water and oxygen and are, on the whole, intolerant to -OH, -COOH, -COR and -NH₂ functionality on the monomer.

More recently a new generation of well defined initiators has been developed which will ROMP strained olefins in the presence of protic solvents such as methanol and water.[10,11] These initiators are based on a ruthenium vinyl carbene as shown in Figure 3.6.

Substitution of the triphenylphosphine ligands for tricyclohexylphosphine ligands gives a more active initiator. Because these initiators tolerate a wide range of monomer functionality[12] they show great potential in the investigation of monomers that previously resisted polymerisation. Termination is achieved by the addition of a vinylether because the ruthenium carbene is unreactive towards aldehydes or ketones.
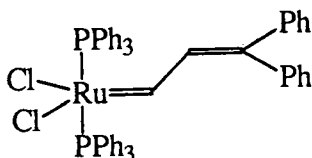
Figure 3.6 Grubbs well defined ruthenium initiators

Initiation and polymerisation mechanisms

ROMP using Schrock type initiators is thought to proceed by the initial co-ordination of the olefin to the metal centre followed by the formation of a metallocyclobutane and then bond reorganisation to give a new repeat unit in the polymer chain and a new carbene, following the sequence first proposed by Chauvin.[13]
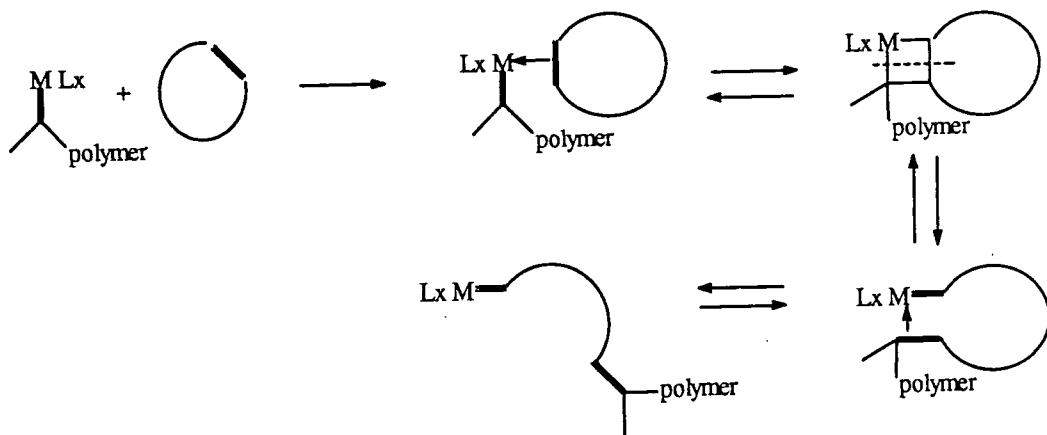
Figure 3.7 Schematic representation of the Chauvin mechanism for ROMP

M for the initiators used in this work was Mo but the same mechanism will also be applicable for W. The symbol Lx represents the associated ligands. Both initiation and propagation are though to proceed via this metallocyclobutane intermediate, for which

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there is good evidence.[14] Termination using an aldehyde or ketone is via a Wittig like reaction.
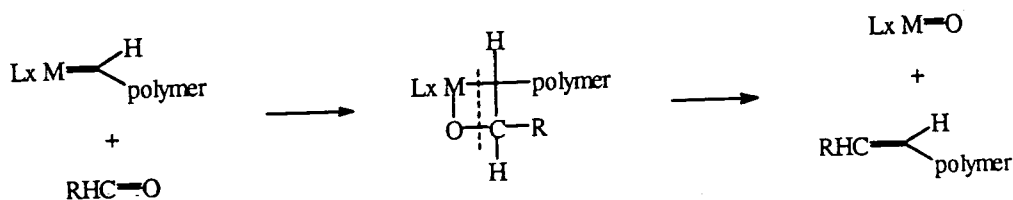
Figure 3.8 Termination mechanism for Schrock type initiators

Due to the fact that carbon carbon double bonds are formed in the polymer chain, intra and intermolecular chain transfer may occur. These are not termination steps but lead to a broadening of the molecular weight distribution and reduce control of the overall molecular weight. Such effects are most common with monocyclic monomers and negligible with polycyclic monomers where the double bonds in the polymer chain are sterically inaccessible.

Monomers and polymers

Ring strain has been proposed as playing a large part in determining which monomers can be easily polymerised. In monocyclic 5,6 and 7 membered rings ring strain is low and consequently the thermodynamics of polymerisation are usually unfavourable making polymerisation very sensitive to reaction conditions such as temperature and monomer concentration. Strained monocyclic (3,4 and more than 8 membered rings) and bicyclic monomers (with strained 5 and 6 membered rings) will polymerise readily under a range of reaction conditions. Bicyclic monomers based on norbornene have been extensively studied due to their ready polymerisation and facile synthesis using the Diels Alder chemistry of cyclopentadiene.[8]

Polymers synthesised from bicyclic rings possess interesting, if complicated, microstructures arising from the carbon carbon double bond and the ring in the repeat
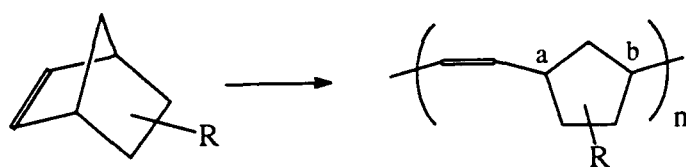
Scheme 3.1

unit. Firstly the carbon carbon double bond allows cis and trans isomers and secondly the two carbon atoms a and b in Scheme 3.1 are chiral centres and introduce tacticity effects into these polymer structures. If the chirality of the centres either side of a double bond are the same then a racemic dyad is formed, if they are different a meso dyad is formed. Sequences of racemic dyads result in syndiotactic polymer whereas sequences of meso dyads result in isotactic polymer. A statistical distribution of racemic and meso dyads gives atactic polymer. These 2 factors combined give the 4 possible structures shown in Figure 3.9.
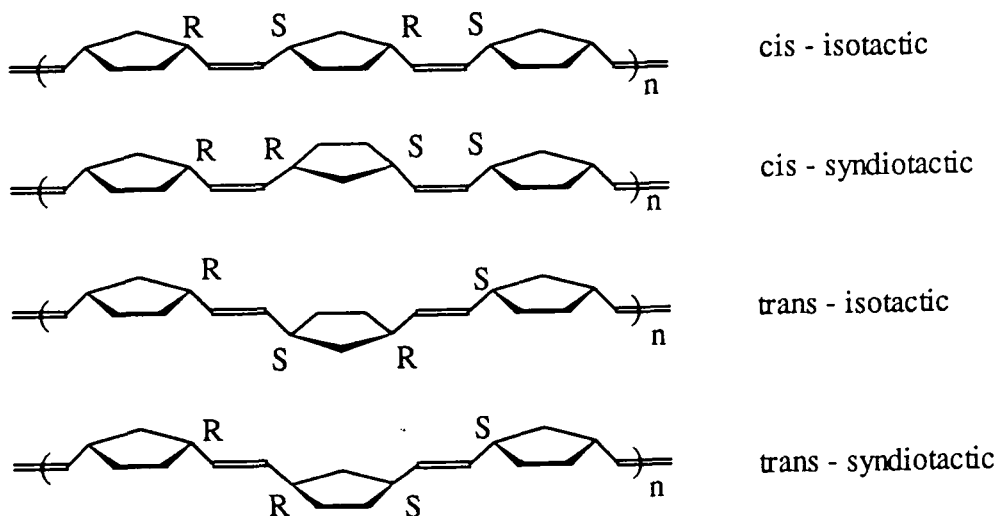
Figure 3.9 Structural isomers in polymers from bicyclic monomers

A further complication arises if the monomer is unsymmetrically substituted. Head-head, head-tail and tail-tail structures will also then be possible (Figure 3.10).
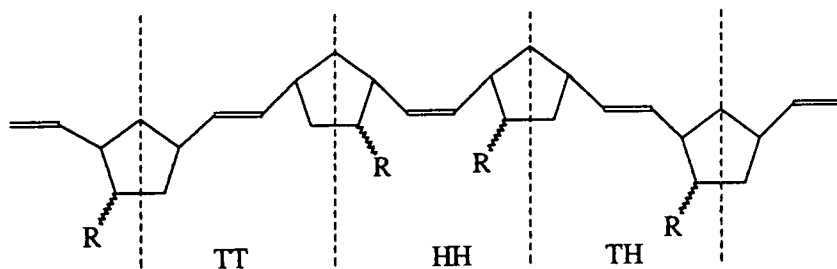
Figure 3.10 Head-head, tail-tail and head-tail structures in a polymer chain

All these factors serve to complicate the overall polymer structure and can make full spectral assignment difficult. Experiment has shown that, amongst other factors, reaction conditions (concentration, temperature and solvent) and choice of initiator controls the exact polymer microstructure. Given this array of possible polymer structures it is worth noting that stereoregular structures can be synthesised by suitable choice of monomer, initiator and reaction conditions.

More detailed reviews of ring opening metathesis polymerisation are available in the literature.[8,15,16]

3.1.2 Conjugated Polymers Via ROMP

The retention of the monomer double bond in the polymer repeat unit makes ROMP attractive as a method of synthesising conjugated polymers. However only a few conjugated polymers have been directly synthesised via ROMP, the technique having been generally limited to the production of precursor polymers. The classic example of this is the 'Durham' route to polyacetylene[17] in which the precursor polymer formed from the ROMP of a substituted cyclobutene undergoes a retro-Diels Alder reaction to give polyacetylene. A more direct route to a substituted polyacetylene is via ROMP of a substituted cycooctatetrene to give polyacetylene without first synthesising a precursor polymer[18] (Scheme 3.2)

Scheme 3.2

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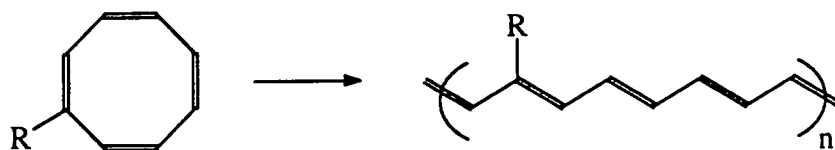
Other approaches to conjugated polymers involve the polymerisation of substituted norbornenes and then elimination to give the desired products[19] (Scheme 3.3).
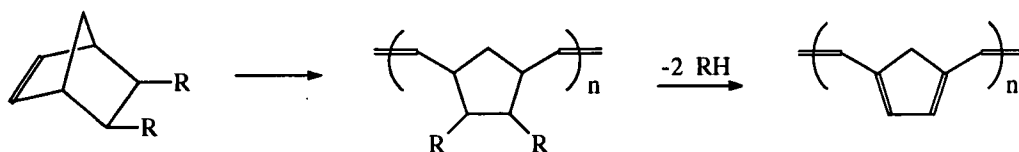
Scheme 3.3

Polymerisation of oxa-norbornadienes gives soluble precursor polymers. The tertiary hydrogens are expected to be labile, since they are α to an oxygen and doubly allylic, and in practice they are readily removed to give conjugated polymer (Scheme 3.4). Substitution at the 2 and 3 positions in the monomer gives soluble polymer.[20]
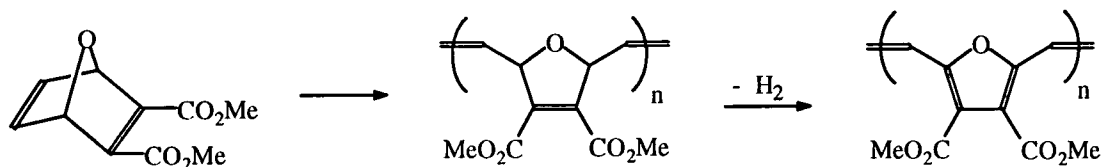
Scheme 3.4

ROMP has also been shown as a suitable way to synthesis 'cross conjugated' polymers where instead of conjugation down the main chain of the polymer conjugation lies across the chain.[21] The polymer synthesised from the ROMP of 3,4-diisopropylidenecyclobutene is a film forming material which on doping with iodine exhibits electrical conductivity up to 200 Scm[-1].
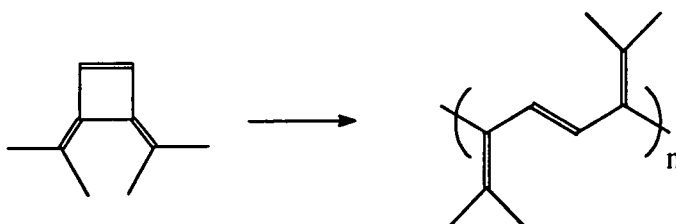
Scheme 3.5

PPV and PPV precursor polymers have also been synthesised by ROMP (see Chapter 2).

Another route to conjugated polymers via ROMP is the synthesis of a precursor polymer which can be converted to conjugated polymer. Harper reported the polymerisation of a dichlorocarbonate substituted norbornene followed by hydrolysis of the polymer via a diketone which is isomerised in situ to give the fully conjugated polymer.[22]
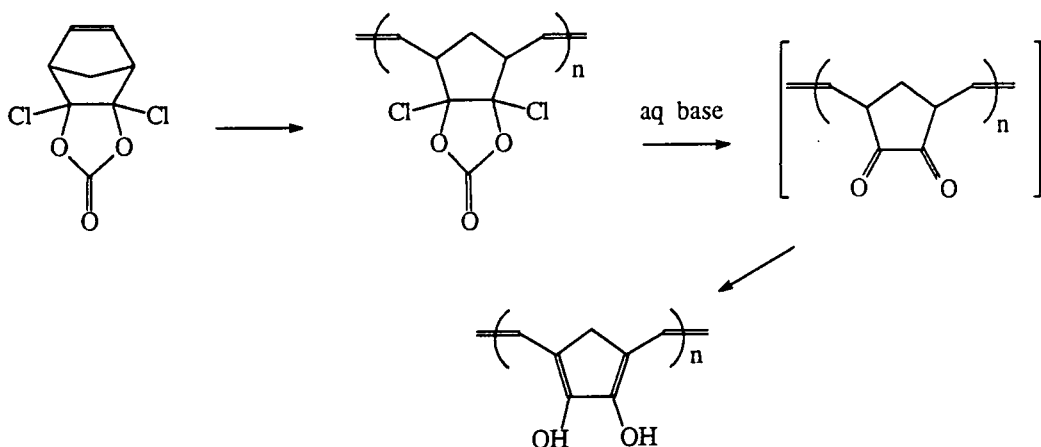
Scheme 3.6

The synthesis above relies on a keto-enol tautomerism and Swager has reported the attempted polymerisation of a p-benzoquinone substituted norbornene to give a polymer that might isomerise in a similar way to give a conjugated polymer[23] (see Figure 3.11)
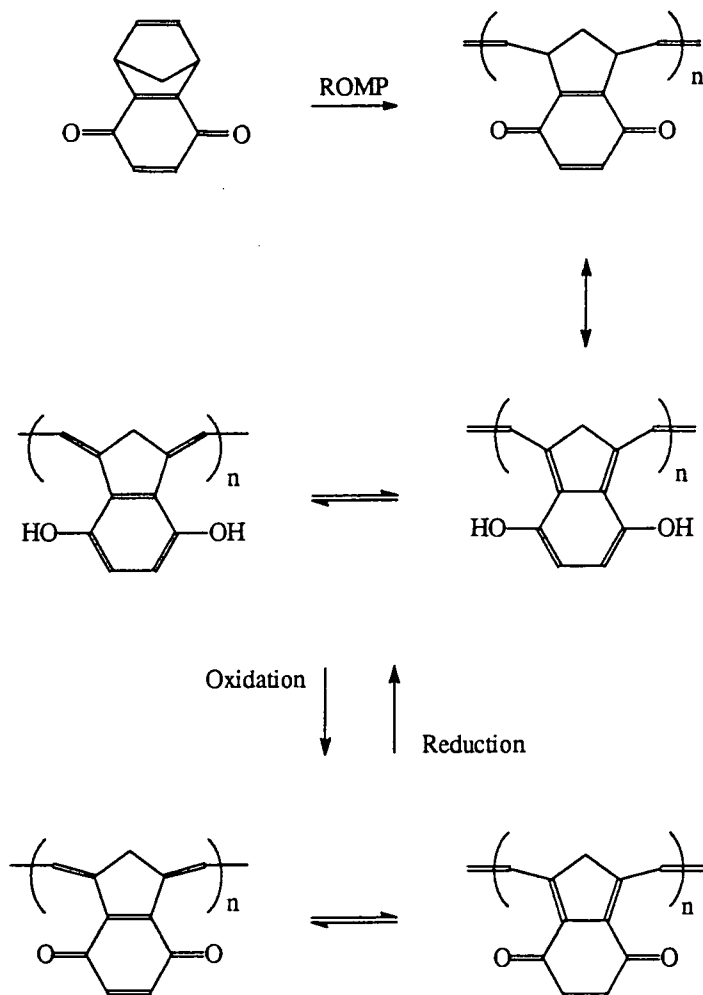
Figure 3.11 Reaction scheme proposed by Swager[23]

One important feature of this potential polymer is that the fully conjugated hydroquinone polymer should be able to be oxidised to give the quinone polymer. Oxidation of hydroquinones proceeds via intermediate species that carry unpaired electrons and single charges.[24] If these intermediate states can be generated along the polymer chain the polymer might be 'n-doped' in a more controllable way than via chemical or electrochemical doping, in which there is no control over where doping induced electronic defects lie on the polymer backbone. However this monomer was not successfully polymerised using a range of classical and well defined initiators but the target polymer was synthesised via the precursor route shown in Scheme 3.7 and gave insoluble conjugated polymer which displayed a conductivity of 5×10^{-4} Scm^{-1} when doped with iodine.
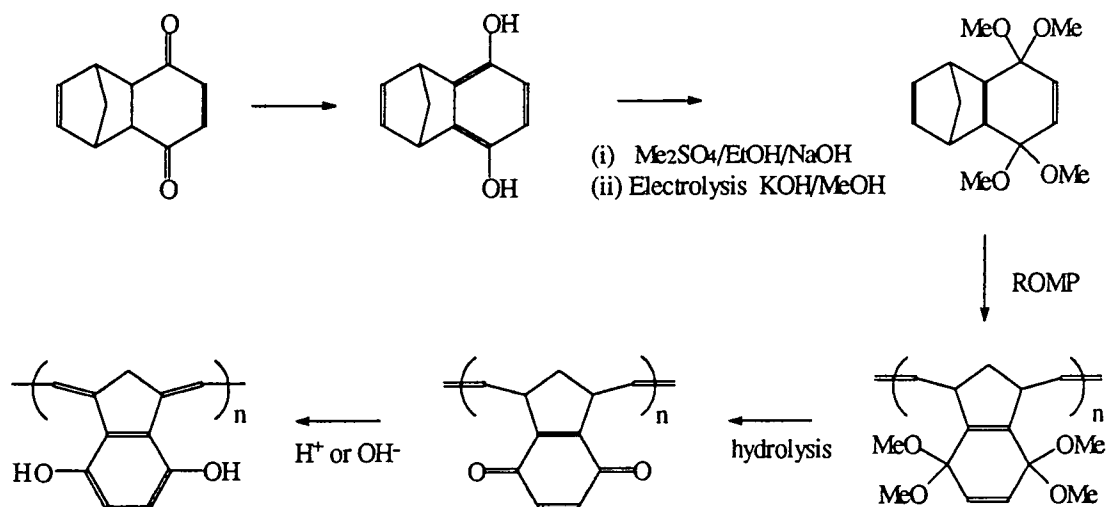
Scheme 3.7

3.1.3 Project Aims

Since the report by Swager[23] of the difficulty of polymerising the p-benzoquinone substituted norbornene, several new initiators have been developed that are more tolerant to monomer functionality. These include the Schrock molybdenum initiator which has been shown to polymerise substituted norbornenes containing ester, cyano, imide and acetate functionalities[15,25] and the Grubbs ruthenium initiator which has been reported to be tolerant to ketone, aldehyde, ester and acid functionality.[12]

It was decided that an attempt to polymerise monomers I, II, III and IV (see below) using these two initiators was sensible and would give a series of polymers (some of which would be fully conjugated) which were related by tautomerism and redox chemistry without the need for the precursor polymers used by Swager.
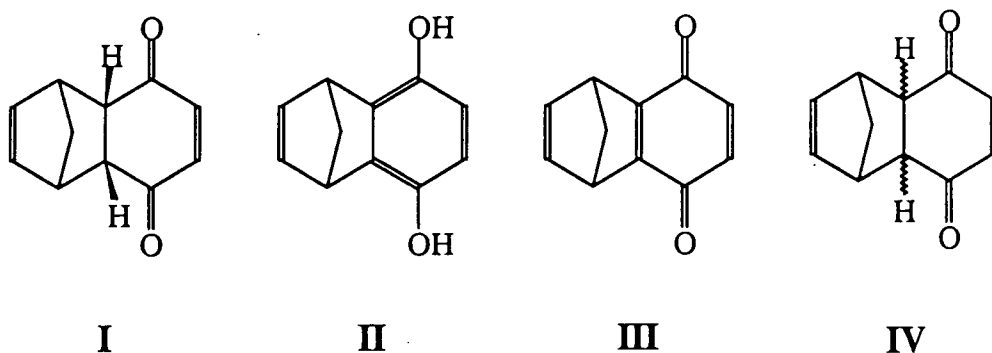
Figure 3.12 Monomers to be polymerised in this work

3.2 RESULTS AND DISCUSSION

3.2.1 Introduction

In 1990 Swager reported[23] the attempted ROMP of III using the classical and well defined initiators shown in Figure 3.13.
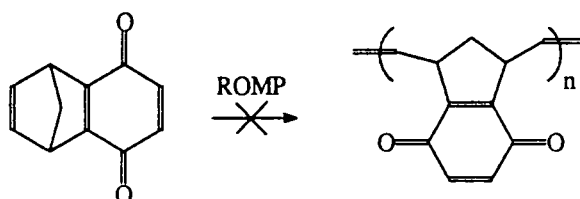
Initiators used : $OsCl_3$, $RuCl_3$, $IrCl_3$, $ReCl_3$, WCl_6:$SnMe_4$, $(CO)_5W=C(OMe)Ph)$,
$W(CHCMe_3)(OCMe_3)_2(N-C_6H_3(CHMe_2)_2)$ and $Ti(\eta-Cp_2)(-CH_2C(Me_2)CH_2-)$

Figure 3.13 ROMP reaction attempted by Swager

These polymerisations were not successful and this lack of success was attributed to the to either the reactivity of the catalysts towards the carbonyl groups of the monomer or the oxidising character of the quinones. To produce polymer a precursor route was used (see Section 3.1.2, Scheme 3.7).

Since that time new initiators have been developed, some of which are tolerant to functional groups on the monomer, in particular, the Schrock type molybdenum centered initiators and the Grubbs type ruthenium initiator shown in Figure 3.14. The only attempt to polymerise these potentially interesting redox monomers was the work of Swager described above and it seemed worthwhile to re-examine these systems with the new initiators. The work described below utilises the monomers I, II, III and IV and, of these, only III appears to have been studied previously.
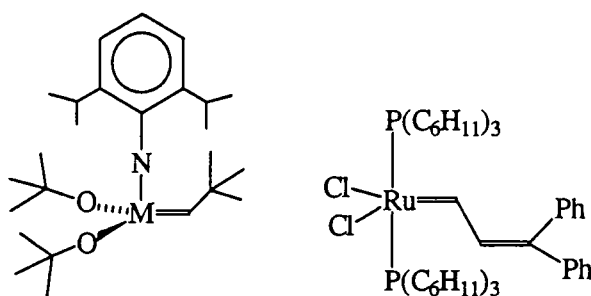
Figure 3.14 Schrock molybdenum and Grubbs ruthenium initiators

ROMP of monomer III and then tautomerism should give the redox polymer system envisaged by Swager without the need for precursor polymer (Scheme 3.8)
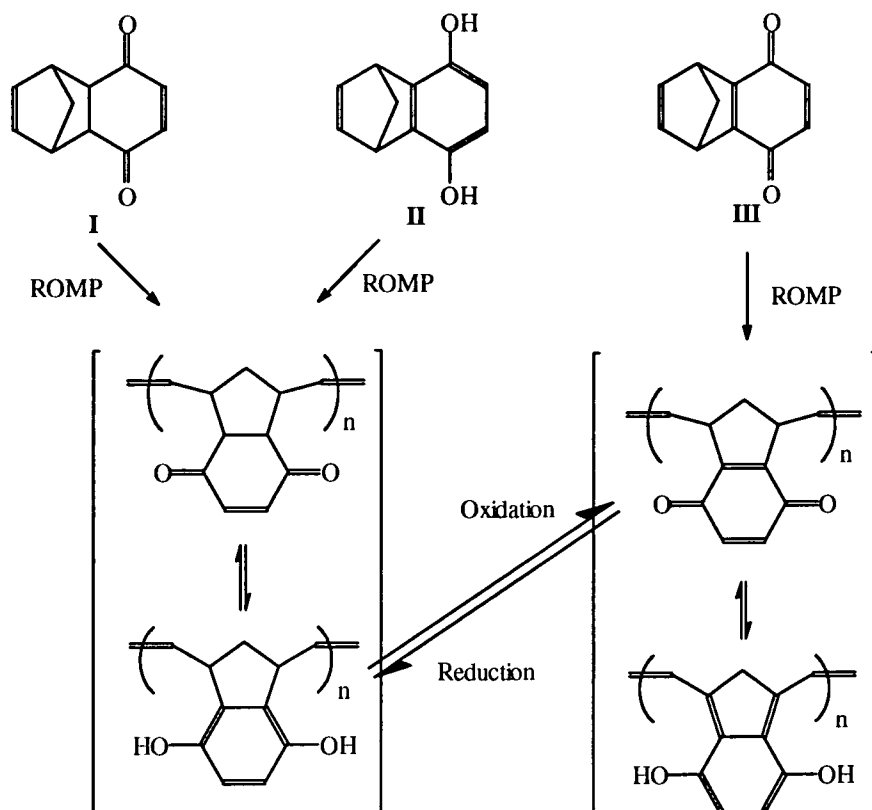
Scheme 3.8

ROMP of monomer I on the other hand should give a non-conjugated polymer which then could be oxidised to give a fully conjugated polymer (Scheme 3.8).

Monomer II however was not expected to be polymerised by the molybdenum initiator due to the presence of the phenolic type -OH groups and this reaction was not attempted. Polymerisations using this type of monomer where the -OH has been replaced by an ester functionality have been successful.[26] The ruthenium initiator, which has been reported to be tolerant to protic solvents[10] and therefore might be expected to be tolerant to the -OH functionality of monomer II was expected to give the same non-conjugated polymer as monomer I which could then be oxidised to give a fully conjugated polymer (Scheme 3.8).

Once in the fully conjugated hydroquinone form these polymers should be able to be either tautomerised to the non-conjugated quinone form (an unwanted reaction) or be oxidised to the fully conjugated quinone form (see Figure 3.15). The fully conjugated hydroquinone and quinone forms should be interconvertable via redox chemistry, possibly electrochemically, and hence it should be possible to control the redox state of such a polymer and the number and type of charge carriers on the chain. In this case
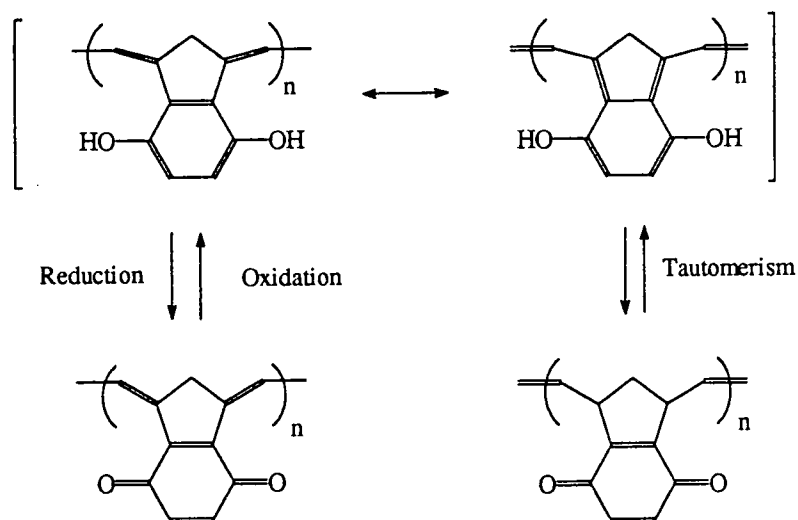
Figure 3.15 Modification of product polymers

such charge carriers could be delocalised radicals, radical anions and anions, that is to say n-type systems, in contrast to most doped conjugated polymers which are p-type systems.

3.2.2 Monomer Synthesis

The four benzoquinone substituted norbornene monomers were synthesised by literature procedures.[27,28] Their nmr and IR spectra are given in Appendix 2 and the assignments of the ^{1}H and ^{13}C nmr spectra are given in Experimental Section 3.3. Assignments were made on the basis of literature values, the splitting patterns seen in the proton nmr and, where necessary to confirm ambiguous assignments, from HETCOR nmr experiments.

Two of the assignments (b and d in Table 3.1) given by Yates and Switlak[28] for endo and exo 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione are given as interchangeable

and are marked with an asterisk. The assignments for the endo isomer were resolved by Cadd[29] using a HETCOR nmr experiment. The exo compound remained unassigned so a HETCOR nmr experiment was run to identify b and d. Assignments from the three sources are given in Table 3.1.

	^{13}C Assignments of endo (I) and exo (IV) 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (Shift ppm)					
Carbon	Yates and Switlak[28]		Cadd[29]		This work	
	I	IV	I	IV	I	IV
a	133.1	137.4	-	-	135.23	137.45
b	48.3*	48.1*	48.7	-	48.72	49.14
c	48.6	44.1	-	-	48.66	44.50
d	48.7*	49.3*	48.3	-	48.29	48.41
e	199.2	199.2	-	-	199.38	199.30
f	141.9	141.7	-	-	142.00	141.79

Table 3.1 ^{13}C nmr assignments of endo and exo 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione

3.2.3 Attempted Polymerisations
Using Schrock type molybdenum initiators

Polymerisation reactions using molybdenum initiators give characteristic ^{1}H nmr signals for the alkylidene hydrogen. The chemical shift of this peak depends on the nature of the ligands attached to the metal and whether the alkylidene is present in an initiating or propagating species (see Figure 3.16)

Figure 3.16 Initiating (left) and propagating (right) alkylidene hydrogens. Molybdenum and its associated ligands are represented as [Mo].

In polymerisation reactions either both initiating and propagating alkylidene hydrogens or just propagating alkylidene hydrogen can be observed by ^{1}H nmr, the two signals differing in chemical shift and multiplicity. If only initiating alkylidene is observed then it can be concluded that monomer has not reacted with the initiator and polymerisation has not yet taken place.

Polymerisations (nmr tube scale) of monomers I and III were attempted using either Mo($=$CHCMe$_3$)(OCMe$_3$)$_2$(N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$) or Mo($=$CHCMe$_2$Ph)(OCMe$_3$)$_2$(N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$) (hereafter referred to as V and VI respectively). Once the solutions of monomer and initiator had been mixed together and stirred for a minimum of 20 minutes they were transferred to an nmr tube with a teflon tap and the ^{1}H nmr spectrum recorded. The attempted polymerisations are detailed in Table 3.2.

Monomer		Initiator		Deuterated Solvent	Evidence of Initiation
	Amount (mmol)		Amount (mmol)		
III	0.182	VI	0.019	benzene	None
III	0.256	VI	0.022	benzene	None
III	0.191	VI	0.018	THF	None
I	0.220	V	0.019	benzene	None

Table 3.2 Attempted polymerisations using Mo initiators

The ratio of monomer to initiator was kept low (approx. 10:1) so that if polymer was formed it would be of low molecular weight and probably soluble. In none of the attempted polymerisations was an alkylidene hydrogen signal observed after mixing monomer and initiator. From this it can be concluded that either the initiator had been deactivated before polymerisation or that polymerisation had occurred and the propagating species had been deactivated. No polymer was observed spectroscopically indicating that the initiator had been deactivated before it was able to initiate polymerisation. The two different initiators were used because the supply of initiator VI ran out before the series of experiments was complete. The reactivity and chemistry of these two initiators can, for the purposes of ROMP, be considered identical.

One possible initiator deactivating reaction is the Wittig type reaction between one of the carbonyl groups of the monomer and the Mo carbene.
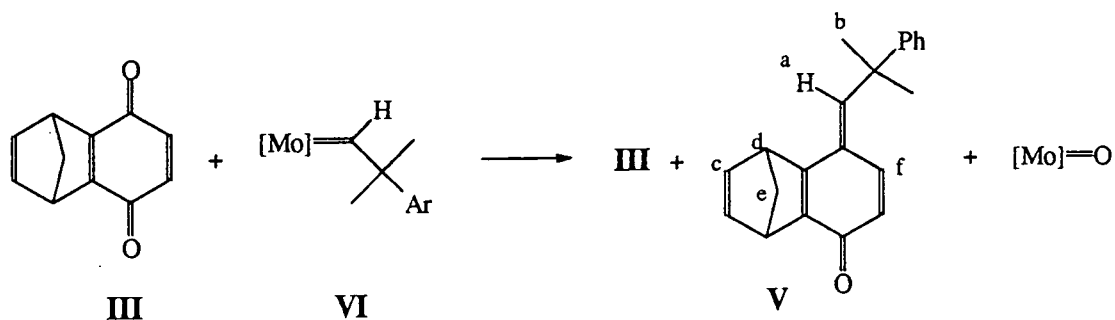
Scheme 3.9

The ^{1}H nmr spectrum of one experiment (Figure 3.17) using monomer III was sufficiently well resolved to make a tentative identification of unreacted monomer and the product from reaction of initiator with a carbonyl compound (Scheme 3.9). The 'capped' monomer (V) was not positively identified, the signals from the monomer hydrogens were expected to obscure hydrogens c,d,e and f of V, b was expected to be a small singlet within the signals between δ1.21 and δ1.42, the aromatic protons may be the small peaks near δ7.00 and the location of peak a could not be ascertained. Evidence for this capping reaction comes from the observed shifts in peak positions for various clearly identified signals of the initiator VI to positions expected for the corresponding molybdenum oxide derivative. Table 3.3 gives the literature assignments of these initiator and molybdenum oxide peaks (recorded in C_6D_6, 400MHz) and the peaks observed in this experiment.

Proton	Initiator VI[30] (shift ppm)	Molybdenum oxide[31] (shift ppm)	Clearly observed in this experiment (shift ppm)
Mo=CHCMe$_2$Ph	11.31 (s)	-	-
N-C$_6$H$_3$(CHMe$_2$)$_2$	4.00 (sept)	4.33 (sept)	4.33
N-C$_6$H$_3$(CHMe$_2$)$_2$	1.27 (d)	1.35 (d)	1.35
OCMe$_3$	1.26 (s)	1.26 (s)	1.26
Mo=CHCMe$_2$Ph	1.70 (s)	-	-

Table 3.3 ^{1}H nmr literature assignments for initiator VI and the corresponding molybdenum oxide derivative
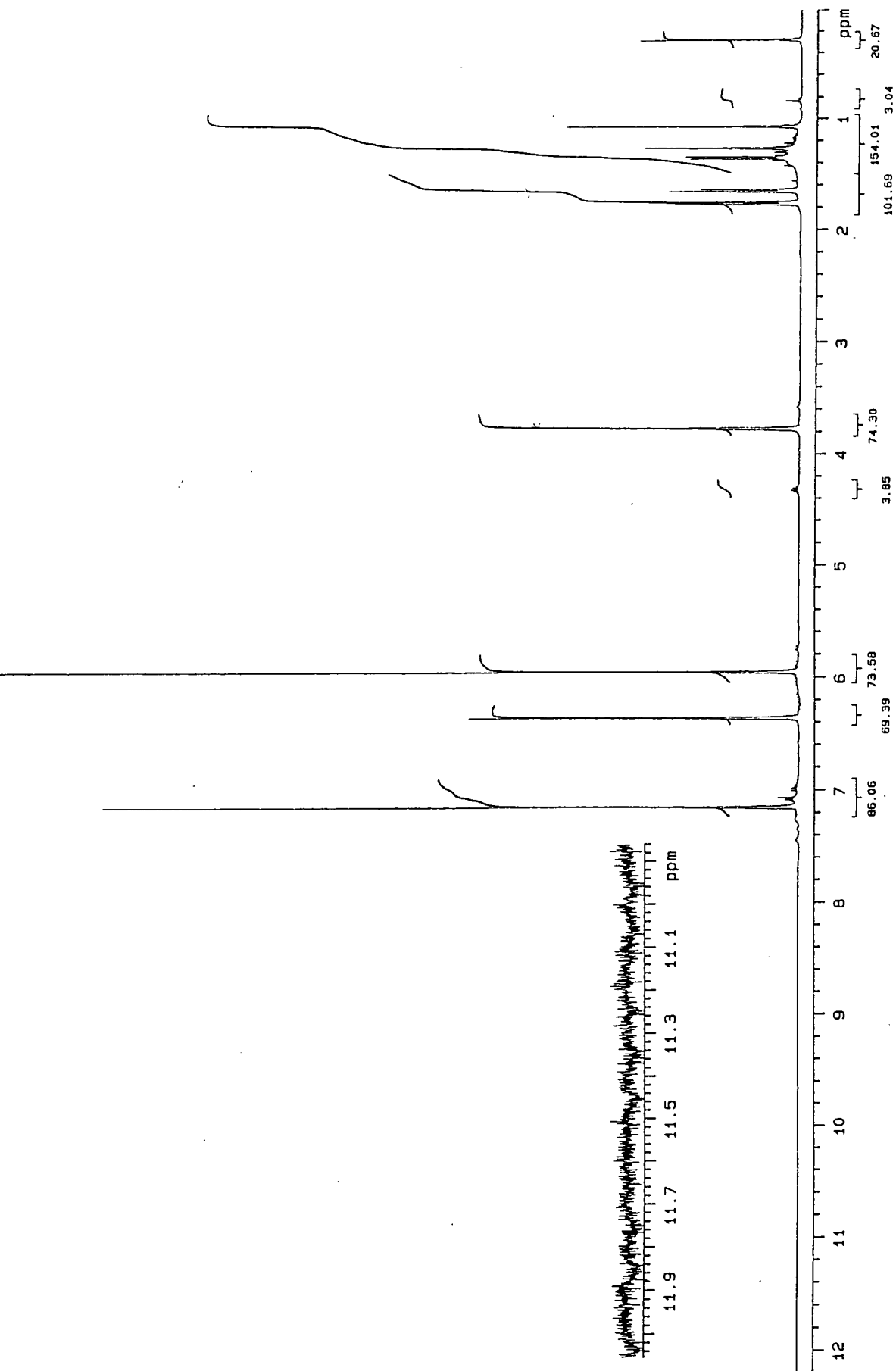
Figure 3.17 ^{1}H nmr spectrum of the results from the attempted polymerisation of III with initiator VI

The good correlation between the observed peaks and the peaks of the molybdenum oxide is an indication that such a capping reaction may be taking place and deactivating the initiator. Other explanations could be the introduction of air or moisture into the reaction which would also cause the formation of the molybdenum oxide. A control experiment using the same reaction technique, solvent (C_6D_6) and initiator with bis(trifluromethyl)norbornadiene successfully produced polymer indicating experimental competence and showing that reaction conditions were not leading to initiator deactivation.

Analysis of the ^{1}H nmr spectrum of the attempted polymerisation of monomer I also showed peaks corresponding to the molybdenum oxide. The peaks at $\delta6.01$, $\delta5.75$, $\delta3.21$, $\delta2.52$, $\delta1.07$. $\delta1.05$ and $\delta0.72$ are assigned to unreacted monomer, the septet at $\delta4.32$ to [Mo=O](N-$C_6H_3(CHMe_2)_2$), the doublet at $\delta1.35$ to [Mo=O](N-$C_6H_3(CHMe_2)_2$) and the singlet at $\delta1.26$ to [Mo=O](OCMe$_3$). Again no peaks could be positively assigned to 'capped' monomer.

These attempted polymerisations were not successful and the lack of success seems to be due to reaction of the monomer functionality with the initiator - a similar problem to that reported by Swager.

Polymerisations with Grubbs type ruthenium initiators
Given the potential tolerance of the ruthenium carbenes to the functionalities possessed by the monomers I, II and III, ROMP using the tricyclohexylphosphine substituted ruthenium initiator (VII) (Figure 3.14) was attempted.

The author is grateful to Dr David Snowden of the IRC in Polymer Science and Technology at the University of Durham who prepared the ruthenium initiator and carried out the attempted polymerisation reactions for his time and efforts.

As with the molybdenum initiators the ruthenium initiators have a characteristic alkylidene proton signal, the chemical shift of which depends (inter alia) on whether it is present as a propagating or initiating species. Also the ruthenium initiators have

characteristic colours for the pure initiator (dark red), propagating species (light red) and terminated or deactivated species (dark green/black). Observation of these colours makes following a polymerisation reaction fairly simple.

Polymerisations were attempted on all four monomers. Experience had showed that exo monomers were often more amenable to polymerisation than the endo monomers so polymerisation of the exo monomer (IV) was also tried. The polymerisation reactions attempted are shown in Table 3.4.

Monomer	Monomer to Initiator Ratio	Solvent	Polymerisation Technique	Evidence of Initiation
I	400:1	benzene	-	none
I	400:1	THF	-	none
I	400:1	dichloroethane	-	none
I	400:1	water	in water with CTAB	none
II	400:1	benzene	-	none
II	400:1	THF	-	none
II	400:1	dichloroethane	-	none
III	400:1	benzene	-	none
III	400:1	THF	-	none
III	400:1	dichloroethane	-	none
IV	10:1	benzene	nmr scale	none

Table 3.4 Attempted polymerisations using ruthenium initiator

Where no details are shown for the polymerisation technique the reaction was carried out with (approx) 500mg of monomer and 10mg of initiator as a solution reaction using the appropriate degassed solvent. The nmr scale reaction was carried out with 40mg of monomer and 3mg of initiator in deuterated solvent. Once the reaction solution had been stirred for 60 minutes it was transferred to a nmr tube with teflon stopper and the ¹H nmr spectrum recorded. Initially a doublet corresponding to initiator alkylidene proton was observed. However after 18 hours this signal could no longer be observed and no other alkylidene signal was observed. Additionally the reaction mixture colour changed from light red to dark green indicating initiator deactivation. One advantage of the ruthenium initiator is that ROMP can be carried out using water as a solvent. This was attempted, using cetyltrimethylammonium bromide as a surfactant. However no

change in solution viscosity was observed and attempted precipitation of product from the polymerisation solution into methanol did not yield polymer.

During the attempted polymerisations shown above, in every case the reaction solution rapidly became dark green on addition of initiator to monomer solution. This colour change from red to green is indicative of initiator deactivation. The degradation reaction of the ruthenium initiator is more complex and less well characterised than that of the molybdenum initiators so analysis of the reaction products was not attempted. However because the initiator changed colour when mixed with monomer and the fact that initiator was not recovered from the reaction mixture it can be concluded that some form of deactivation reaction occurred. Since there are established examples of the polymerisation of monomers carrying all the individual structural features of monomers I to IV, namely, benzonorbornadienes, hydroxyls and carbonyls, it must be concluded that the deactivation is a result of the specific structures present, the redox systems. Presumably there is redox chemistry as the first step in the deactivation process but in the view of the scarcity and cost of the initiators investigation was abandoned at this point.

3.3 EXPERIMENTAL

3.3.1 Reagents and Apparatus

All organic reagents were purchased from Aldrich Chemical Co. and used as received unless indicated otherwise. Melting points were obtained on an Electrothermal digital melting point apparatus and are reported without correction. Infra-red spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. The ^1H and ^{13}C nmr spectra were recorded on either a Varian Gemini 200MHz or a Varian VXR 400MHz spectrometer. Chemical shifts are reported in parts per million (δ) and are referenced to internal TMS.

The IR and nmr spectra for all compounds are recorded in Appendix 2.

The polymerisation reactions were performed in a modified Miller Howe dry box under an inert atmosphere of oxygen-free nitrogen. The working conditions were 2-6 ppm

oxygen 5-10ppm H_2O. Apparatus was transferred into and out of the box via two vacuum/nitrogen ports.

Deuterated chloroform and perdeuterated tetrahydrofuran for the polymerisation reactions were respectively dried with P_2O_5 and sodium wire and degassed before use.

3.3.2 Synthesis of Monomers

Synthesis of endo 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (I)

The method of Albrecht[27] was followed. A solution of freshly distilled cyclopentadiene (22.05g, 0.33moles) in methanol (20ml) was added dropwise over 20 minutes to a stirred slurry of p-benzoquinone (39.66g, 0.37moles, sublimed) in methanol (80ml) at -70°C. During the reaction the mixture was kept under a slight positive pressure of N_2. Once the addition was complete the mixture was stirred for 60 minutes at -70°C and then allowed to warm slowly to room temperature over 4 hours. Cooling the reaction mixture in a freezer for 60 minutes resulted in the precipitation of yellow crystals which were collected, dried and recrystallised three times from petroleum spirit (60-80) to give product (37.05g, 0.21moles, 64%, m.p.72.1-73.0°C, lit.[27] 77-78°C and[28]76-77°C). Found C,75.8; H,5.7; O,18.5% (calculated for $C_{11}H_{10}O_2$: C,75.8; H,5.8; O,18.4). ^1H nmr (400MHz, $CDCl_3$), (Appendix 2.1) and ^{13}C nmr (100MHz, $CDCl_3$), (Appendix 2.2) assignments are shown in Table 3.5; IR (KBr disc) 3037.2cm^{-1} (w, olefinic C-H stretch), 2991.5, 2945.4, 2873.7cm^{-1} (w, alkyl C-H stretch), 1677.5cm^{-1} (s, quinone C=O), 1603.9cm^{-1} (s, quinone C=C), (Appendix 2.3).
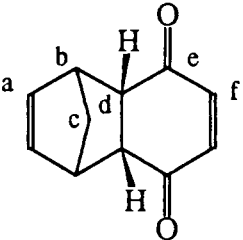
| | | endo - 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (I) |

	^{13}C (shift ppm)	^1H (multiplicity) (shift ppm)	coupling (Hz)
a	135.23	6.07 (t, 2H)	1.6
b	48.72	3.55 (m, 2H)	-
c	48.66	anti - 1.55 (dt, H) syn - 1.43 (br d, H)	1.6, 8.4 8.4
d	48.29	3.23 (m, 2H)	-
e	199.38	-	-
f	142.00	6.58 (s, 2H)	-

Table 3.5 ^1H and ^{13}C nmr assignments for I

Synthesis of 1,4-dihydro-1,4-methanonaphthalene-5,8-diol (II)

Sodium hydrogen carbonate (2.6g, 10% w/w)was added to a stirred solution of I (26.05g, 150mmol) in methanol (300ml) and the mixture stirred for 120 minutes after which time it was poured into distilled water (1000ml). Organic product was extracted with diethyl ether (6x200ml), organic portions combined, dried (MgSO$_4$) and solvent removed to give a sticky orange oil. This oil was recrystallised (with some difficulty) from boiling chloroform to give colourless crystals of pure product which when dried on the vacuum line changed into an off white powder (9.57g, 55mmol, 36%, m.p.142.8-143.7°C, lit.[32]144.0-144.5°C). Found C,75.7; H,5.8; O,18.5% (calculated for C$_{11}$H$_{10}$O$_2$: H,75.8; H,5.8; O,18.4%). ^1H nmr (400MHz, d^6-DMSO), (Appendix 2.4) and ^{13}C nmr (100MHz, d^6-DMSO), (Appendix 2.5) assignments are shown Table 3.6. IR (KBr disc) 3185.3cm^{-1} (s, O-H stretch), 2983.9, 2936.1, 2862.8cm^{-1} (w, aliphatic C-H stretch), 1621.6cm^{-1} (w, isolated C=C), 1602.5cm^{-1} (w, aromatic C=C), (Appendix 2.6).
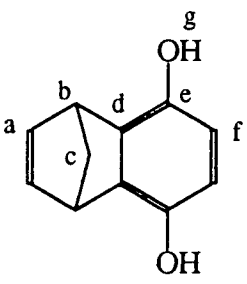
	^{13}C (shift ppm)	^{1}H (multiplicity) (shift ppm)	coupling (Hz)
a	142.36	6.73 (d, 2H)	1.6
b	46.18	4.05 (m, 2H)	-
c	68.61	2.05, 1.97 (2x dd, 2H) (syn and anti)	1.2, 6.8
d	136.40	-	-
e	144.17	-	-
f	113.51	6.19 (s, 2H)	-
g	-	8.35 (s, 2H)	-

The structure shown above the table is 1,4-dihydro-1,4-methanonaphthalene-5,8-diol (II), with labeled positions a–g.

Figure 3.6 ^{1}H and ^{13}C nmr assignments for II

Synthesis of 1,4-dihydro-1,4-methanonaphthalene-5,8-dione (III)

Manganese dioxide (5.24g, 63mmol) was added to a stirred solution of II (3.69g, 21mmol) in diethyl ether (80ml). The mixture was stirred for 120 minutes after which time it was filtered through Celite filter aid to remove the inorganic solids. Solvent was evaporated to give an orange oil which was recrystallised twice from petroleum spirit (60-80) to give orange crystals of III (0.86g, 5mmol, 23%, m.p.67.1-67.6°C, lit.[32] 66-67°C). Found C,76.8; H,4.8; O,18.4% (Calculated for $C_{11}H_8O_2$: C,76.7; H,4.7; O,18.6%). ^{1}H nmr (400MHz, $CDCl_3$), (Appendix 2.7) and ^{13}C nmr (100MHz, $CDCl_3$), (Appendix 2.8) assignments are given in Table 3.7. IR (KBr disc) 3064.2cm^{-1} (w, olefinic C-H stretch), 2979.4, 2943.3, 2873.9cm^{-1} (w, aliphatic C-H stretch), 1649.7 cm^{-1}(s, quinone C=O), (Appendix 2.9).
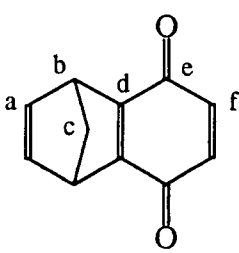
	1,4-dihydro-1,4-methanonaphthalene-5,8-dione (III)

(structure labeled a, b, c, d, e, f with O at top and O at bottom)

	^{13}C (shift ppm)	^1H (multiplicity) (shift ppm)	coupling (Hz)
a	135.68	6.87 (t, 2H)	2.00
b	73.81	4.10 (m, 2H)	-
c	48.36	2.33 and 2.27 (2x dd, 2H) syn and anti	1.6, 7.2
d	160.67	-	-
e	184.00	-	-
f	142.47	6.57 (s, 2H)	-

Table 3.7 ^1H and ^{13}C nmr assignments for III

Synthesis of exo 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (IV)

The method of Yates[28] was used. Freshly distilled cyclopentadiene (28.10g, 0.42moles) was added dropwise to a stirred solution of p-benzoquinone (20.00g, 0.185moles, sublimed) in methanol (200ml) at room temperature and the mixture stirred for 120 minutes. During the reaction the mixture was kept under a slight positive pressure of N_2. Cooling the reaction mixture in a freezer for 120 minutes resulted in the precipitation of yellow crystals (the 2:1 adduct) which were collected. p-Benzoquinone (24.53g, 0.227moles) was added to a boiling solution of the 2:1 adduct in p-xylene (300ml) and this mixture refluxed for 40 minutes before pouring into hexane (1200ml). This gave a green/black precipitate which was removed and the solution put in the freezer for 120 minutes. More green/black solid precipitated and was removed before solvent was stripped from the solution to give an orange oil. This oil was recrystallised from boiling hexane to give orange crystals and an orange solution which when the solvent was removed yielded an orange oil. These two products both contained a mixture of endo and exo 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione in the ratios endo:exo, 4:1 and 3:1 respectively. Flash chromatography (2.5g crude product, 100g silica - 60 mesh, 4:1 hexane:ethyl acetate, 1500ml) of the orange crystals (which contained no impurities unlike the orange oil) gave exo 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-

5,8-dione. This was recrystallised from petroleum spirit 60-80 to give pure product

(0.41g, 2.4mmol, m.p.83.5-83.9°C, lit.[28] 80.5-81.5°C). Found C,75.8; H,5.8; O,18.4%

(calculated for $C_{11}H_{10}O_2$: C,75.8; H,5.8; O,18.4%). ^{1}H nmr (400MHz, CDCl$_3$),

(Appendix 2.10) and ^{13}C nmr (100MHz, CDCl$_3$), (Appendix 2.11) assignments are

shown in Table 3.8. IR (KBr disc) 3060.0cm^{-1} (w, olefinic C-H stretch), 2994.0, 2935.9,

2871.9 cm^{-1} (m, aliphatic C-H stretch), 1666.4 cm^{-1} (s, quinone C=O), 1606.9 cm^{-1}

(m, quinone C=C), (Appendix 2.12).
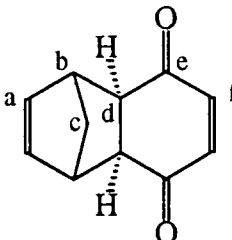
		exo - 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (IV)	
	^{13}C (shift ppm)	^{1}H (multiplicity) (shift ppm)	coupling (Hz)
a	137.44	6.32 (d, 2H)	2.0
b	49.14	3.29 (m, 2H)	-
c	44.50	anti - 1.37 (br d, H) syn - 1.27 (br d, H)	9.6 9.6
d	48.41	2.52 (m, 2H)	-
e	199.30	-	-
f	141.79	6.76 (s, 2H)	-

Table 3.8 ^{1}H and ^{13}C nmr assignments for IV

Note: For the ^{1}H nmr peak assignments the signal from proton 'a' in all four compounds is expected to be a doublet of doublets, if the spectra is first order, with a three bond coupling to the vicinal 'b' proton and a four bond coupling to the other 'b' proton. This peak appears as a pseudo triplet in compounds I and III and a pseudo doublet in compounds II and IV.

3.3.3 Attempted Polymerisations

Reactions using molybdenum initiators

In a typical polymerisation attempt, a solution of III (31.3mg, 0.182mmol) in C_6D_6

(320μl) was added to a stirred solution of molybdenum initiator (10.0mg, 0.0182mmol)

in C_6D_6 (320μl). The mixture was stirred for 15 minutes before being transferred to a

nmr tube with an air tight teflon stopper. The ^{1}H nmr spectrum was then run within 60 minutes of adding the monomer to initiator. Experimental results are given in Section 3.2.3.

Reactions using ruthenium initiators

These attempted polymerisations were carried out by Dr. David Snowden at the IRC laboratories in Durham.

In a typical solution polymerisation attempt using organic solvent, a solution of ruthenium initiator (12mg, 0.013mmol) in degassed benzene (0.50ml) was added to a stirred solution of II (0.904g, 5.2mmol) in degassed benzene (3ml). The reaction mixture was stirred for several hours and any colour changes indicating polymerisation or deactivation of catalyst were noted.

In a typical polymerisation using water as a solvent, a solution of ruthenium initiator (12mg, 0.012mmol) in 1,2-dichloroethane (0.5ml) was added to a stirred mixture of II (0.911g, 5.2mmol), cetyltrimethylammonium bromide (1.5g, 4.1mmol) and degassed water (10ml). The reaction mixture was stirred overnight at 55°C and any colour change of the reaction mixture noted.

Experimental results are given in Section 3.2.3.

3.4 CONCLUSIONS

The work reported by Swager led us to believe that given suitable initiators the benzoquinone polymers could be synthesised directly via ROMP without need for a precursor polymer. The work in this chapter involved using initiators that were known to tolerate monomer functionality much better than previously used classical or well defined initiators. However the monomers were found not to be tolerated by either the Schrock type molybdenum of Grubbs type ruthenium initiators. For the molybdenum initiator, deactivation by reaction of the initiator carbene with the monomer carbonyl functionality has been proposed although not proved. Further reaction of monomer with initiator on a scale large enough to allow full ^{1}H and ^{13}C nmr characterisation would have confirmed this proposal but given the high cost and lengthy preparation of the initiator this was considered a waste of valuable material. The deactivation mechanism of the ruthenium initiator was not investigated. Reasons as to why the monomers used should not be tolerated by the initiator probably lie in the potential reactivity of the quinone with the initiator. Polymerisation of these monomers using different initiators may indeed one day be possible giving a novel route to potentially interesting conjugated polymers.

3.5 REFERENCES

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CHAPTER 4

An Investigation of a Potential Synthesis of Polyaniline and Polyaniline Related Polymers via a Novel Triphenylarsine Oxide Catalysed Process

4.1 INTRODUCTION

4.1.1 Polyaniline

History

The material now known as polyaniline was first reported in the mid-nineteenth century by Letheby.[1] Fritzche[2] attempted to analyse what were then known as the 'Aniline Blacks' while Nietski investigated their use as cotton dyes.[3] Oxidation of aniline was found to produce not one distinct compound but a series of materials in different oxidation states. Since then there has been considerable but intermittent effort in investigating the properties, chemistry and structure of these materials. During the 1950's and 60's novel and improved synthetic methods were developed including electrochemical oxidation.[4] Since 1977, the year in which metallic conductivity of doped polyacetylene[5] was demonstrated, interest in conjugated polymers has surged and with the demonstration[6] that doping polyaniline gives a conducting material, research into polyaniline has also increased dramatically. The number of publications is huge and is increasing rapidly, for example STN International On-Line Computer File records over 3000 publications and patents concerning polyaniline in the period 1986-1995. Polyaniline is regarded as a cheap and stable material[7] and has been identified as having potential commercial applications. Given the volume of literature available this introduction will be brief but will draw out the information salient to this project. Comprehensive reviews are available.[7,8,9]

Initial work by Green and Woodhead[10] and Willstatter[11] proposed that polyaniline was an eight ring molecule whose various forms were dictated by the number of benzenoid and quinonoid rings present. This concept has been retained to this day except that the molecules are believed to be polymeric chains rather than octamers. Polyaniline is conventionally represented in three different forms, each of which has its own trivial name.
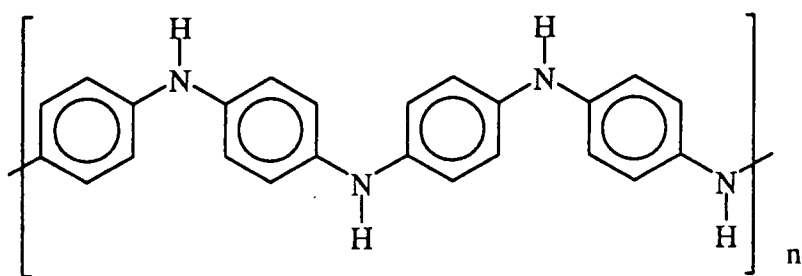
Figure 4.1 Leucoemeraldine form of polyaniline
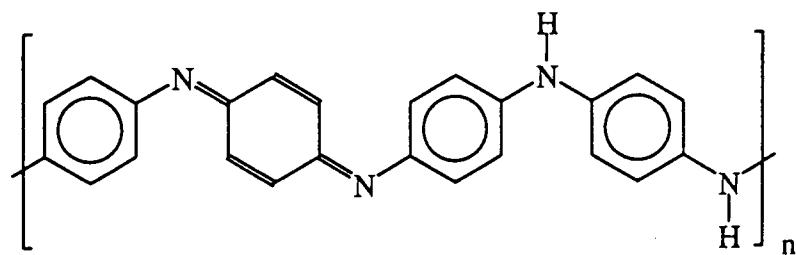
Figure 4.2 Emeraldine form of polyaniline
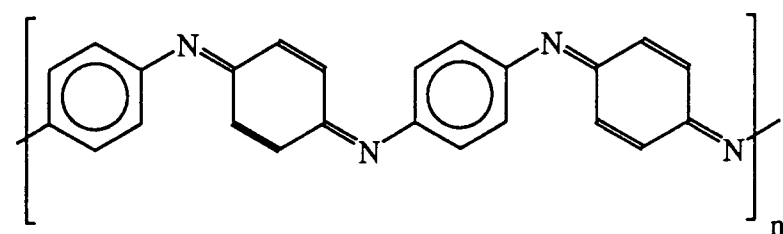
Figure 4.3 Pernigraniline form of polyaniline

These three structures can be represented by the generalised structure shown in Figure 4.4 where the average oxidation state of the polymer, (1-y), can vary from zero (completely reduced polymer - leucoemeraldine), to 0.5 ('half oxidised' polymer - emeraldine) to 1 (fully oxidised polymer - pernigraniline).
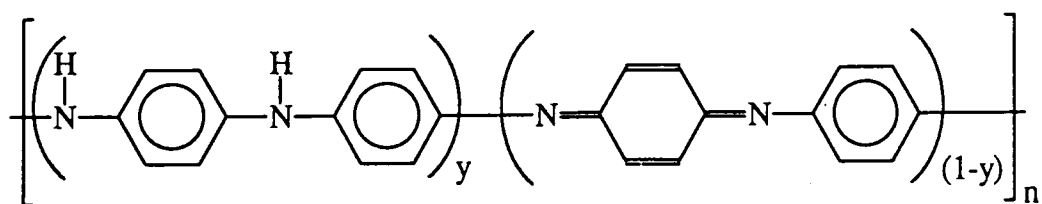
Figure 4.4 Generalised structure for polyaniline

Interconversion between these various forms of polyaniline is achieved through chemical or electrochemical oxidation or reduction. Protonation of the imine nitrogens to give the corresponding salts is possible and provides an added complication to the range of possible structures for polyaniline.

Synthesis

Polyaniline is generally synthesised via chemical or electrochemical oxidation of aniline. It is agreed that the characteristics of the polymer produced depend on the exact method of synthesis.[12]

Chemical oxidation involves the reaction of aniline with a suitable oxidising agent and then isolating the resulting polymer. One of the more commonly used systems is ammonium peroxydisulphate, $(NH_4)_2S_2O_8$ in aqueous HCl.[6] Once synthesised, the polymer containing mixture is neutralised and the emeraldine form is collected. This method gives polymer which is soluble in NMP (N-methyl-2-pyrrolidinone) and the soluble portion is reported as having Mw = 78,000 and Mn = 26,000 (GPC, 0.5wt% LiCl in NMP, polystyrene standards).[13] Conversion of this material to the other forms is possible.[14] Other authors use different oxidising agents, in the presence of different acids and solvents using a range of reaction conditions.[7] Different synthetic routes give small variations in the detailed properties of the products.

Electrochemical synthesis of polyaniline is achieved via oxidation of aniline at an inert electrode, usually platinum, producing a film of the polymer. The potential at the electrode can be either fixed (0.7-1.2V) or cycled (-0.2 to 0.7-1.2V). As with the chemical syntheses, the use of a variety of solvents, concentrations of reagents and pH ranges have been reported.[7]

One drawback to using the oxidation of aniline as a synthetic route to polyaniline is that the formation of benzidine as a side product is well established.[15] Benzidine is known to be carcinogenic[16] so synthetic routes to polyaniline that avoid its possible formation are to be preferred.

Other routes to polyaniline have been developed including gas-phase plasma synthesis,[17] which does not involve solvent or oxidant, and vapour deposition of the emeraldine form onto quartz at 350°C which is said to give polymer which is less contaminated by oxygen.[18] Step growth condensation polymerisation of suitable monomers can, in principle, give polymer without the need for an oxidising agent. For example, the product of condensation polymerisation of 1,4-phenylenediamine and succinosuccinic acid (see below) can be decarboxylated to give poly(p-phenyleneamineimine)[19] - the pernigraniline form of polyaniline. Polyanilines substituted either at the nitrogens or on the rings can also be synthesised by using the appropriate monomers.[20,21]

Physical and chemical properties

Generally polyanilines are thought to be insoluble materials. However polyaniline is soluble in concentrated acids[22] and some low molecular weight fractions have been shown to be soluble in THF.[12] Solubility can be increased by attachment of side chains making the polymers soluble in aqueous[23] or organic solvents.[20,22] In addition the emeraldine form synthesised by some routes is soluble in NMP and this allows characterisation of the polymer.[13] Samples can be solution processed to give free-standing flexible films.[14]

One of the principle interests in polyaniline is its conductivity. The leucoemeraldine, emeraldine and pernigraniline forms shown above are all insulating. Oxidative doping of the leucoemeraldine form or protonic acid doping of the emeraldine form produces the polymer in its conducting form known as the emeraldine salt (see Scheme 4.1).

Protonic acid doping of polyaniline involves treating the emeraldine form (insoluble in aqueous acid and base) with HCl and then collecting and drying the polymer. Conductivity, which is dependent on pH, increases by the order of ~10^{-10} to 1-5 Scm^{-1}.[6] Protonic acid doping, unlike redox doping, does not involve a change in the number of electrons associated with the polymer backbone. Conductivities of 300 Scm^{-1} have been reported.[13]

$\sigma = 10^{-10} \text{ Scm}^{-1}$

No change in number of electrons on backbone | H⁺ protic acid doping

Emeraldine hydrochloride
$\sigma = 1\text{-}5 \text{ Scm}^{-1}$

No change in number of protons on backbone | Chemical or electrochemical oxidative doping

$\sigma = 10^{-10} \text{ Scm}^{-1}$
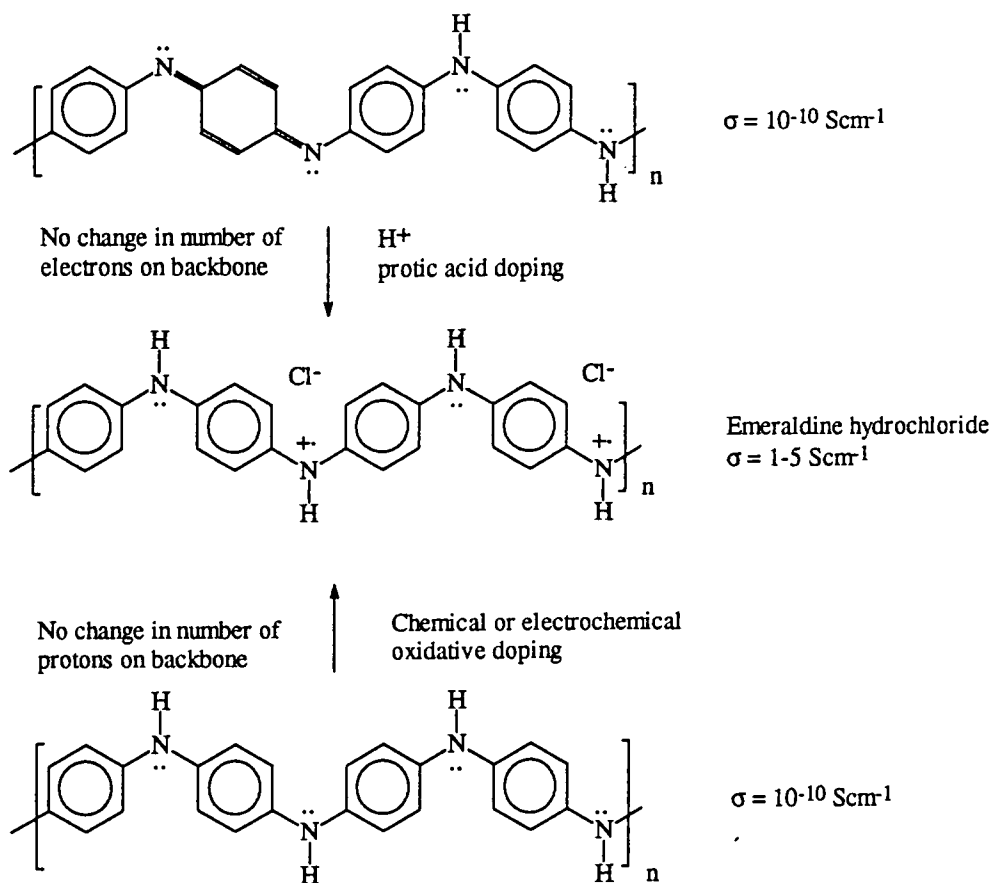
Scheme 4.1

Interconversion between the various forms is possible via oxidation and reduction. This can be chemical or electrical. Usually interconversion can be effected without any change in molecular weight which indicates that no chain scission or cross linking occurs.[24]

Structural studies

Most authors agree that the structure of polyaniline can be represented in one of the forms shown above, that is a regular structure of alternating six carbon rings and nitrogens with the rings in either the benzenoid or quinonoid form. It is also accepted that the forms show the average state of the polymer and do not represent the exact sequence of benzenoid and quinonoid rings. However, very few studies take into consideration the possibility of defects in the polymer chain, be they 1,2 or 1,3 links, benzidine, hydrazine or carbazole type structures. The structure of polyaniline has been 'proved' several ways.

The simplest method is to synthesise fully characterisable model compounds and oligomers and then spectroscopically compare these materials with conventionally synthesised polyaniline. Examples include N,N'-diphenyl-1,4-phenylenediamine, [4-(phenylamino)phenyl]-1,4-phenylenediamine and their oxidised forms[25,26] (Figure 4.5) and phenyl capped octaaniline[27] (Figure 4.6). These studies have shown that, within the limits of the analytical techniques employed, the characteristics of polyaniline were consistent those of the model compounds and the authors conclude that polyaniline can indeed be represented by one of the forms shown above.

n = 1,2,3
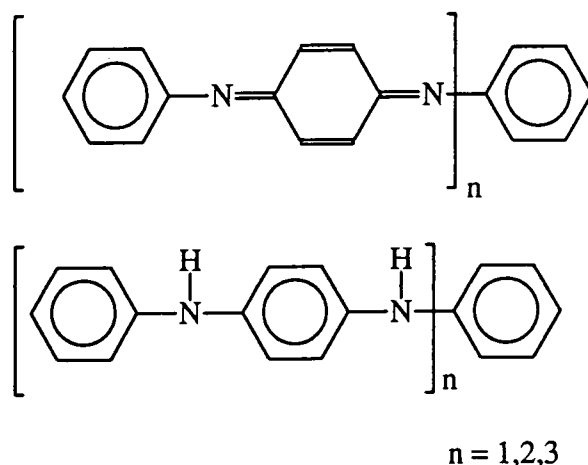
Figure 4.5 Polyaniline oligomers used in structural studies[25,26]
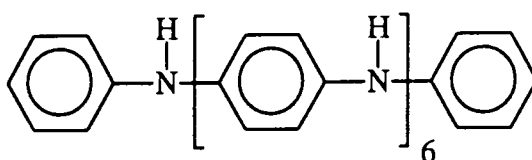
Figure 4.6 Phenylcapped octaaniline

Secondly polyaniline can be synthesised unambiguously via a non-oxidative method and the polymer produced compared to conventional polyaniline. One example of this is the approach of Wudl.[19] The polymer made by the condensation polymerisation of 1,4-phenylenediamine and succinosuccinic acid is decarboxylated to give, after spontaneous atmospheric oxidation, polyaniline in which the alternation of rings and

nitrogens has to be perfect. Spectra, electrochemistry and magnetic properties of this polymer matched those of polyaniline very closely and the authors concluded that the two materials were the same.
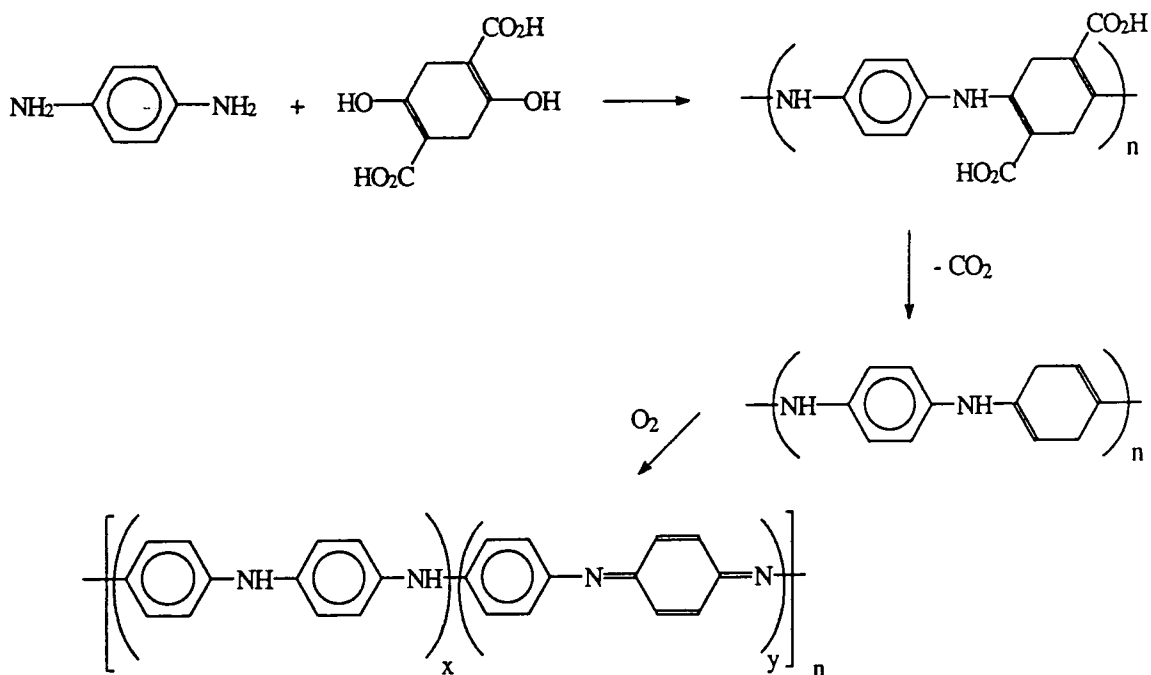
Scheme 4.2

A third approach has involved obtaining high resolution nmr spectra of conventionally produced soluble polyaniline.[24] This study on polyaniline itself showed that the vast majority (>95%) of the leucoemeraldine and emeraldine forms were of the postulated structure. However, for the emeraldine form, defects were detected in the polymer chain. By comparison with model compounds the presence of carbazole type structures and amine ring substituents were essentially ruled out. However the detection of minor peaks indicated that 1,2 substitution, benzidine and phenyl hydrazine type structures could not be excluded.

4.1.2 Arsine Imines

Organic arsenic compounds form ylids in the same way as the better known organic phosphorus compounds. These arsonium ylids are relatively easy to prepare and tend to be more reactive than their phosphorus counterparts. General reviews on arsonium ylids are available.[28,29] Likewise arsine imines (containing a As=N bond), which are the

analogues of compounds containing a P=N bond, are known. The properties of the arsine imines (which are discussed below) are in many instances identical to those of the arsonium ylids and similar arguments concerning their stability and reactivity can be constructed.

The arsenic - nitrogen bond is often represented as an arsenic nitrogen double bond but it has a dipolar form which makes a contribution to the overall structure.

$$R_3As{=}N{-}R' \quad \longleftrightarrow \quad R_3\overset{+}{A}s{-}\overset{-}{N}{-}R'$$
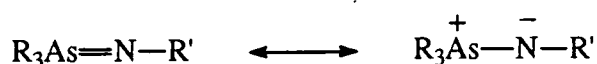
Scheme 4.3

Dipole measurements, ^1H and ^{13}C nmr studies, IR spectroscopy[28] and X-ray crystallography[29] of arsonium ylids suggest that, compared to the phosphonium ylids, the dipolar form is more favoured than the covalent form. One reason for these observations could be that the $p\pi$-$d\pi$ overlap between carbon and arsenic is less efficient than the analogous overlap between carbon and phosphorus due to arsenic having a more diffuse d-orbital. Similar arguments should apply for arsine imines which have been shown[30] to have a significant dipolar contribution to their structure although direct comparisons with compounds containing a phosphorus nitrogen double bond have not been reported.

Factors affecting the stability of arsine imines mirror those affecting arsonium ylids and include the nature of the groups attached to the arsenic atom and the nature of the groups attached to the imine nitrogen. For example, if electron withdrawing groups, which are capable of conjugation with the imine nitrogen, are present electron delocalisation will aid stabilisation of the dipolar form (Scheme 4.4).

$$R_3\overset{+}{A}s{-}\overset{-}{N}{-}\underset{\underset{O}{\|}}{C}{-}R \quad \longleftrightarrow \quad R_3\overset{+}{A}s{-}N{=}\underset{\underset{O^-}{|}}{C}{-}R$$
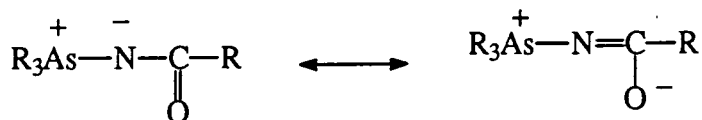
Scheme 4.4

Introduction of electron donating species into the aromatic groups attached to the arsenic stabilises the ylid as does replacement of the aromatics with alkyl groups.[28] These factors affect both the stability and reactivity of the arsine imine. Overall arsine imines, even the less stabilised forms, are reported[28] to be more stable than arsonium ylids.

Synthesis

Arsine imines can be synthesised in several ways, many of which are analogous to routes to arsonium ylids.

a) Salt method

Initially an arsonium salt is formed and then the imine is freed by treatment with a suitable base.[31]

$$Ph_3As \ + \ ClNH_2 \ \longrightarrow \ Ph_3\overset{+}{As}-NH_2 \ \overset{-}{Cl} \ \xrightarrow[NH_3 \ (l)]{NaNH_2} \ Ph_3As{=\!\!=}NH$$
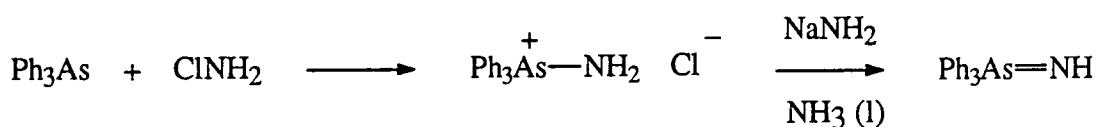
Scheme 4.5

b) From arsenic halides

Reaction of an arsine di or trihalide with a primary amine in the presence of triethylamine gives the corresponding arsine imine[32,33] (Schemes 4.6, 4.7). This method also allows the

$$Ph_3AsCl_2 \ + \ 2 \, H_2NAr \ \xrightarrow[Et_3N]{} \ Ph_3As{=\!\!=}NAr \ + \ 2 \, Et_3N.HCl$$

Scheme 4.6

$$Ph_2AsCl_3 \ + \ 2 \, H_2NAr \ \xrightarrow[Et_3N]{} \ Ph_2(ArNH)As{=\!\!=}NAr \ + \ 3 \, Et_3N.HCl$$
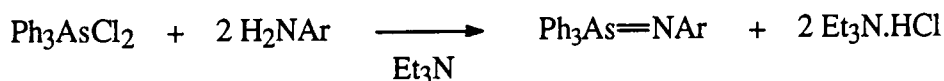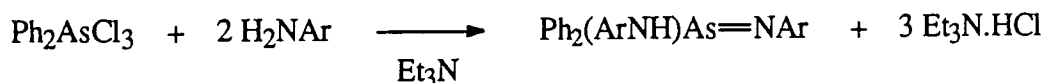
Scheme 4.7

synthesis of arsenic (III) imines (Scheme 4.8) rather than the more common arsenic (V) imines.

$$\text{ArAsCl}_2 \quad + \quad \text{H}_2\text{NAr'} \quad \xrightarrow[\text{Et}_3\text{N}]{} \quad \text{ArAs}{=}\text{NAr'} \quad + \quad 2\,\text{Et}_3\text{N.HCl}$$
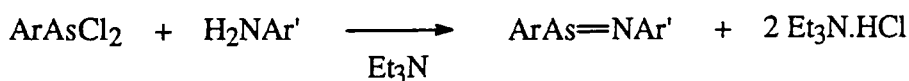
Scheme 4.8

c) From triphenylarsine oxide

Triphenylarsine oxide reacts with both aryl and acyl isocyanates[30,34,35] to give arsine imines with the evolution of carbon dioxide.

$$\text{Ph}_3\text{As}{=}\text{O} \quad + \quad \text{ArNCO} \quad \xrightarrow{\hspace{1cm}} \quad \text{Ph}_3\text{As}{=}\text{NAr} \quad + \quad \text{CO}_2$$
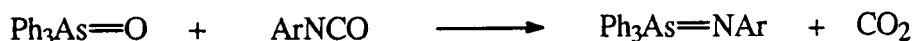
Scheme 4.9

Similarly triphenylarsine oxide reacts with N-sulphinylamines,[35] via what is assumed to be the same reaction mechanism, releasing sulphur dioxide.

d) From nitrenes

Triphenylarsine has been shown to be sufficiently nucleophilic to act as a suitable trapping compound for electron deficient nitrenes,[36] producing a triphenylarsine imine (Scheme 4.10).

$$\text{Ph}_3\text{As} \quad + \quad \text{XN:} \quad \xrightarrow{\hspace{1cm}} \quad \text{Ph}_3\text{As}{=}\text{NX}$$

Scheme 4.10

e) From triphenylarsine and lead tetracetate

This is a one pot reaction in which triphenylarsine, lead tetracetate and an amide are heated together to give the arsine imine.[37] Initially the reaction was thought to produce a nitrene from lead tetracetate and amide but this has been shown not to be the case and the reaction proceeds via an isolatable bisacetoxytriphenylarsine intermediate.

$$\text{Ph}_3\text{As} \quad + \quad \text{Pb(OAc)}_4 \quad \xrightarrow{\hspace{1cm}} \quad \text{Ph}_3\text{As(OAc)}_2 \xrightarrow[\text{RCONH}_2]{} \quad \text{Ph}_3\text{As}{=}\text{NCOR}$$
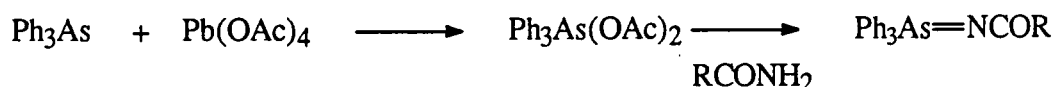
Scheme 4.11

f) From triphenylarsine

The original synthesis[38] of an arsine imine was from the reaction of triphenylarsine and sodium N-chloro-p-toluenesulphonamide (chloramine T). This reaction has been shown not to be particularly straightforward and is not generally used in the synthesis of arsine imines.

$$Ph_3As \quad + \quad [p\text{-}MeC_6H_4SO_2NCl]^- \; Na^+ \quad \longrightarrow \quad Ph_3As{=}NSO_2C_6H_4Me$$
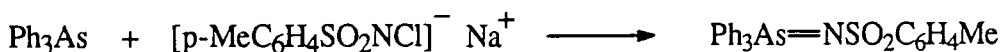
Scheme 4.12

Chemistry

The characteristic chemistry of the arsine imines is governed by the As=N bond and the fact that they are more reactive than their phosphorus counterparts. Arsine imines are hydrolysed by aqueous base[30,39] or acid[30] and some of the unstabilised forms (for example triphenylarsine phenylimine) are hydrolysed by atmospheric moisture.[32] Hydrolysis produces an arsine oxide and an amine.

$$Ph_3As{=}NPh \quad \longrightarrow \quad Ph_3AsO \quad + \quad PhNH_2$$
$$H^+, OH^- \text{ or } H_2O$$
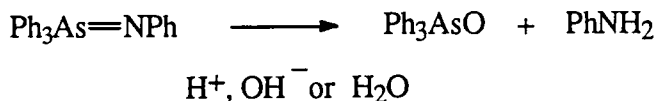
Scheme 4.13

Arsine imines can be alkylated with methyl iodide which, in the case of triphenylarsine benzoylimine,[30] occurs at either the imine nitrogen or carbonyl oxygen (Scheme 4.14); they are also acylated using acyl halides.[31]
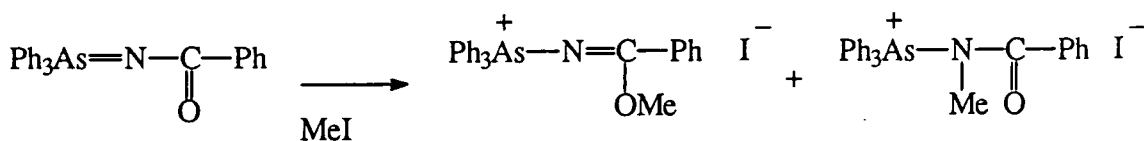
Scheme 4.14

One useful reaction of the arsine imines is their reaction with carbonyl compounds to give imines and arsine oxide.[34]

$$Ph_3As=N-Ph \quad \rightleftharpoons \quad \left[\begin{array}{c} Ph_3As-N-Ph \\ | \quad | \\ O-CR_2 \end{array} \right] \quad \longrightarrow \quad Ph_3As=O$$

$$+ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad +$$

$$O=CR_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad R_2C=NPh$$
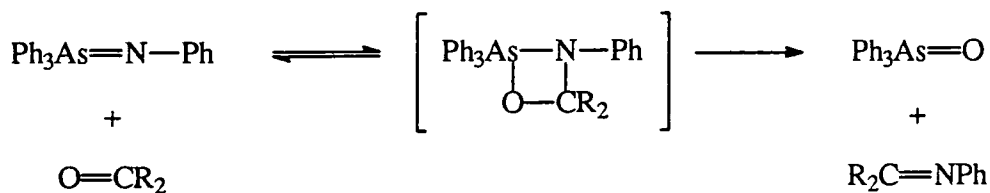
Scheme 4.15

The reaction was thought to proceed via a non-isolatable four membered ring intermediate, which parallels the mechanism of the Wittig reaction, but studies of the mechanism of the analogous phosphine imine reaction[40] suggests that this reaction proceeds via a betaine rather than the cyclic intermediate. Studies on arsonium ylid reactions[41] suggest that betaine formation does not occur and the reaction proceeds via the cyclic intermediate. No similar mechanistic studies on the reactions of arsine imines have been found and all reports in the literature show the reactions proceeding via the cyclic intermediate without betaine formation.

Similarly arsine imines have been shown to react with compounds containing double bonds such as isocyanates, nitrobenzenes and isothiocyanates[34] (no reports of reaction with olefins have been found). Reaction of a triphenylarsine imine, generated from triphenylarsine oxide and phenylisocyante, with phenylisocyante results in the formation of diphenylcarbodiimide and triphenylarsine oxide.[35] Comparison of this reaction and that involving triphenylphosphene oxide[42] highlights some differences between phosphorus and arsenic.

$$Ph_3AsO \quad \longrightarrow \quad \left[\begin{array}{c} Ph_3As-O \\ | \quad | \\ Ph-N-C=O \end{array} \right] \quad \longrightarrow \quad Ph_3As=N-Ph$$

$$+ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad +$$

$$Ph-NCO \qquad\qquad\qquad\qquad\qquad\qquad\qquad CO_2$$

$$Ph_3As=NPh \quad \longrightarrow \quad \left[\begin{array}{c} Ph_3As-NPh \\ | \quad | \\ O-C-NPh \end{array} \right] \quad \longrightarrow \quad Ph_3AsO$$

$$+ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad +$$

$$O=C=NPh \qquad\qquad\qquad\qquad\qquad\qquad Ph-N=C=N-Ph$$
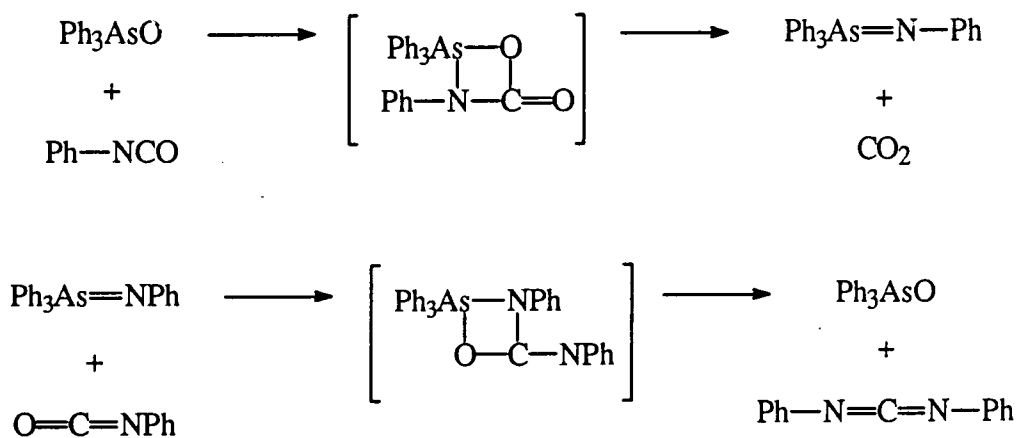
Scheme 4.16

In the case of phosphorus, in the second step in the sequence of reactions of triphenylphosphine oxide with phenylisocyanate the reaction of the first product, triphenylphosphine imine, with phenylisocyanate is 10^5 - 10^7 times faster than the reaction of phenylisocyanate with the starting triphenylphosphine oxide.[43] If this were the case for arsenic, which is expected to be more reactive than the phosphene imine, isolation of the arsine imine would be very difficult. However, it is possible to prevent reaction of arsine imine with phenylisocyante by simply controlling the reaction conditions. Below 5°C no carbodiimide is formed and the arsine imine can be isolated whereas at higher temperature (60°C) reaction to form carbodiimide proceeds. This difference between arsenic and phosphorus allows control of arsine imine reactions. It is worth reiterating that whatever the ratio of the rates within a particular two step reaction (see carbodiimide formation above), arsine imines are more reactive than their phosphorus counterparts.[34]

Other reactions include reaction with carbon disulphide to give a carbodiimide and an isothiocyanate[34] and the reaction of triphenylarsine N-tosylimine with phenyllithium to give pentaphenylarsine[44] (Scheme 4.17).

$$Ph_3As{=}NSO_2PhCH_3 \quad + \quad Ph\,Li \quad \longrightarrow \quad Ph_5As$$
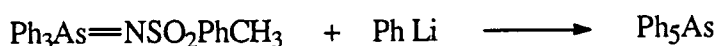
Scheme 4.17

4.1.3 Project Aims

It has been shown that there may be some uncertainty concerning the structure of polyaniline in its various forms.[24] Literature studies on the structure of polyaniline (see above) show that for the most part polyaniline exists in of one of the forms shown above. However these studies, with few exceptions, do not identify or account for any structural defects in 'conventionally' synthesised polyaniline. Therefore an investigation into the synthesis of polyaniline and the development of a synthetic route to exclusively one form the polymer via a method that does not involve conditions potentially leading to either protonation/deprotonation or oxidation/reduction was of interest. This is what this project aimed to address.

4.2 RESULTS AND DISCUSSION

4.2.1 Introduction

In 1973 Froyen reported the synthesis of N,N'-diphenyl-2,5-cyclohexadiene-1,4-diimine from phenylisocyanate, triphenylarsine oxide and p-benzoquinone.[34]

$$Ph_3As=O \quad + \quad PhNCO \quad \longrightarrow \quad Ph_3As=N-Ph$$
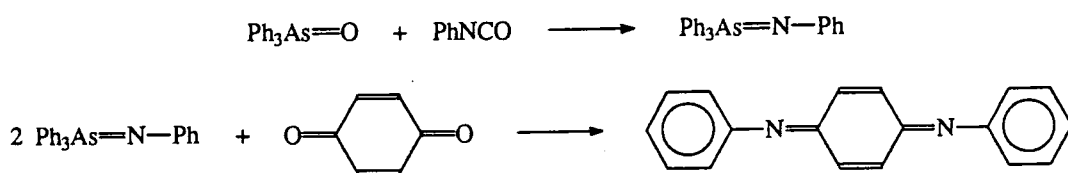
Scheme 4.18

This reaction was reported to proceed in 'quantitative' yield and, by substituting a diisocyanate for phenylisocyanate, appeared to show potential as the coupling reaction in an AA BB type polycondensation. In principle, using p-benzoquinone and 1,4-phenyldiisocyanate, this reaction could be used to synthesise polyaniline in its pernigraniline form (Scheme 4.19).
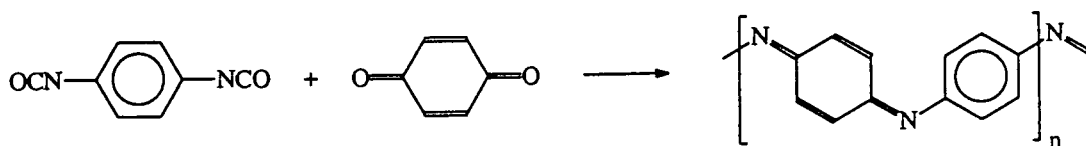
Scheme 4.19

Simply varying the diisocyanate or quinone used would allow a series of polyaniline related polymers to be synthesised.
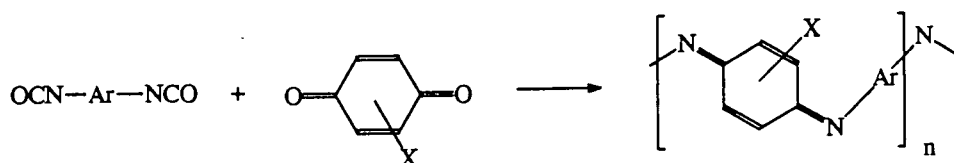
Ar = any aromatic
X = H, Ar, R, Hal, etc.

Scheme 4.20

4.2.2 Synthesis of Triphenylarsine Phenylimine

Triphenylarsine phenylimine was synthesised according to Froyen[34,35] to show that this coupling reaction was suitable for use as a polymerisation reaction. Initial attempts resulted in formation of diphenyl urea rather than the expected triphenylarsine phenylimine. This was attributed to the reaction of phenylisocyanate with residual water from either solvent, the water of crystallisation of triphenylarsine oxide or wet glassware and bad experimental technique. Solvent (initially toluene and then benzene) was rigorously dried according to standard methods[45] (distilled from sodium) and experimental technique was improved and perfected to exclude air and moisture. Triphenylarsine oxide was freed from water of crystallisation by azeotropic distillation (Dean Stark distillation) with benzene.[30,36] The mole% residual water was calculated from the integrals of the ^{1}H nmr spectrum which contained only two sets of signals, one for the aromatic hydrogens of triphenylarsine oxide and one for those of water. This gave a measure of the amount of water present in a sample of triphenylarsine oxide which could be used for comparison between samples. Table 4.1 shows the mole% water in a sample of triphenylarsine oxide before and after azeotropic distillation with benzene. It can be seen that the triphenylarsine oxide supplied had approximately one water molecule for each arsenic atom, whereas the dried material had approximately one water for seventy arsenic atoms.

Drying Method	Mole% water (from ^{1}H nmr)
None	45
Azeotropic distillation with benzene	0.7

Table 4.1 Mole% water in a sample of triphenylarsine oxide before and after drying

Using this dried triphenylarsine oxide, the synthesis of triphenylarsine phenylimine was re-examined. The method reported by Froyen proved to be ineffective in all of many experiments as only mixtures of triphenylarsine phenylimine, triphenylarsine oxide and aniline could be obtained. Components of the product mixtures were identified by ^{1}H and ^{13}C nmr and HETCOR and DEPT nmr experiments. The hydrogen and carbon peak assignments for the three components are shown in Table 4.2 and typical ^{13}C nmr and ^{1}H nmr in Figures 4.7 and 4.8. In each case all the nmr signals could be accounted for in

terms of a mixture of these three compounds but the proportion of the product that was arsine imine never exceeded 60 mole%.
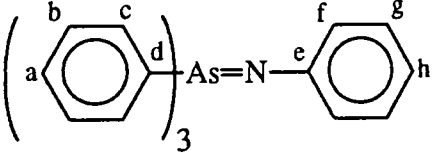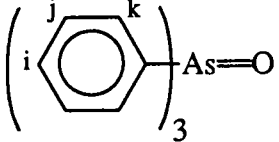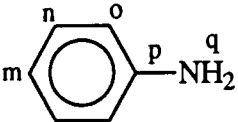
A:				
	Triphenylarsine Phenylimine			
		^{13}C (δ)	^{1}H (multiplicity) (δ)	coupling (Hz)
	a	131.74	7.52 (m)	-
	b	129.35	7.52 (m)	-
	c	132.09	7.77 (dd, 6H)	7.2, 0.8
	d	130.97	-	-
	e	156.75	-	-
	f	120.69	6.77 (dd, 2H)	7.2, 1.2
	g	128.57	6.96 (t, 2H)	7.2
	h	114.80	6.50 (dt, H)	7.2, 1.2
B:				
	Triphenylarsine Oxide			
	i	131.99	7.52 (m)	-
	j	131.38	7.52 (m)	-
	k	129.21	7.73 (dd, 6H)	7.2, 0.8
	l	132.83	-	-
C:				
	Aniline			
	m	118.33	6.76 (td, H)	7.6, 0.8
	n	129.15	7.14 (t, 2H)	7.6
	o	114.96	6.66 (d, 2H)	7.6, 0.8
	p	probably 146-148	-	-
	q	-	3.66 (s, 2H)	-

Table 4.2 Peak assignments for the triphenylarsine phenylimine, triphenylarsine oxide and aniline mixture

When the reaction mixture was left for 24 hours in the nmr tube the ratio of triphenylarsine oxide to triphenylarsine phenylimine increased with time and new peaks appeared in the spectrum which were identified as aniline. This change was attributed to
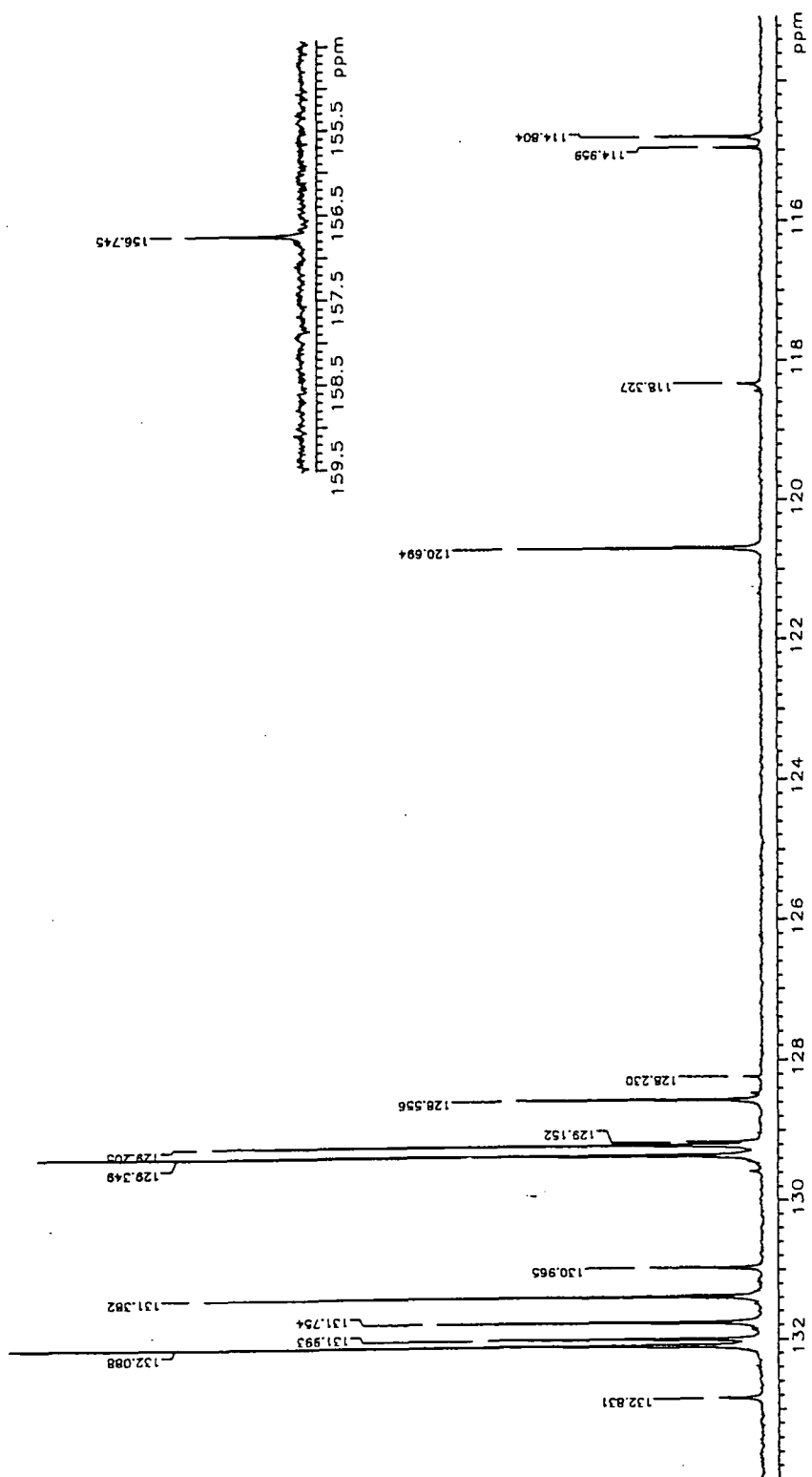
Figure 4.7 ^{13}C nmr spectrum of the products (triphenylarsine phenylimine, triphenylarsine oxide and aniline) from a typical preparation of triphenylarsine phenylimine

137
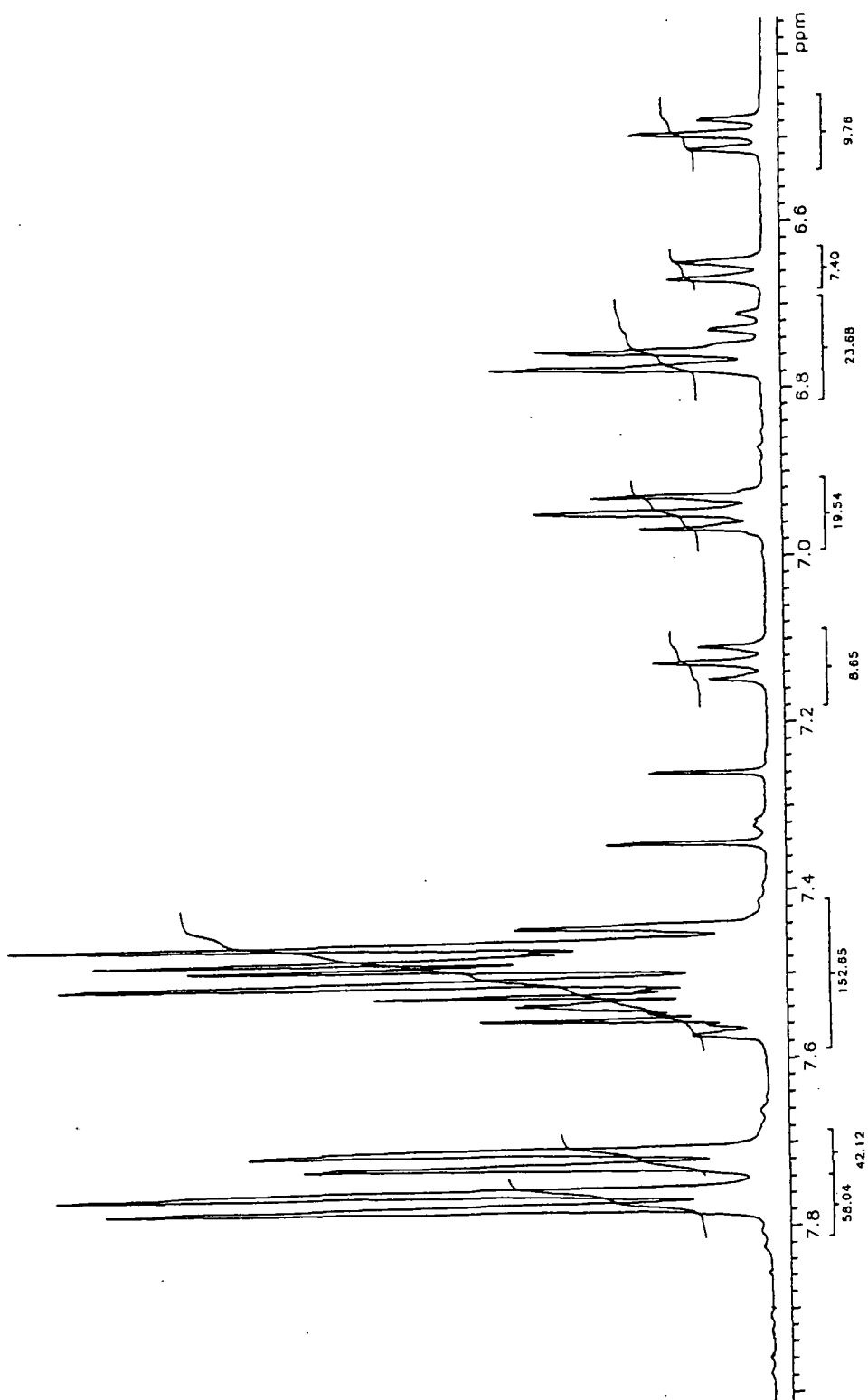
Figure 4.8 ^{1}H nmr spectrum of the products (triphenylarsine phenylimine, triphenylarsine oxide and aniline) from a typical preparation of triphenylarsine phenylimine

the hydrolysis of triphenylarsine phenylimine. To confirm this a drop of water was added to the sample and when the spectrum was re-analysed only triphenylarsine oxide and aniline remained. Clearly, the synthesis and isolation of triphenylarsine phenylimime and was very sensitive to water.

Attempts to isolate triphenylarsine phenylimine from the reaction mixture resulted in its hydrolysis to triphenylarsine oxide and aniline. To limit the extent to which this occurred, the second stage of the reaction, addition of p-benzoquinone, was carried out as soon as the triphenylarsine phenylimine had been synthesised. Because triphenylarsine oxide and aniline are unreactive towards triphenylarsine phenylimine these side products were regarded as inert impurities and no attempt was made to remove them before reaction with p-benzoquinone. The amount of triphenylarsine phenylimine present in the mixture was estimated from the ratio of the integral of the aromatic ortho hydrogen of the arsine imine phenylenes to the integral of the aromatic ortho hydrogen of the arsine oxide phenylenes (ratio of hydrogens c and k in Table 4.2).

4.2.3 Reactions of Triphenylarsine Phenylimine

Triphenylarsine imine was reacted with p-benzoquinone to give the desired 2:1 adduct, N,N'-diphenyl-2,5-cyclohexadiene-1,4-diimine. The yield of this reaction was poor and product was never isolated in a pure state from the reaction mixture. Characterisation data is given in Section 4.3.3 and spectra in Appendix 3. Bearing in mind the theoretical constraints on polymer molecular weight for step growth polycondensation reactions imposed by the Carrothers equation, a low yield coupling reaction would give a polymer with a low degree of polymerisation. Because the yields were not sufficient to isolate product it would be a sensible assumption that high molecular weight polymer could not be produced. With the benefit of hindsight this might have been a sensible place to end this project. However one potential advantage of this synthetic route is that triphenylarsine oxide is produced as a product in the reaction and possibly could be used in catalytic rather than stoichiometric quantities. Given this potential advantage, further investigation of this reaction and attempts at polymerisation were considered sensible.

Once the coupling reaction had been shown to work (even if in low yield), reaction of a diisocyanate, 4,4′-methylene bis(phenylisocyanate), with triphenylarsine oxide to give 4,4′-methylene bis(triphenylarsine phenylimine) (I) (Figure 4.9) was attempted. As with
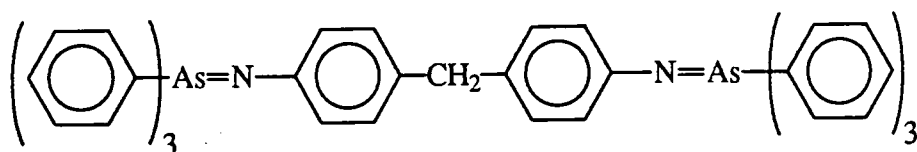
Figure 4.9 4,4′-methylene bis(triphenylarsine phenylimine) (I)

the synthesis of triphenylarsine phenylimine, I proved difficult to separate from triphenylarsine oxide and was identified only by nmr spectroscopy. Tentative assignment of the ^{13}C nmr spectra, Figure 4.10, is given in Table 4.3. The ^{1}H nmr spectrum was not assigned and is given in Appendix 3.15. Assignments are based on the chemical shifts of the starting materials, of triphenylarsine phenylimine and from HETCOR nmr spectra (Appendix 3.17).

	4,4′-methylene bis(triphenylarsine phenylimine)

Carbon	Shift (δ)
a	131.67
b	129.32
c	132.15
d	131.29
e	154.26
f, f′	120.51, 120.40
g, g′	129.13, 129.05, 128.97
h	128.64
i	(one of) 40.31, 40.10, 40.07
triphenylarsine oxide	132.83, 132.07, 131.41, 129.27
benzene	128.27
(all other peaks unassigned)	-

Table 4.3 ^{13}C nmr assignments of 4,4′-methylene bis(triphenylarsine phenylimine)
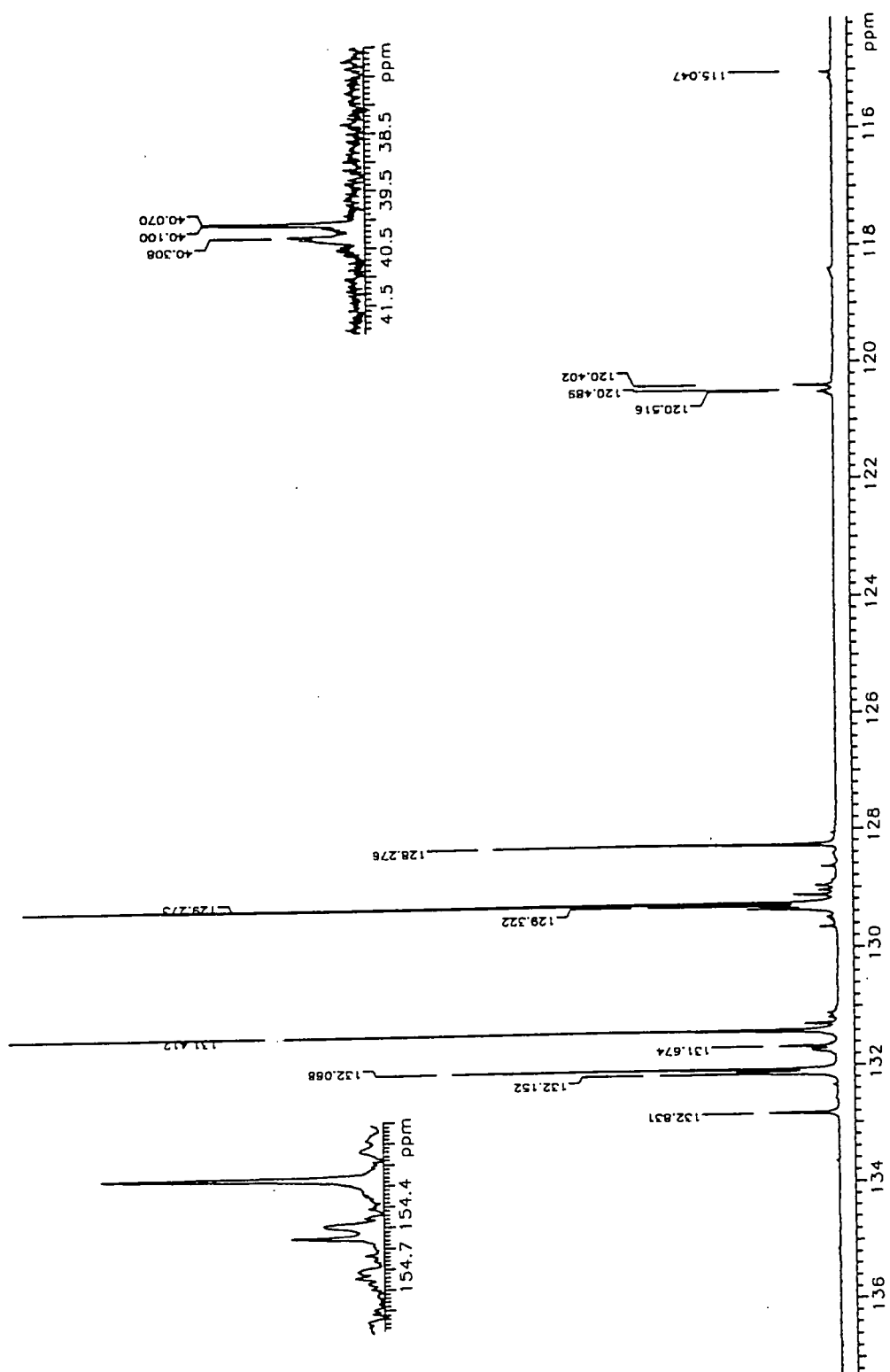
Figure 4.10 ^{13}C nmr spectrum of the reaction mixture containing 4,4′-methylene bis(triphenylarsine phenylimine)

Polymerisation of this diarsine imine with p-benzoquinone, to give a polyaniline type
polymer, was attempted.
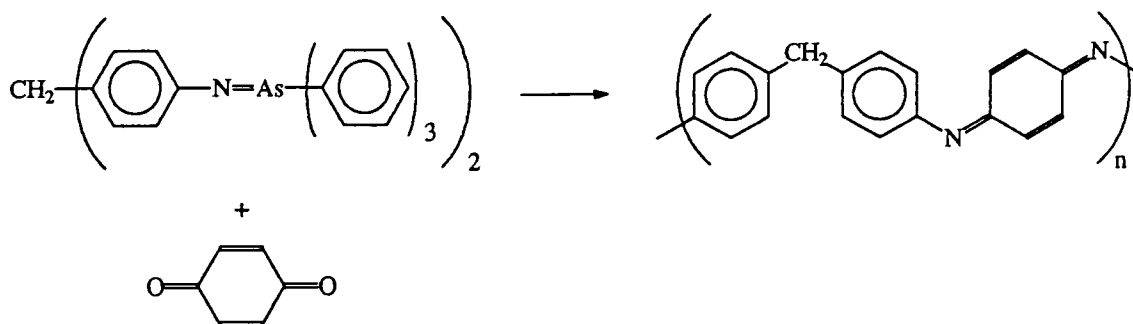
Scheme 4.21

To prevent hydrolysis of the diarsine imine (I), it was synthesised in the presence of
p-benzoquinone so immediate coupling reaction could occur. Several different ratios of
triphenylarsine oxide to isocyanate and p-benzoquinone were tried (see Section 4.3.3)
and in each case no polymer was detected. However the 2:1 adduct (ABA type trimer-
Table 4.4) of p-benzoquinone and 4,4'-methylene bis(phenylisocyanate) was detected by
nmr. Assignments, again tentative, of the ^{13}C nmr spectrum (Figure 4.11) are given in
Table 4.4. These were made on the basis of the chemical shifts of N,N'-diphenyl-2,5-
cyclohexadiene-1,4-diimine and N-phenyl-2,5-cyclohexadiene-4-imine-1-one (1:1 adduct
of triphenylarsine phenylimine and p-benzoquinone). The ^{1}H nmr spectrum is given in
Appendix 3.18.

Synthesis of 4,4'-methylene bis(triphenylarsine phenylimine) and then addition of
p-benzoquinone was also attempted but also only gave the same ABA type trimer and
triphenylarsine oxide. Reaction mixtures were stirred for between 20 and 24 hours at
room temperature and in each case only the ABA type trimer was synthesised. Extended
reaction over three days at room temperature was also attempted but still did not
produce polymer. Reflux of the reaction mixture was not attempted as this would have
resulted in the formation of a polycarbodiimide. In all attempts at polymerisation the
product mixture contained unreacted starting materials as well as the ABA trimer.
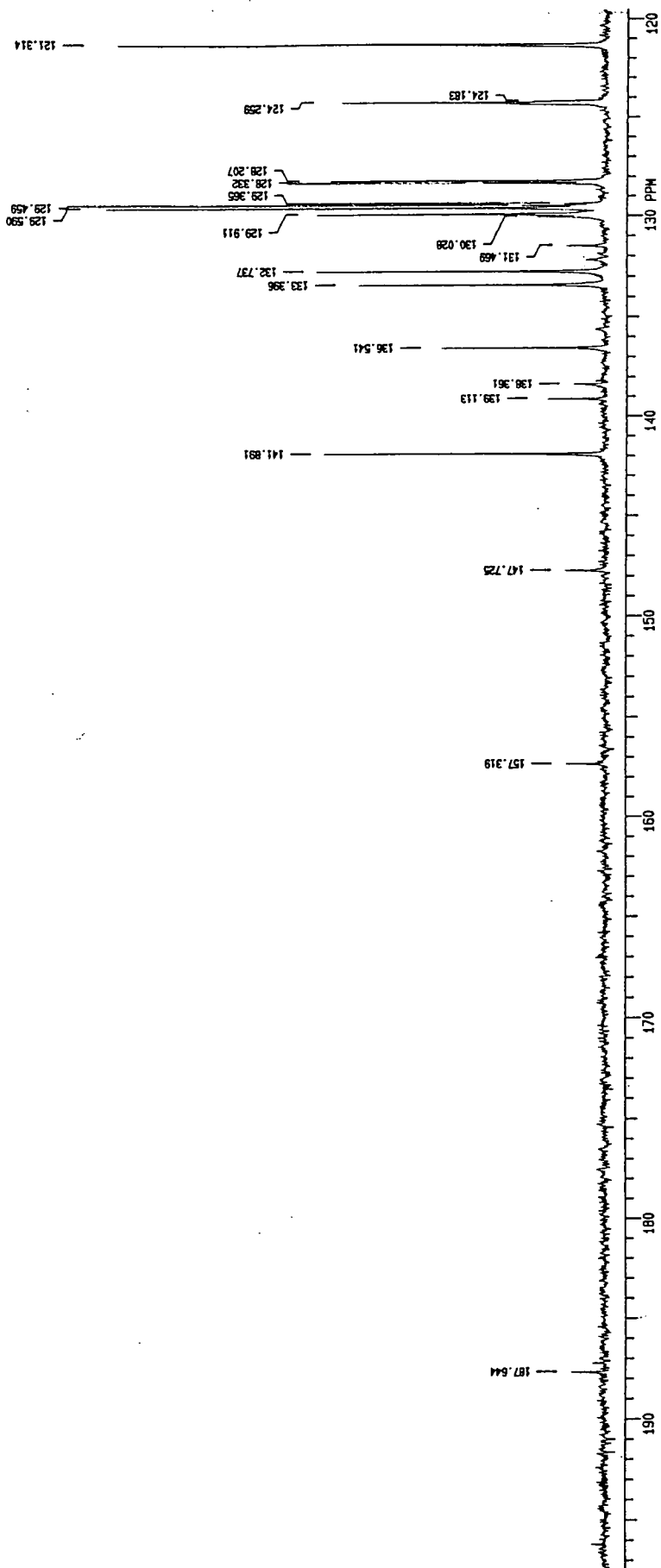
Figure 4.10 ^{13}C nmr spectrum of 4,4′-methylene bis(N-phenyl-2,5-cyclohexadiene-4-imine-1-one) - (ABA type trimer)

143
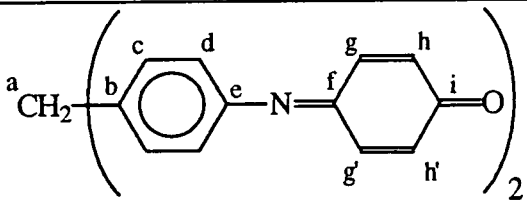
Carbon	Shift (δ)

4,4′-methylene bis(N-phenyl-2,5-cyclohexadiene-4-imine-1-one) (ABA type trimer)

Carbon	Shift (δ)
a	40.87
b	139.11
c	129.59
d	121.31
e	147.72
f	157.32
g, g′	141.89, 128.21
h, h′	133.40, 132.74
i	187.64
triphenylarsine oxide	132.15, 131.47, 129.36
p-benzoquinone	184.40, 136.54
4,4′-methylene bis(phenylisocyanate)	138.36, 129.91, 124.26, 124.18, 40.72

Table 4.4 ^{13}C nmr peak assignments for the ABA type trimer

Hydrolysis of I or other side reaction was not detected. These results show that generating the arsine imine (I or triphenylarsine phenylimine) in the presence of p-benzoquinone under 'dry' conditions allows the coupling reaction to take place without the competition of side reactions and indicates that the degree of polymerisation was limited by the coupling reaction. At this point the project was abandoned without having successfully made the target polymer since eighteen months of the author's research training period had already elapsed.

4.3 EXPERIMENTAL

4.3.1 Reagents and Apparatus

All organic reagents were purchased from Aldrich Chemical Co. and used as received unless indicated otherwise. Melting points were obtained on an Electrothermal digital melting point apparatus and are reported without correction. Infra-red spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. The ^{1}H and ^{13}C nmr spectra

were recorded on either a Varian Gemini 200MHz or a Varian VXR 400MHz spectrometer. Chemical shifts are reported in parts per million (δ) and are referenced to internal TMS.

The IR and nmr spectra for all compounds are recorded in Appendix 3.

All reactions involving triphenylarsine oxide and triphenylarsine phenylimine were performed under a positive pressure of dry N_2 using oven dried glassware and dried solvents.

Purification and drying of triphenylarsine oxide

Triphenylarsine oxide (Flukka Chemicals) was recrystallised twice from toluene and stored under N_2 (m.p.194.2-195.2°C, lit.[30,36,46] 192°C). Before use, in order to remove the associated water of crystallisation,[36] triphenylarsine oxide was dried by Dean Stark distillation with benzene for a minimum of 4 hours. Once cooled to room temperature reactions were carried out using the resulting triphenylarsine oxide solution.

Purification and drying of benzene

Thiophene free benzene was refluxed over sodium under N_2, distilled, degassed, stored under N_2 and used within 4 hours.

4.3.2 Synthesis of Model Compounds

Synthesis of diphenylurea

Phenylisocyanate (3.00ml, 3.29g, 28mmol) was added to a stirred solution of aniline (3.00ml, 3.07g, 33mmol) in ethanol (20ml). The white precipitate, which formed rapidly, was collected by filtration and recrystallised from toluene/ethyl acetate to give diphenylurea as flaky white crystals (1.36g, 6.4mmol, 23%, m.p.234.5-235.2°C, lit.[47] 238-239°C). ^{1}H nmr (DMSO, 200MHz) δ6.99 (tt, 8.4Hz, 1.2Hz, 2H, Ar-$\underline{H}$), δ7.30 (dt, 8.4Hz, 1.2Hz, 4H, Ar-$\underline{H}$), δ7.47 (dd, 8.4Hz, 1.2Hz, 4H, Ar-$\underline{H}$), δ8.68 (s, 2H, N-$\underline{H}$) (Appendix 3.1); ^{13}C nmr (CDCl$_3$, 50MHz) δ118.14, δ121.78, δ128.7 (all aromatic $\underline{C}$-H), δ139.68 (aromatic $\underline{C}$-NH), δ152.50 ($\underline{C}$=O), (Appendix 3.2); IR (KBr disc) 3325.8cm^{-1}

(m, secondary amide N-H stretch), 3024.2cm^{-1} (w, aryl C-H stretch), 1648.8 and 1555.7cm^{-1} (s, secondary amide C=O), 1594.1 and 1497.5cm^{-1} (s, aryl-H vibration), (Appendix 3.3).

Synthesis of diphenyl carbodiimide

The method of Monagle[42] was used. To neat phenylisocyanate (15ml, 16.44g, 138mmol) under N$_2$ triphenylarsine oxide (0.60g, 19mmol) was added with stirring. Once the vigorous effervescence had ceased the yellow solution was stirred at 80°C for 4 hours. On cooling an oil formed which was vacuum distilled (>1mmHg, 118-120°C) to give a colourless liquid (3.72g, 19mmol, 28%). Found C,81.2; H,5.0; N,13.8% (calculated for C$_{13}$H$_{10}$N$_2$: C,80.4; H,5.2; N,14.4%). ^{1}H nmr (400MHz, CDCl$_3$) δ7.31 (tt, 7.8Hz, 2.2Hz, 4H, Ar-H), δ7.16 (m, 6H, Ar-H), (Appendix 3.4); ^{13}C nmr (100MHz, CDCl$_3$) δ124.35, δ125.75, δ129.66 (all aromatic C-H), δ 135.1 (N=C=N), δ138.59 (aromatic C-N=), (Appendix 3.5); IR (neat) 3061.5, 3025.7cm^{-1} (m, aryl-H stretch), 2137.5cm^{-1} (s, carbodiimide N=C=N), 1589.1, 1486.2cm^{-1} (s, aryl C-H vibration), (Appendix 3.6). On standing for several days under N$_2$ this material formed a hard, insoluble and intractable white solid.

Synthesis of N,N′-diphenyl-2,5-cyclohexadiene-1,4-diimine using lead (IV) oxide

Lead (IV) oxide (0.93g, 3.9mmol) was added to a stirred solution of N,N′-diphenyl-1,4-phenylenediamine (0.34g, 1.3mmol) in chloroform (30ml) and the mixture stirred for 60 minutes during which time the colour changed from brown to dark red. The mixture was filtered, residual solids washed with chloroform (2x 20ml), organic portions combined and solvent removed to give an orange powder. Crude product was recrystallised from cyclohexane to give N,N′-diphenyl-2,5-cyclohexadiene-1,4-diimine as an orange powder (0.26g, 1.0mmol, 77%, m.p.186.5-186.8°C (lit.[48] 185-186°C). ^{1}H nmr (CDCl$_3$, 400MHz, Appendix 3.7) and ^{13}C nmr (CDCl$_3$, 100MHz, Appendix 3.8) were consistent with those reported in the literature.[49] IR (KBr disc) 3042.1cm^{-1} (m, aryl C-H stretch), 1577.6cm^{-1} (s, quinone type C=C or α,β-unsaturated imine C=N), (Appendix 3.9).

4.3.3 Reactions Involving Triphenylarsine Oxide

<u>Preparation of triphenylarsine phenylimine</u>

In a typical reaction a solution of phenylisocyanate (1.05ml, 1.10g, 9.7mmol) in benzene (20ml) was added dropwise to a stirred slurry of triphenylarsine oxide (2.72g, 8.4mmol) in benzene (150ml) at 0°C, keeping the temperature of the reaction mixture between 4 and 5°C. A white precipitate was deposited from a yellow solution. Once the addition was complete the mixture was heated for 10 minutes between 60 and 70°C to dissolve all solid at which point the reaction flask was cooled quickly to room temperature. Solvent was removed by freeze drying and the resulting white solid recrystallised from benzene/hexane to give an off white powder. The product was identified as a mixture of triphenylarsine phenylimine, triphenylarsine oxide and aniline using ^{13}C nmr spectroscopy, HETCOR nmr (Appendix 3.12) and reference compounds. For discussion of the ^{1}H nmr (Appendix 3.10) and ^{13}C nmr (Appendix 3.11) spectra see Section 4.2.

<u>Preparation of N,N'-diphenyl-2,5-cyclohexadiene-1,4-diimine using triphenylarsine phenylimine</u>

In a typical reaction, p-benzoquinone (0.52g, 4.8mmol) in benzene (10ml) was added dropwise to a stirred solution of triphenylarsine phenylimine (approx. 7.2mmol, impure, prepared as described above) in benzene (80ml) at room temperature. The clear yellow solution rapidly became brick red and was stirred for a further 60 minutes. Solvent was removed by freeze drying to give an orange/red solid which was washed with cold (-20°C) diethyl ether (2x20ml) to extract product. The ether solutions were combined and solvent removed to give a red solid which was recrystallised twice from cyclohexane to give crude product. N,N'-diphenyl-2,5-cyclohexadiene-1,4-diimine was identified using nmr spectroscopy as a component of this mixture but complete isolation and characterisation were not achieved. The characteristic peaks which allowed identification of the components are given below. ^{1}H nmr (CDCl$_3$, 200MHz) δ6.74 (m, Ar-<u>H</u>), δ6.92 (m, Ar-<u>H</u>), δ7.18 (m, Ar-<u>H</u>), δ7.36 (m, Ar-<u>H</u> and As-Ph-<u>H</u>), δ7.54 (m, As-Ph-<u>H</u>), δ7.71 (m, As-Ph-<u>H</u>), δ9.39 (s, Ph-N<u>H</u>-CO), (Appendix 3.13); ^{13}C nmr (CDCl$_3$, 50MHz) N,N'-diphenyl-2,5-cyclohexadiene-1,4-diimine, δ120.52, δ120.59 (both aromatic <u>C</u>-H), δ124.57 (N=C-<u>C</u>H=CH), δ125.16 (N=C-<u>C</u>H=CH and aromatic <u>C</u>-H), δ128.93, δ128.98 (both aromatic <u>C</u>-H), δ136.52, δ137.69 (both N=C-<u>C</u>H=CH), δ149.99

(aromatic C-N=C), δ158.45 (N=C-CH=CH), triphenylarsine oxide, δ129.56, δ131.36, δ132.45 (all aromatic C-H), diphenylurea, δ118.76, δ121.67, δ128.61 (all aromatic C-H), δ139.98 (aromatic C-NH), δ153.8 (imide C=O), (Appendix 3.14).

Attempted Preparation of 4,4'-methylene bis(triphenylarsine phenylimine)

4,4'-Methylene bis(phenylisocyanate) (4.35g, 17.3mmol) in benzene (50ml) was added dropwise to a stirred slurry of triphenylarsine oxide (11.20g, 34.7mmol) in benzene (160ml) at 0°C, keeping the temperature of the reaction mixture was between 4 and 5°C. The previously colourless solution instantly became pale yellow and the white precipitate remained. Once the addition was complete the mixture was allowed to warm slowly to room temperature over 60 minutes and was then refluxed for 120 minutes during which time about half of the solid dissolved and the solution became darker yellow in colour. Removal of the precipitate by filtration gave a clear yellow solution which was freeze dried to give a yellow solid. The ^{1}H (Appendix 3.15), ^{13}C (Figure 4.10) and HETCOR (Appendix 3.16) nmr spectra of this crude material indicated the presence of 4,4'-methylene bis(triphenylarsine phenylimine) (for discussion of the ^{13}C nmr spectrum see Section 4.2).

Attempted polymerisation of 4,4'-methylene bis(phenylisocyanate) and p-benzoquinone - method 1

In a typical reaction, triphenylarsine oxide (0.17g, 0.5mmol) in benzene (15ml) was added dropwise to a stirred solution of 4,4'-methylene bis(phenylisocyanate) (5.76g, 23mmol) and p-benzoquinone (2.53g, 23mmol) in refluxing benzene (50ml). The initially yellow solution became instantly red and was refluxed for a further 30 minutes. On cooling to room temperature the mixture was freeze dried to give a red powder. The ^{1}H nmr (Appendix 3.17) and ^{13}C nmr (Figure 4.11) spectra indicated only starting material and ABA type trimer were present (see discussion in section 4.2). The ratios of reagents used in the attempted polymerisation of 4,4'-methylene bis(phenylisocyanate) and p-benzoquinone are shown in Table 4.5.

Reaction	Ratio p-benzoquinone	Ratio diisocyanate	Ratio Ph₃AsO	Solvent	Result
1	1	1	1	benzene	no polymer
2	1	1	1/8	benzene	no polymer
3	1	1	1/50	benzene	no polymer

Table 4.5 Reaction ratios used in the attempted polymerisation of 4,4′-methylene bis(phenylisocyanate) and p-benzoquinone - method 1

Attempted polymerisation of 4,4′-methylene bis(phenylisocyanate) and p-benzoquinone - method 2

p-Benzoquinone (0.51g, 4.8mmol) was added to a stirred solution of 4,4′-methylene bis(triphenylarsine phenylimine) (3.85g, 4.8mmol, prepared as described above) under N_2 at room temperature. The pale yellow solution became red and was stirred for 5 hours. Solvent was removed by freeze drying to give a red solid which was washed twice with cold (-20°C), dry diethyl ether (2x20ml) to extract product. Solvent was removed by freeze drying to give crude product which nmr spectroscopy showed to be triphenylarsine oxide and ABA type trimer. ^{1}H nmr (CDCl₃, 200MHz) triphenylarsine oxide: δ7.54 and δ7.72 (m, both aromatic C-H̲), ABA type trimer: δ4.04 (s, 2H, Ar-CH̲₂-Ar), δ6.52, δ6.57, δ6.67, δ6.72, δ6.89, δ7.12, δ7.18, δ7.28 (m, 16H, aromatic C-H̲), benzene: δ7.36 (s, aromatic C-H̲), diethyl ether: δ1.21 (t, 6H, CH̲₃-CH₂), δ3.47 (q, 4H, CH̲₂-CH₃), (Appendix 3.18); ^{13}C nmr (CDCl₃, 50MHz) triphenylarsine oxide, δ129.38, δ131.48, δ132.21 (aromatic C̲-H), ABA type trimer: δ121.31 (aromatic C̲-H), δ128.20 (N=C-C̲H=C), δ129.59 (aromatic C̲-H), δ132.73, δ133.40, δ141.89 (all N=C-C̲H=C), δ147.73 (aromatic C̲-N), (Appendix 3.19); IR (KBr disc) 3051.5cm⁻¹ (w, aryl C-H stretch), 1643.1cm⁻¹ (s, quinone C=O), 1617.5cm⁻¹ (m, quinone C=C), (Appendix 3.20).

4.4 CONCLUSIONS

Although the coupling reaction of phenylisocyanate and p-benzoquinone looked, on paper, promising when it was attempted it proved to be impossible to obtain high yields of N,N′-diphenyl-2,5-cyclohexadiene-1,4-diimine. Initially this was due to the side reactions of phenylisocyanate and then triphenylarsine phenylimine with moisture. Once moisture was excluded from the reaction, the synthesis and reaction of both triphenylarsine phenylimine and 4,4′-methylene bis(triphenylarsine phenylimine) with p-benzoquinone were shown to be possible.

Polymerisation using 4,4′-methylene bis(phenylisocyanate) did not give high molecular weight material using the methods tried. Only material approximating to an ABA type trimer was produced. At the end of these polymerisation attempts, only unreacted starting materials and ABA trimer were detected in the reaction mixture indicating that the problem of side reactions with water had been overcome and that further reaction to give higher molecular weight oligomers might indeed have been possible using, perhaps, greatly extended reaction times. More severe reaction conditions were excluded since elevated temperatures were known to result in carbodiimide formation. Given the inability to produce oligomers of any significant molecular weight this project was abandoned.

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APPENDIX 1

Spectra from Chapter 2
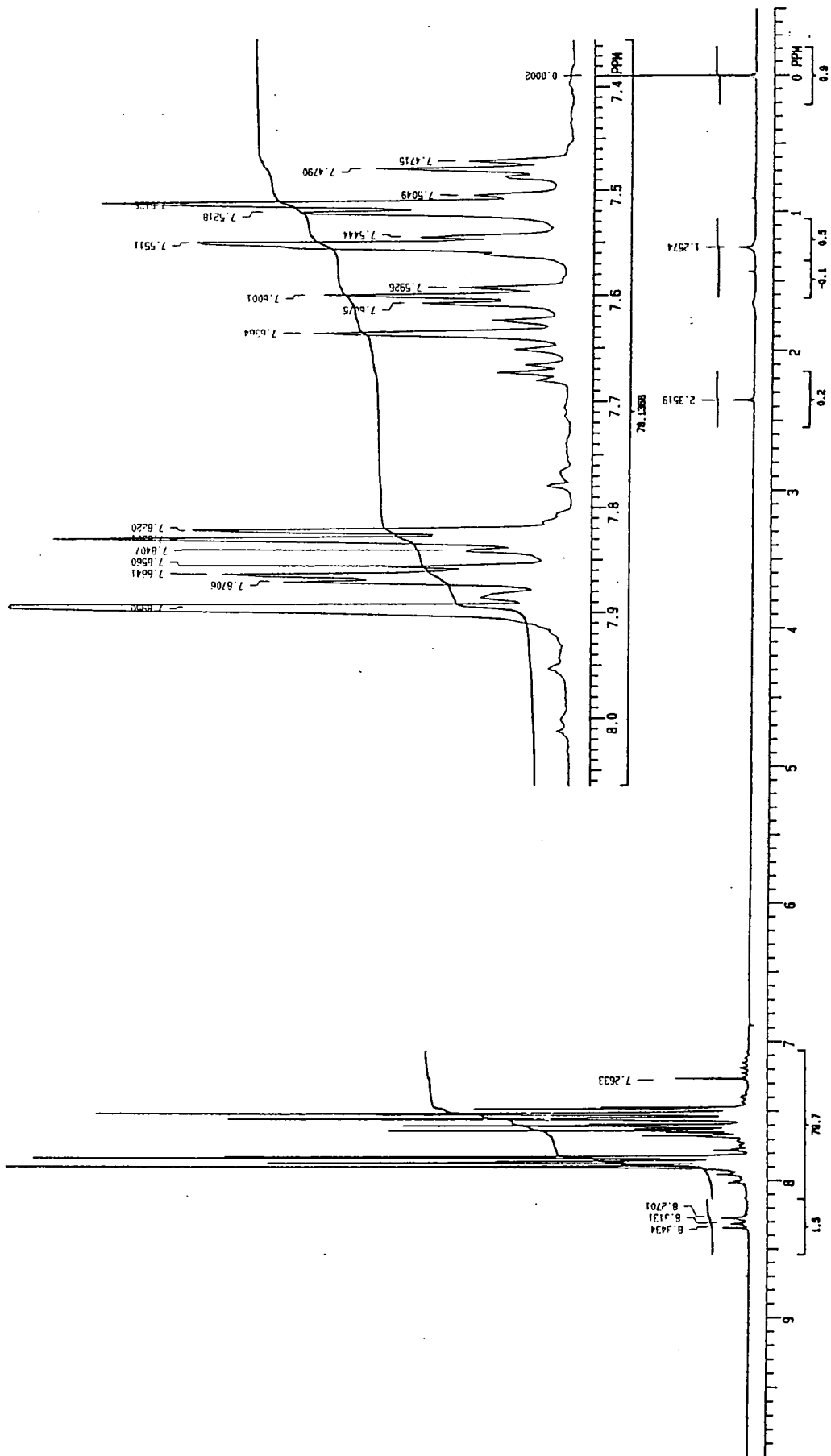
Appendix 1.1 ^{1}H nmr spectrum of 1,4-dibenzoylbenzene (II)
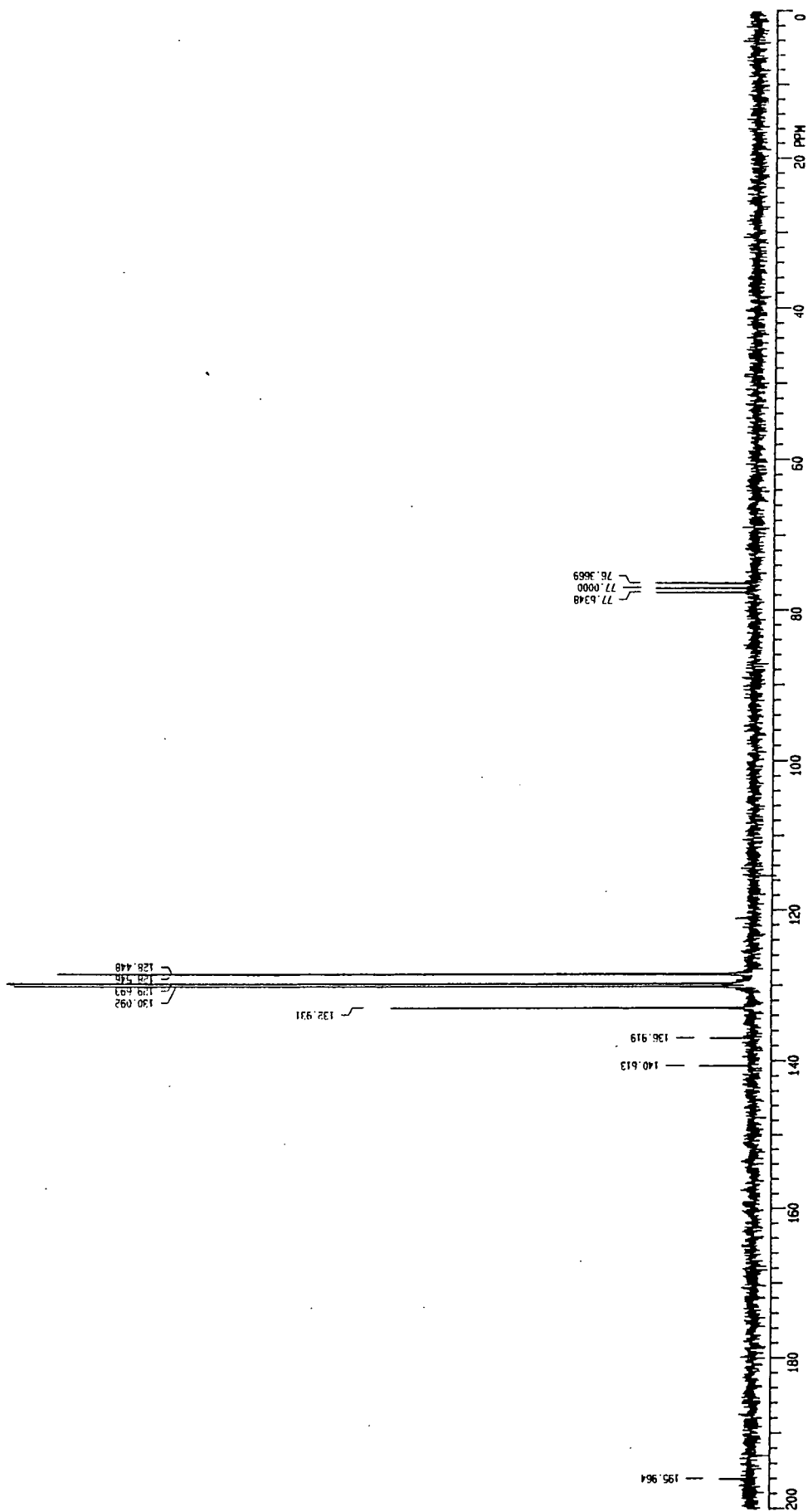
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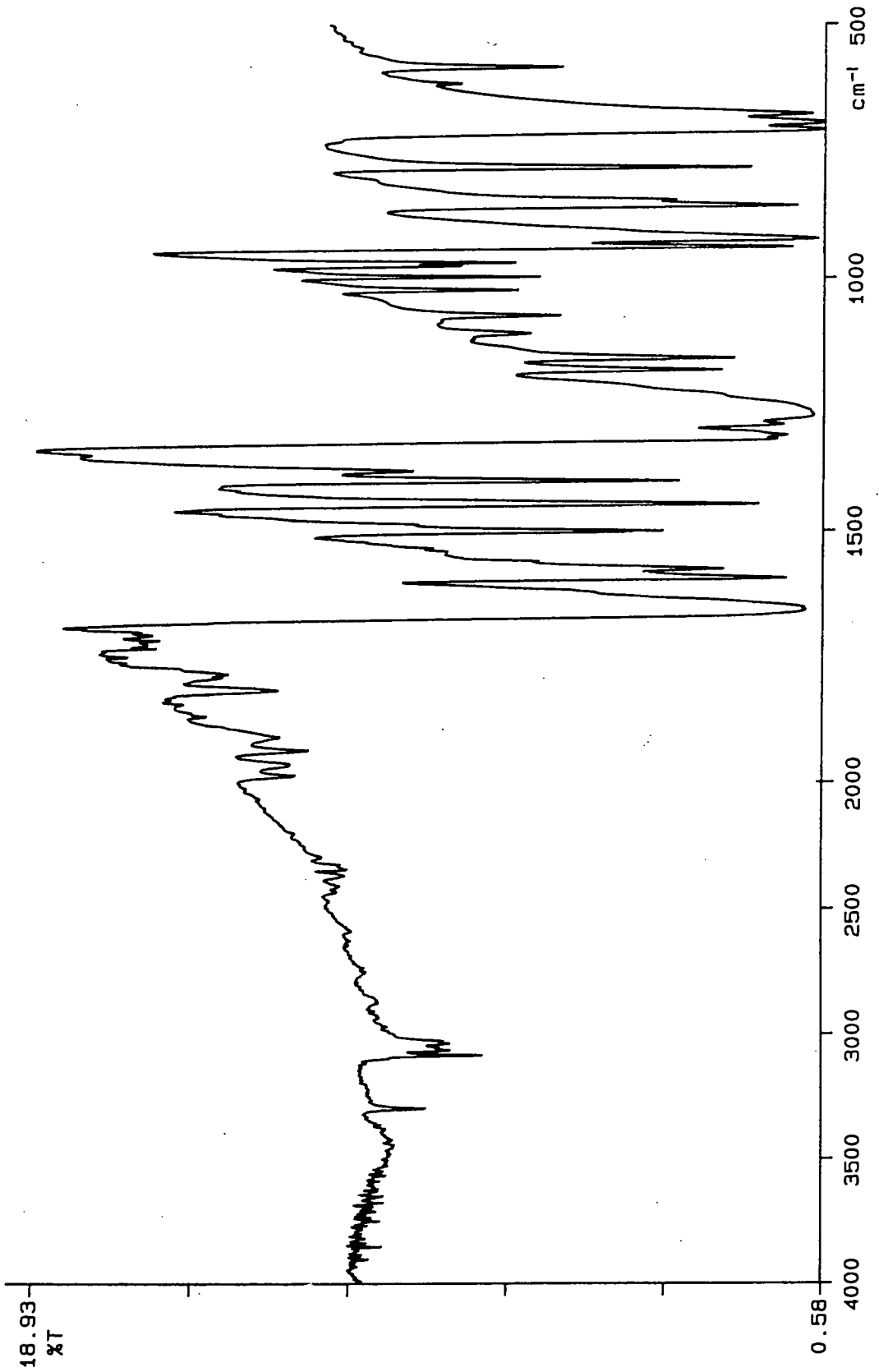
Appendix 1.3 IR spectrum of 1,4-dibenzoylbenzene (II)
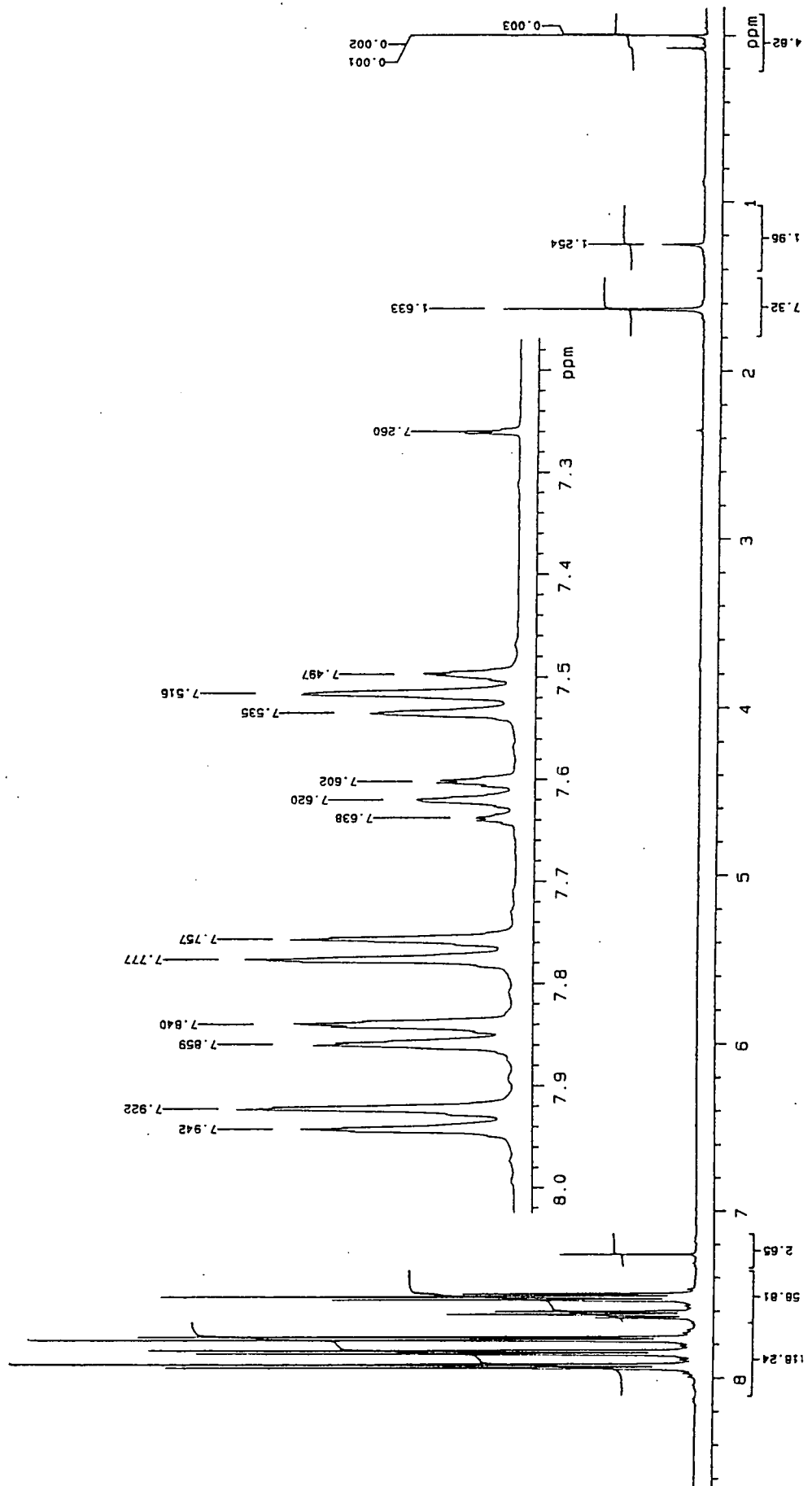
Appendix 1.4 ¹H nmr spectrum of 4,4′-dibenzoyldiphenyl (I)
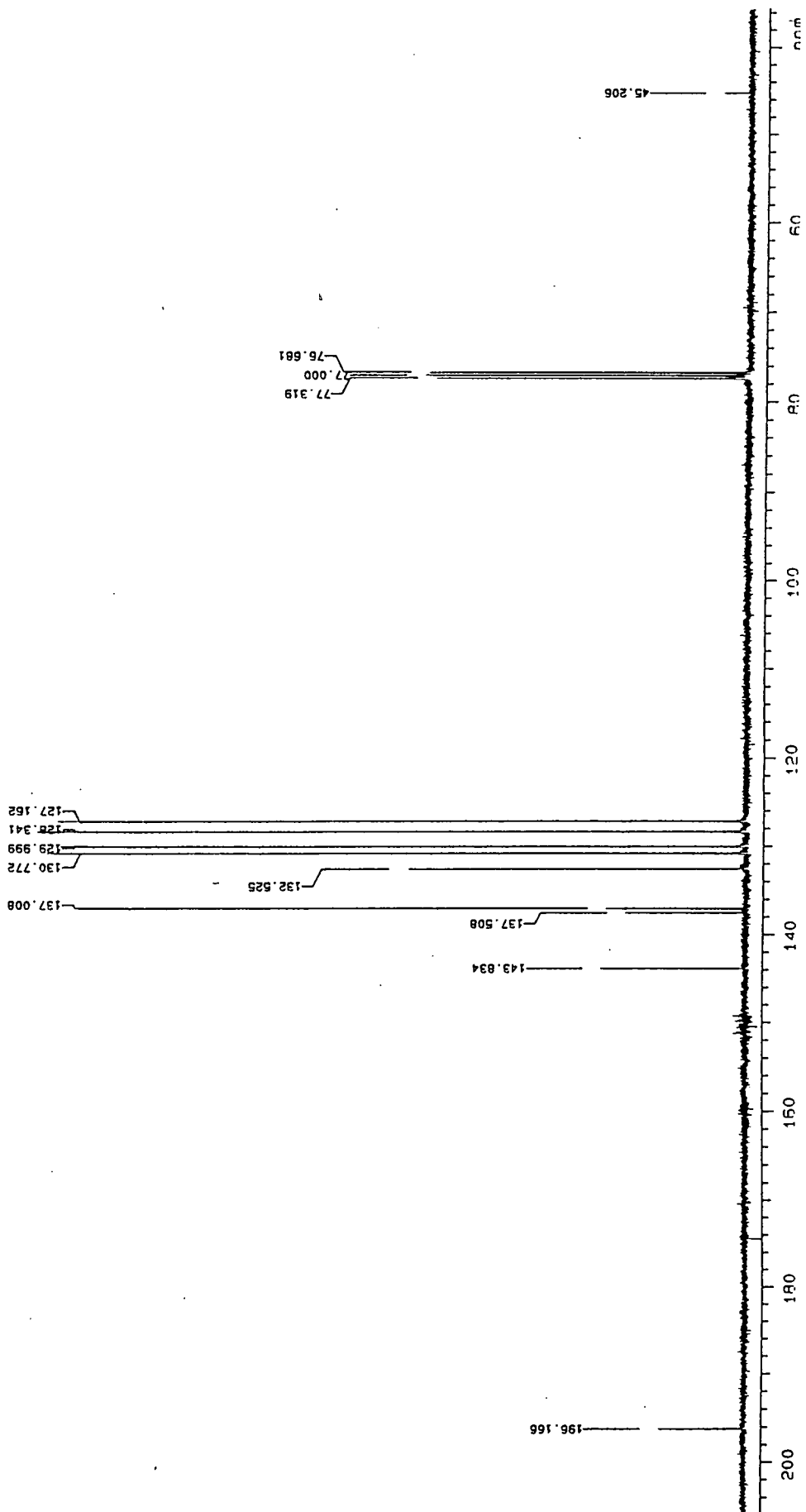
Appendix 1.5 ^{13}C nmr spectrum of 4,4′-dibenzoyldiphenyl (I)
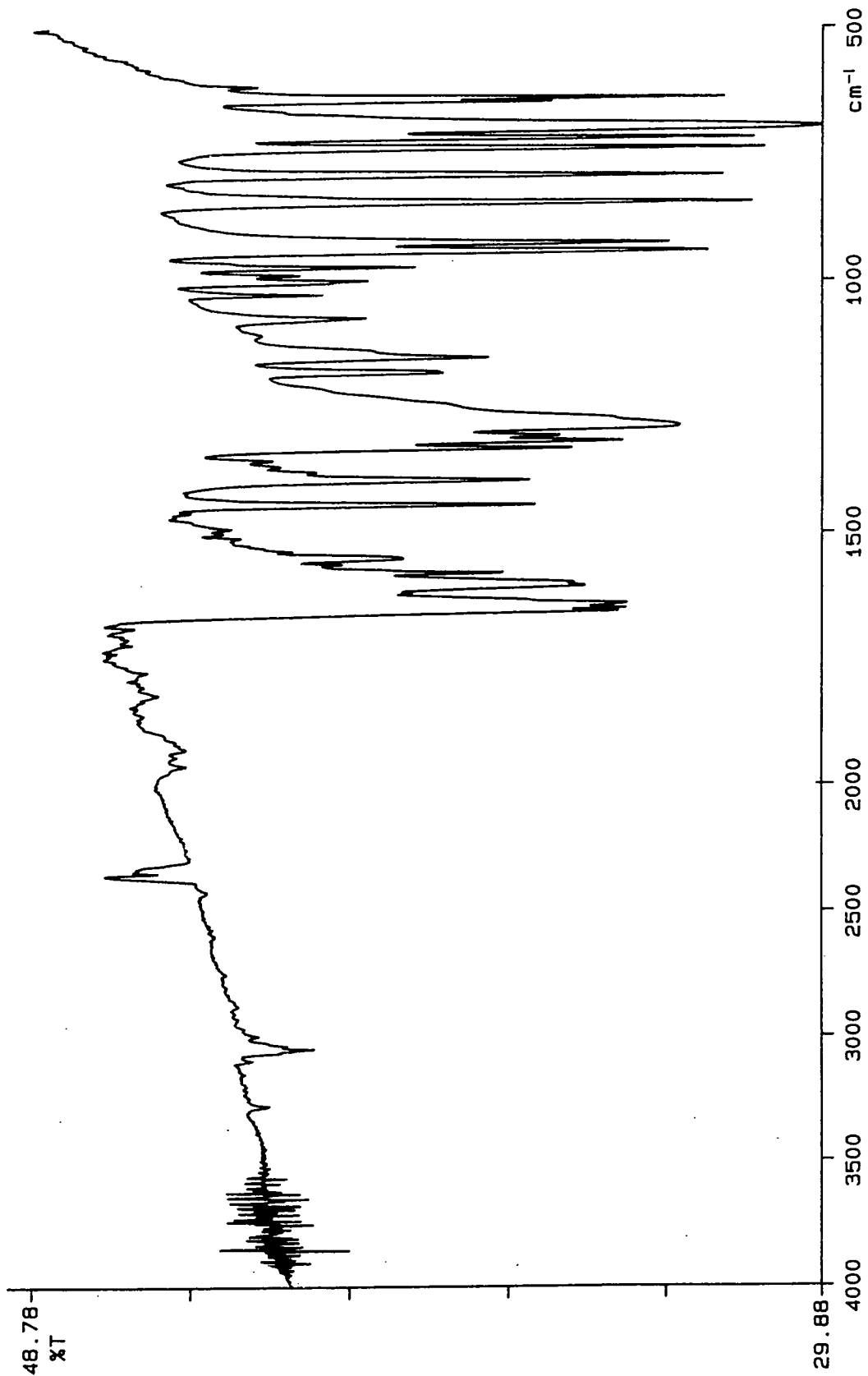
Appendix 1.6 IR spectrum of 4,4′-dibenzoyldiphenyl (I)
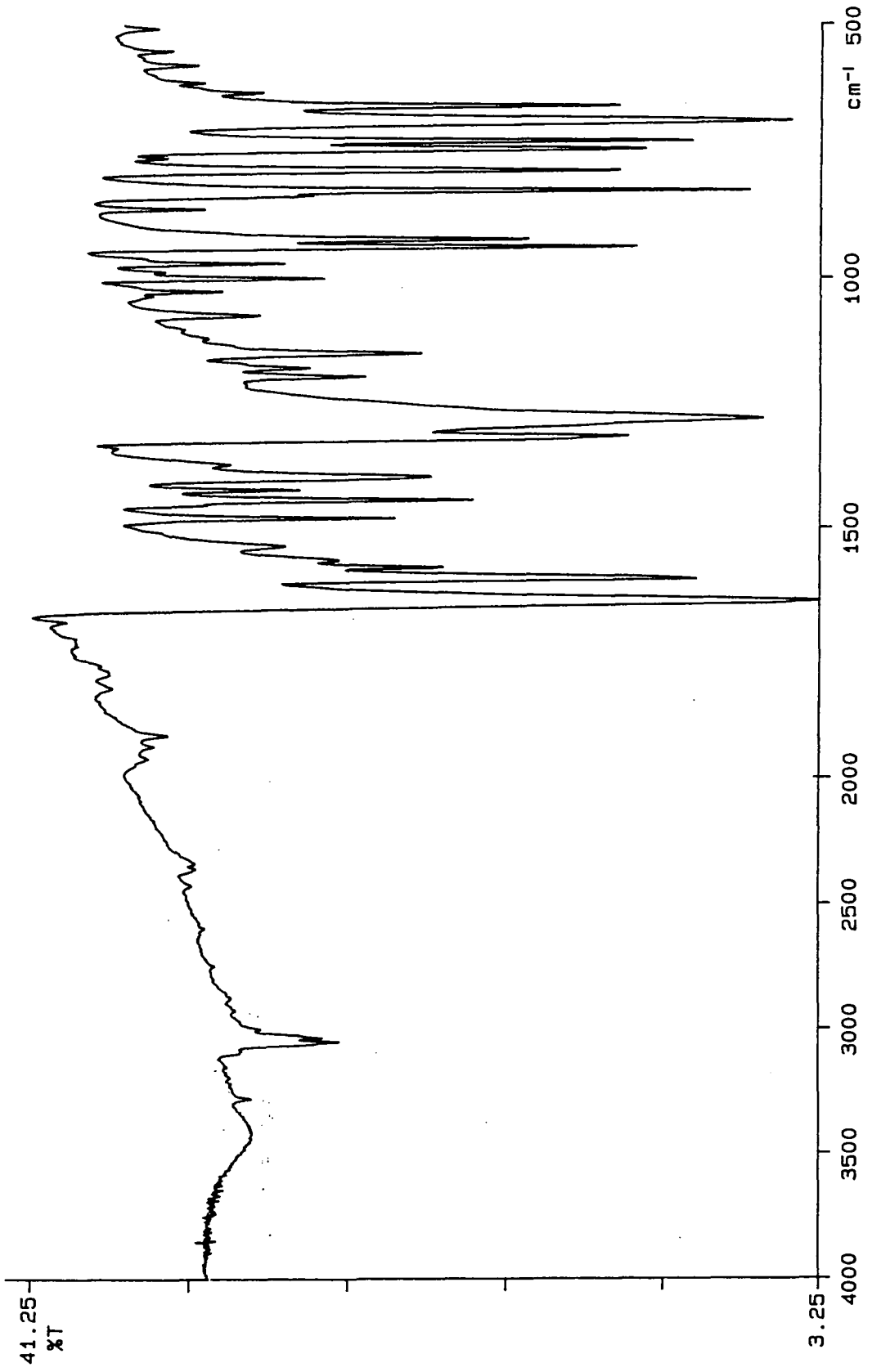
Appendix 1.7 IR spectrum of 4,4″-dibenzoyl-p-terphenyl (IV)
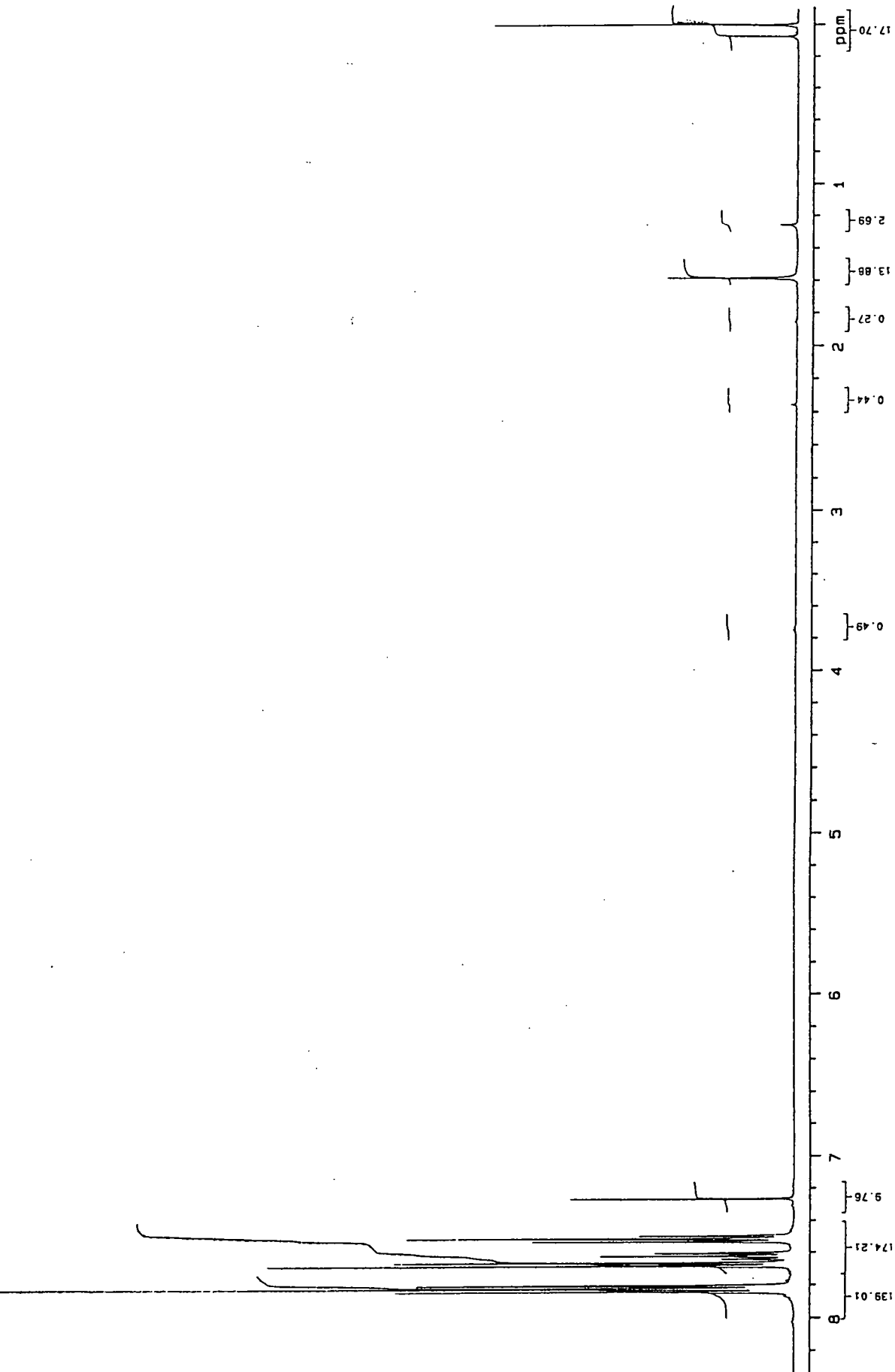
Appendix 1.8 ^{1}H nmr spectrum of 4,4′-dibenzoyldiphenylacetylene (V)

81.469

126.889

128.383
129.872
130.087
131.665
132.623

137.212
137.281

195.858

190

180

170

160

150

140

130

120

110

100

ppm
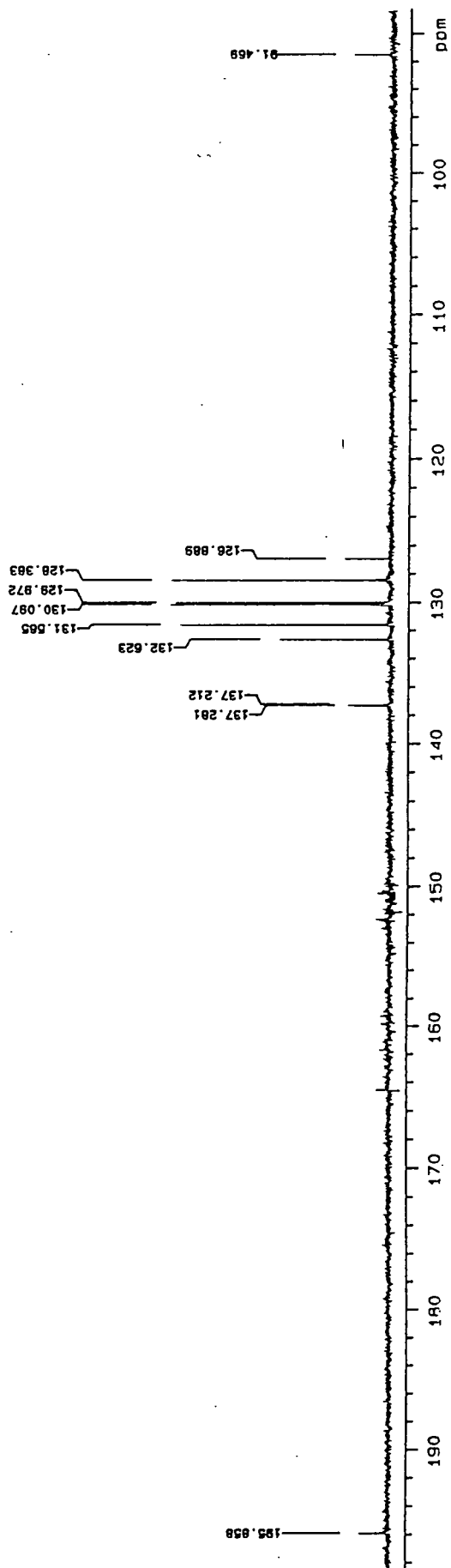
Appendix 1.9 ^{13}C nmr spectrum of 4,4′-dibenzoyldiphenylacetylene (V)
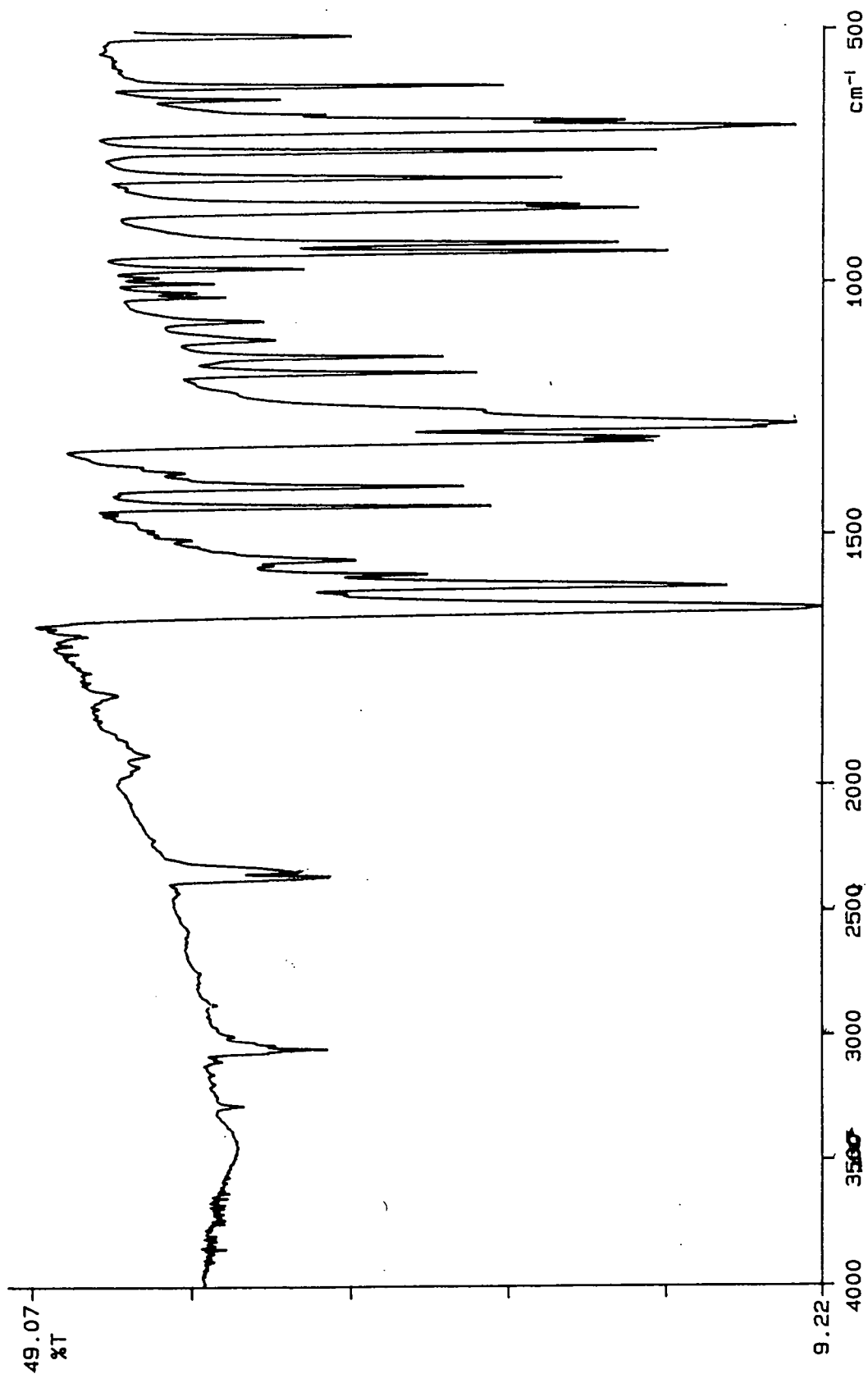
Appendix 1.10 IR spectrum of 4,4′-dibenzoyldiphenylacetylene (V)
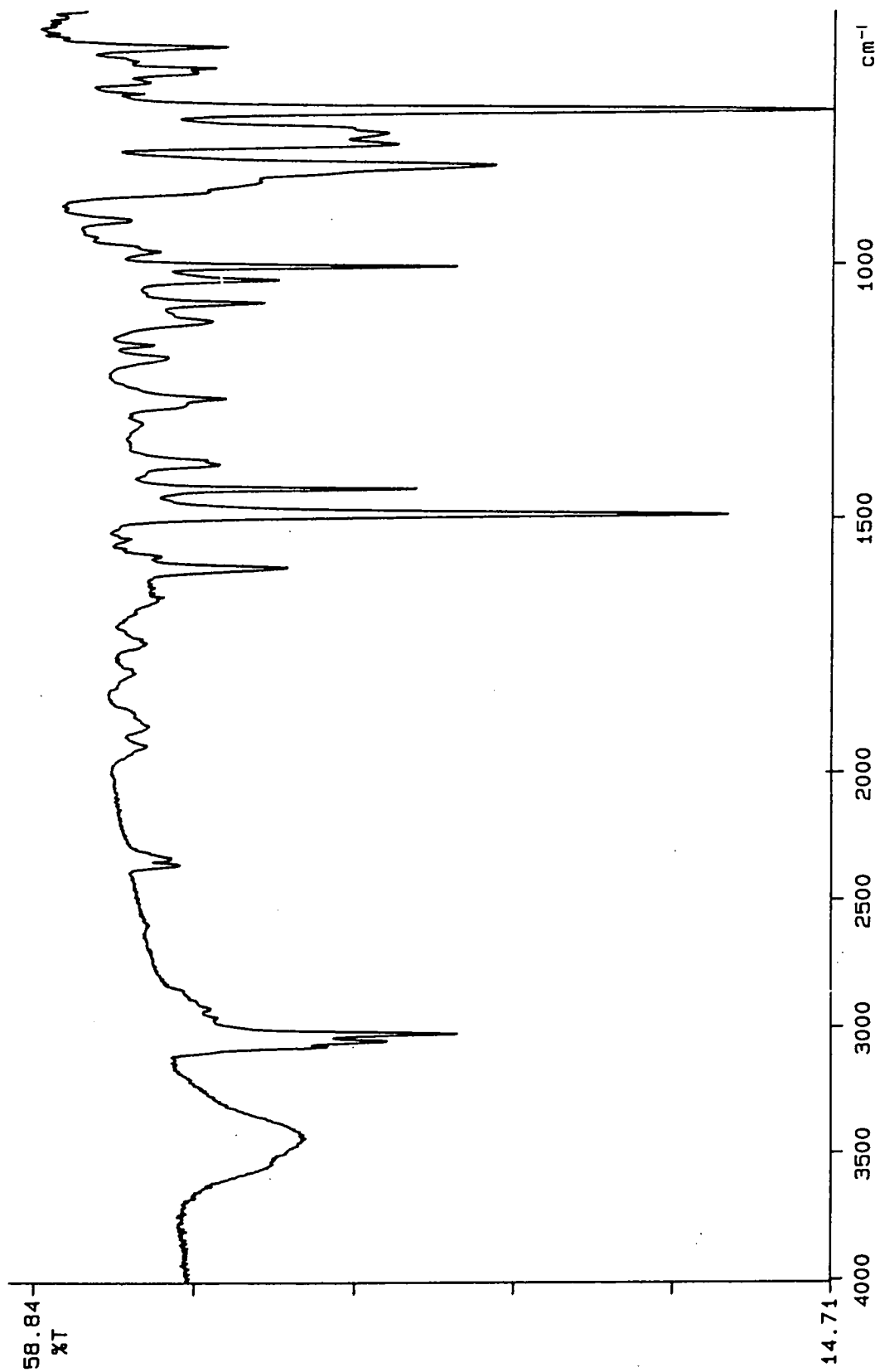
Appendix 1.11 IR spectrum of poly(4,4′-diphenylene diphenylvinylene)
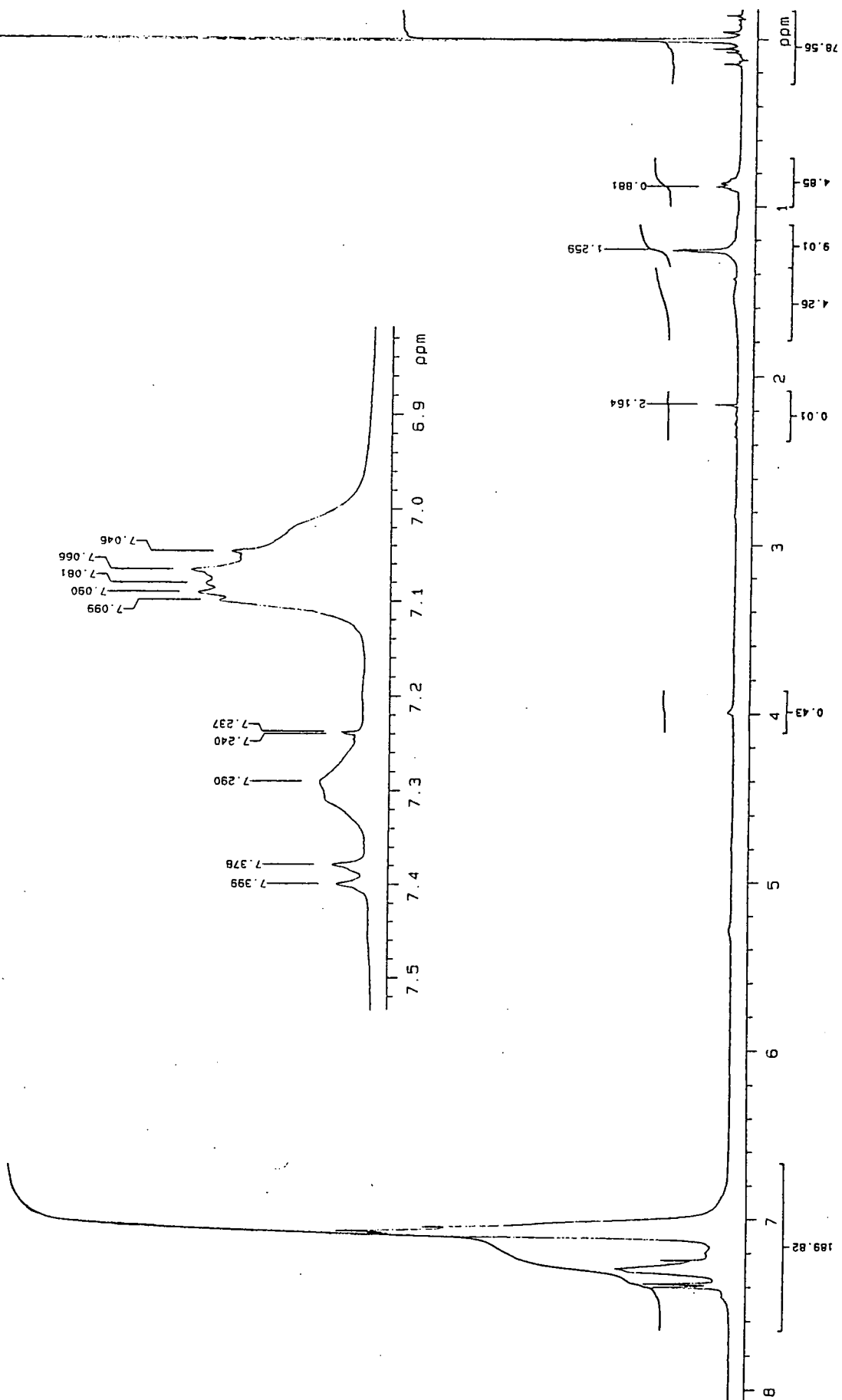
Appendix 1.12 ^{1}H nmr spectrum of poly(4,4′-diphenylene diphenylvinylene)
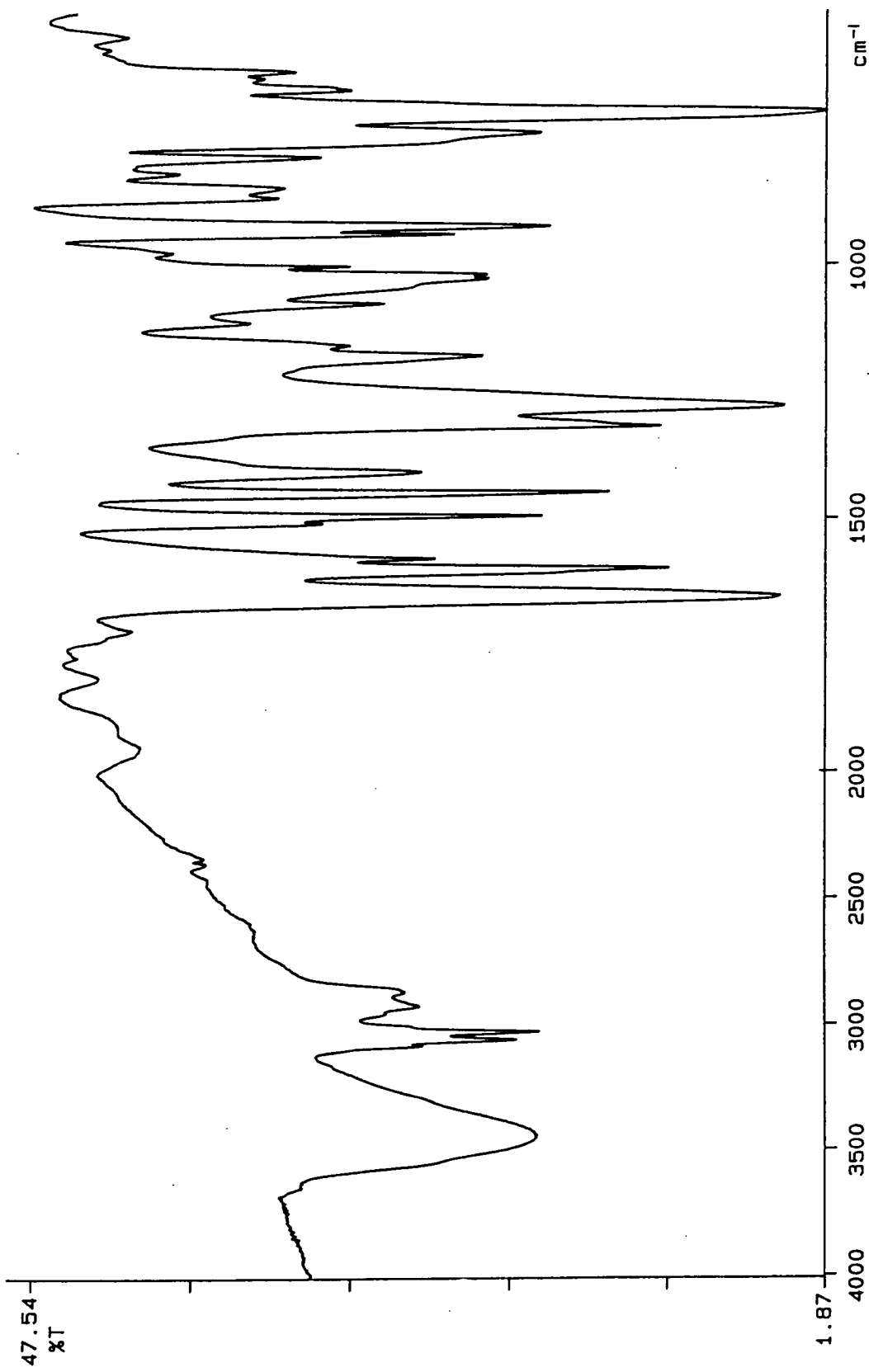
Appendix 1.13 IR spectrum of the products from the attempted polymerisation of 1,4-dibenzoylbenzene
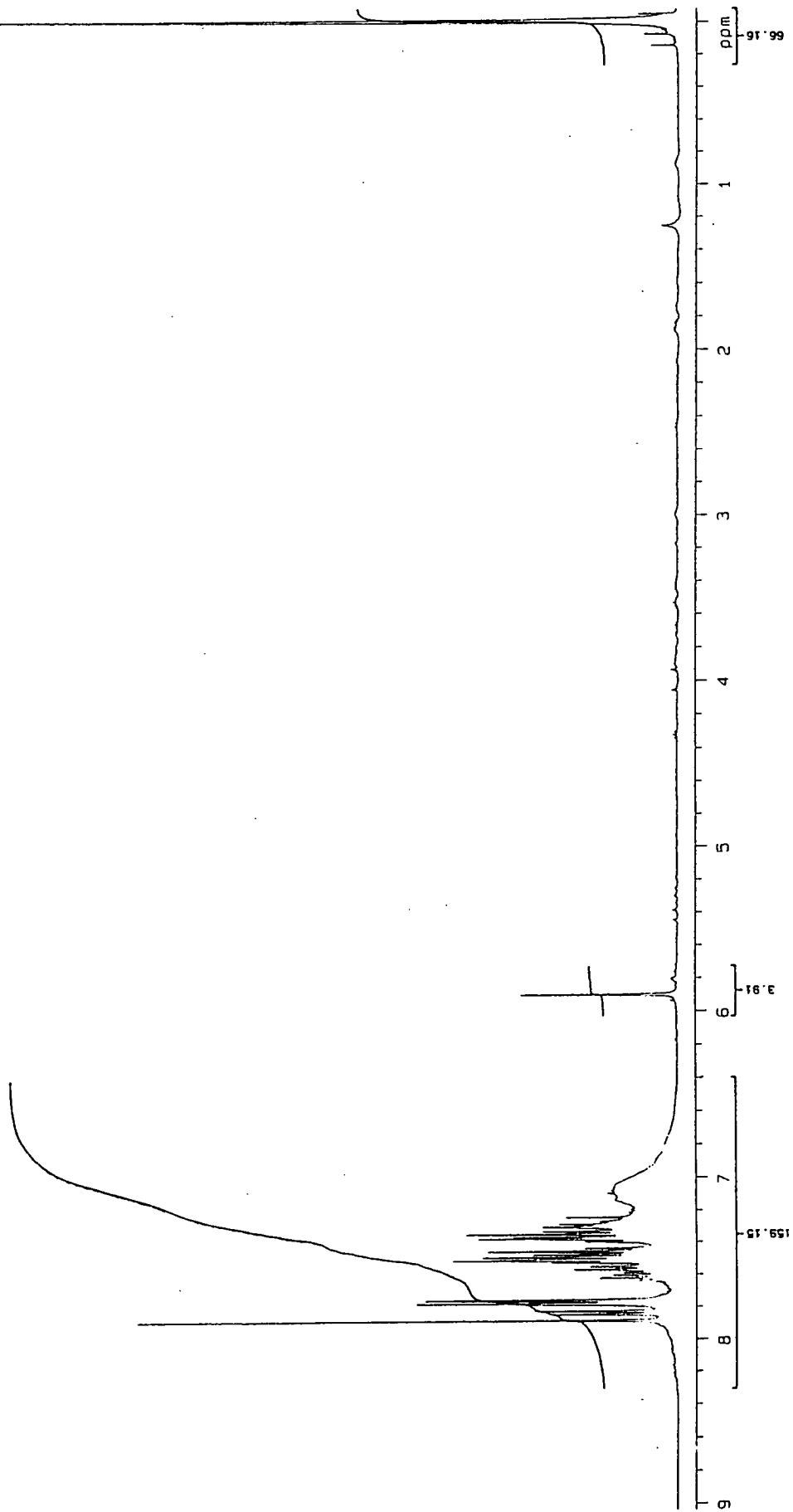
Appendix 1.14 ^{1}H nmr spectrum of the products from the attempted polymerisation of 1,4-dibenzoylbenzene
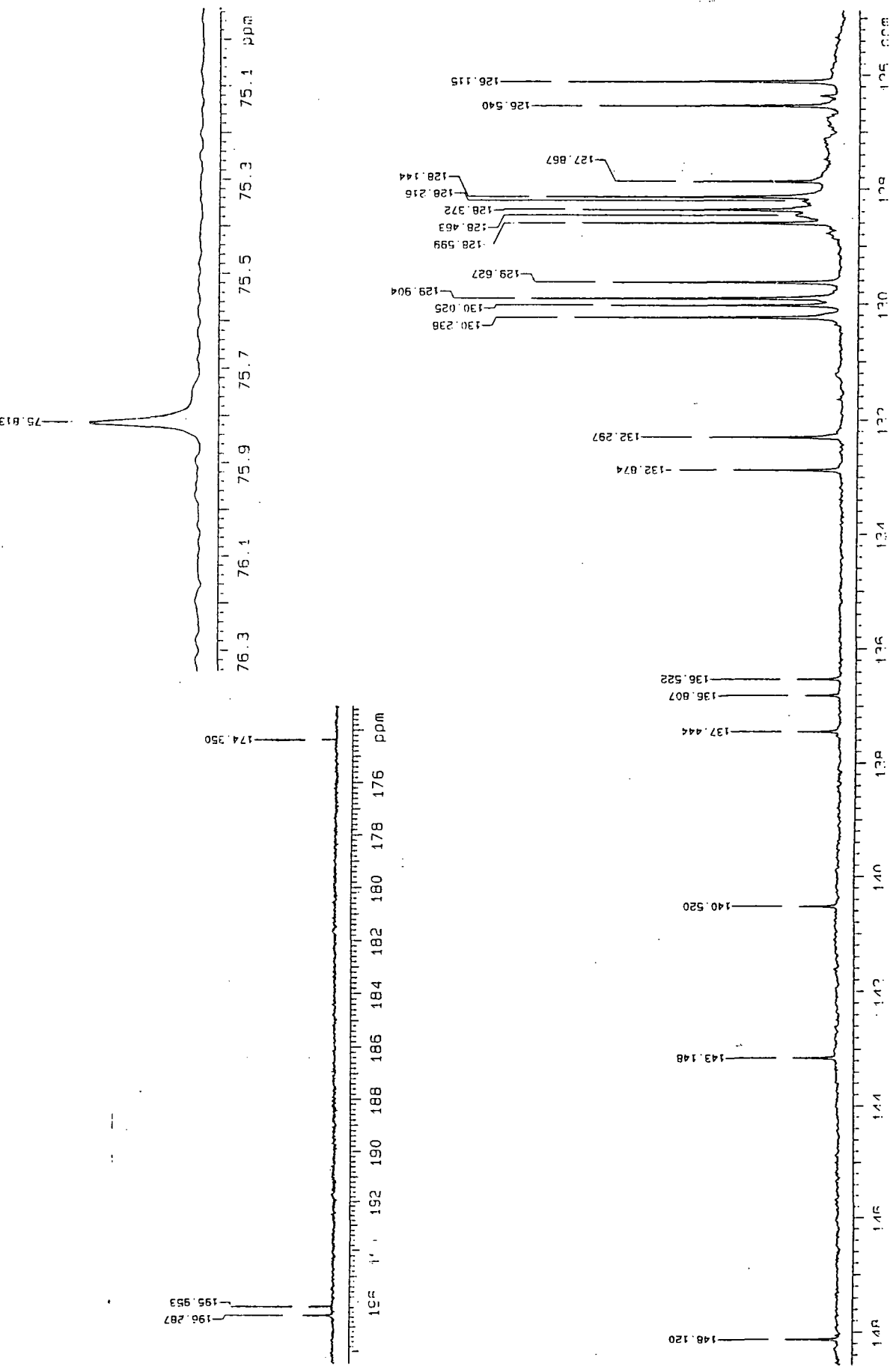
Appendix 1.15 ^{13}C nmr spectrum of the products from the attempted polymerisation of 1,4-dibenzoylbenzene
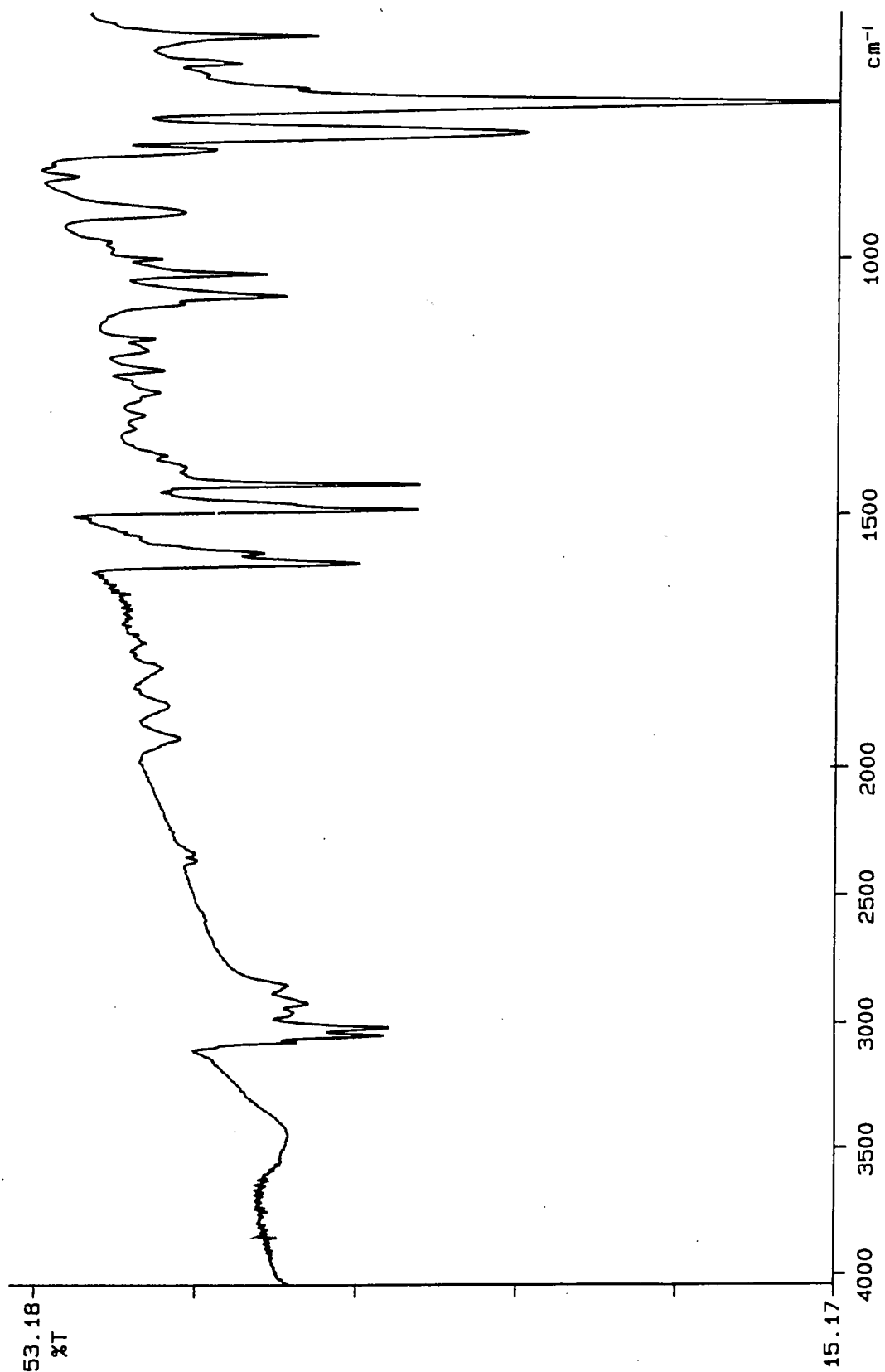
Appendix 1.16 IR spectrum of poly(1,3-diphenylene diphenylvinylene)
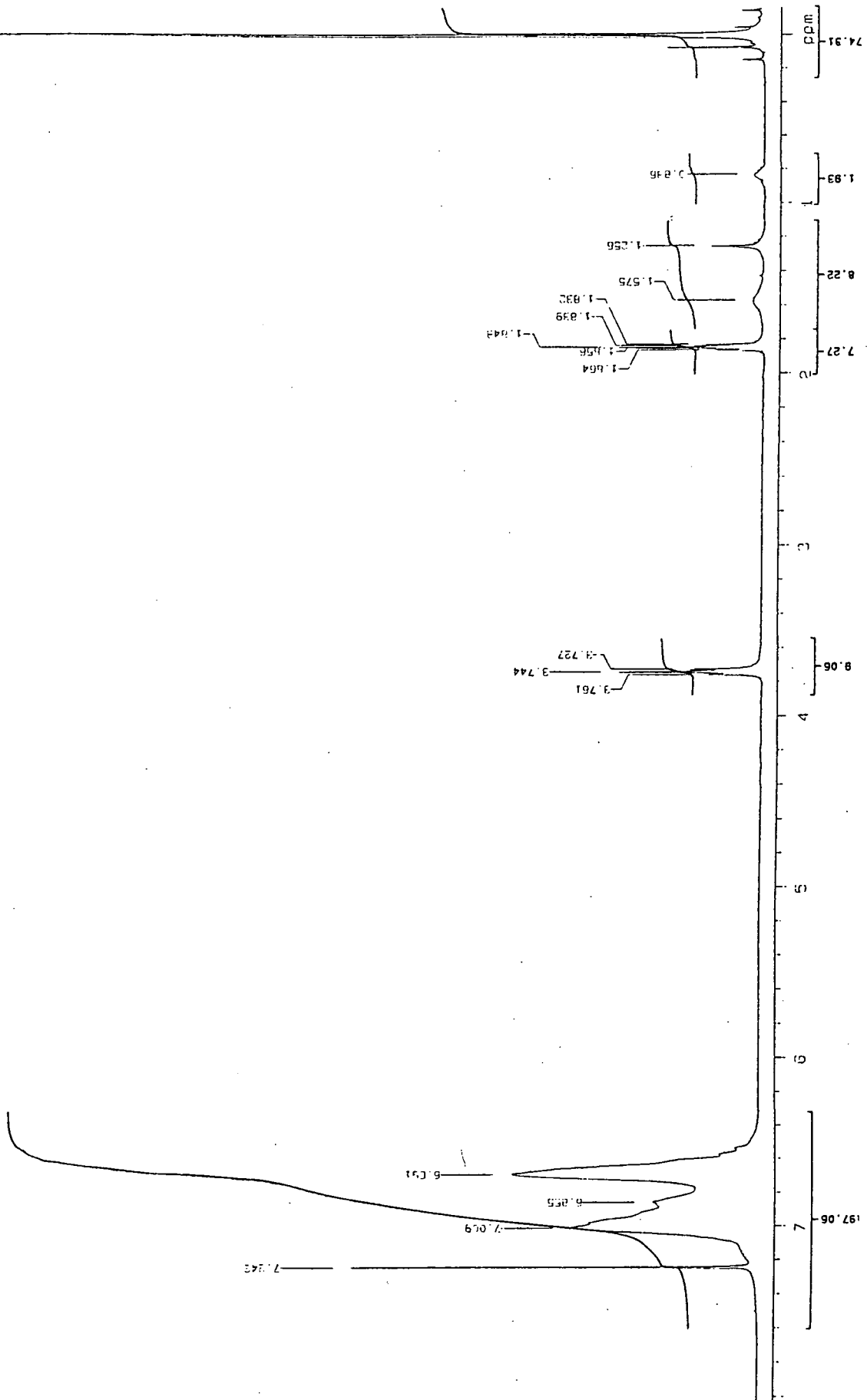
Appendix 1.17 ¹H nmr spectrum of poly(1,3-diphenylene diphenylvinylene)
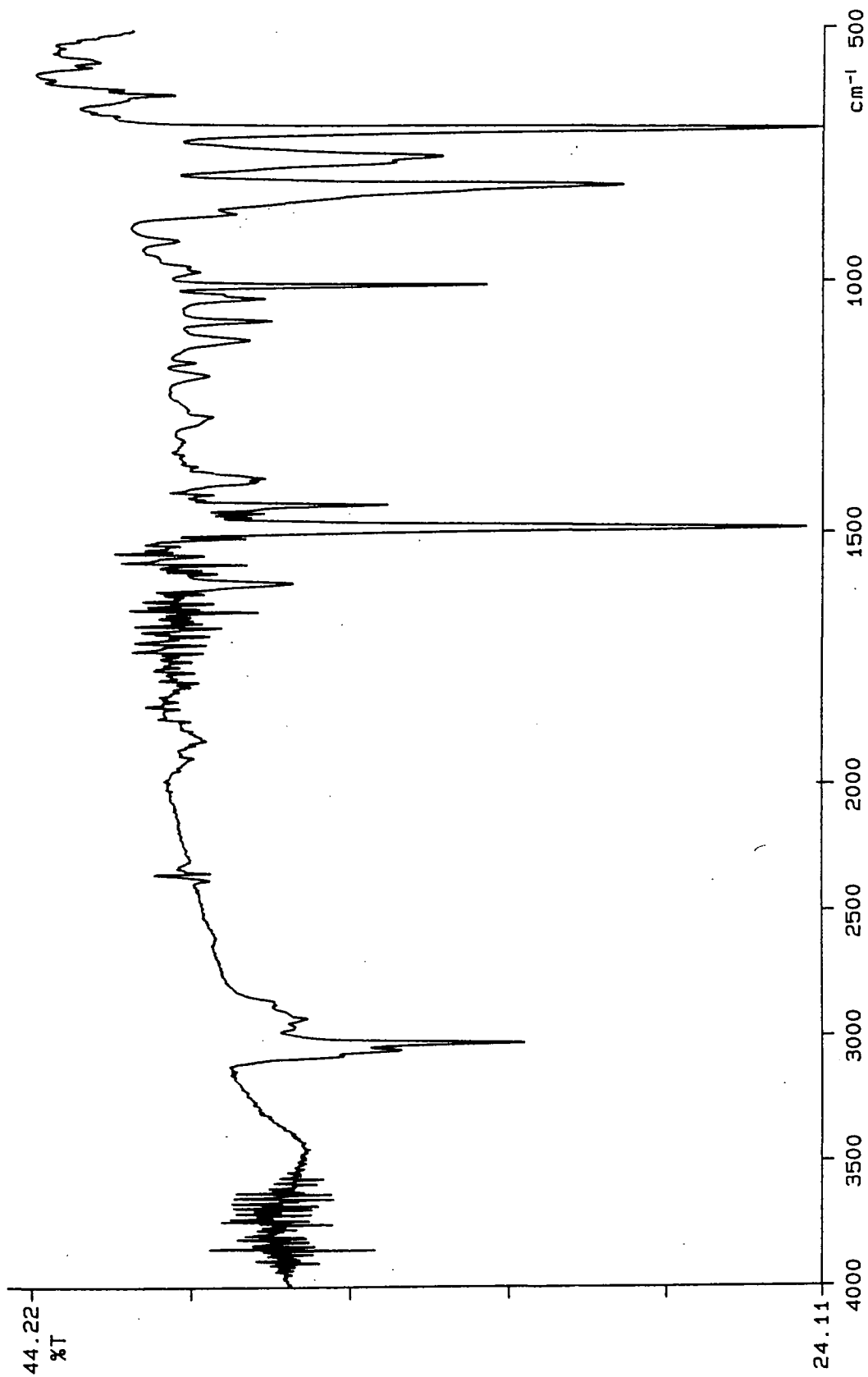
Appendix 1.18 IR spectrum of poly(4,4''-terphenylene diphenylvinylene)

A1 - 19
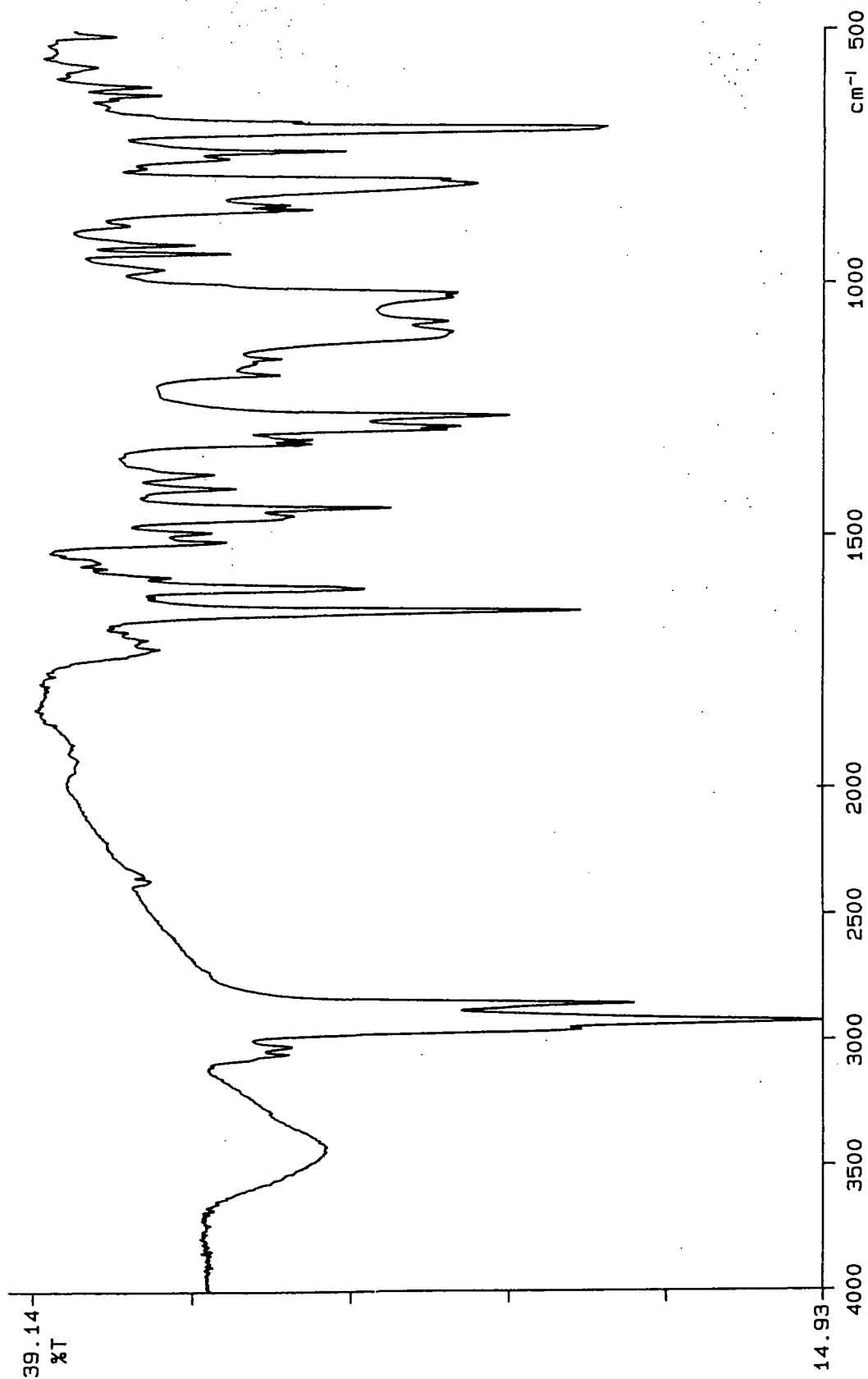
Appendix 1.19 IR spectrum of the products from the attempted polymerisation of 4,4′-dibenzoylphenylacetylene
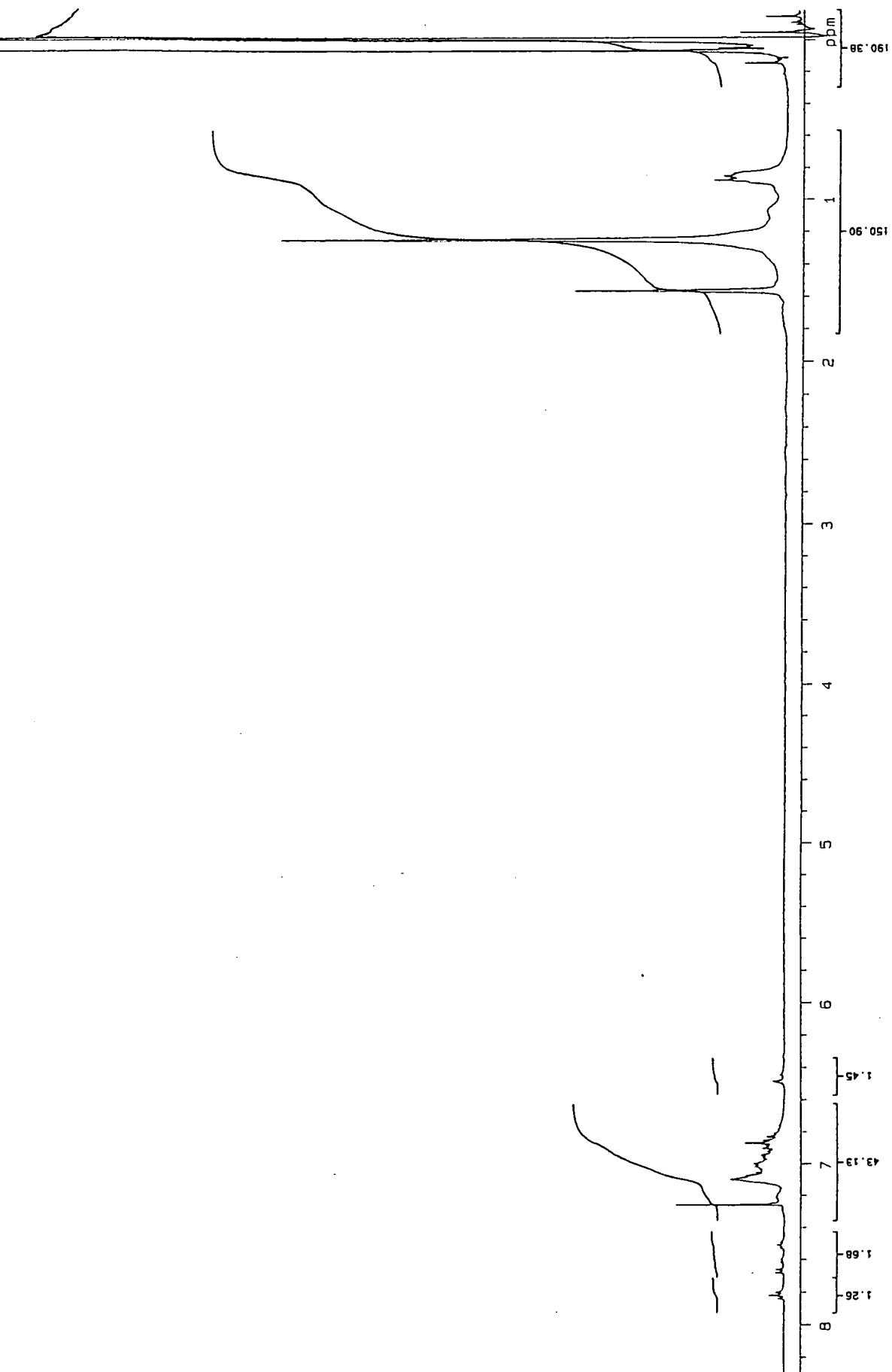
Appendix 1.20 ¹H nmr spectrum of the products from the attempted polymerisation of 4,4′-dibenzoylphenylacetylene
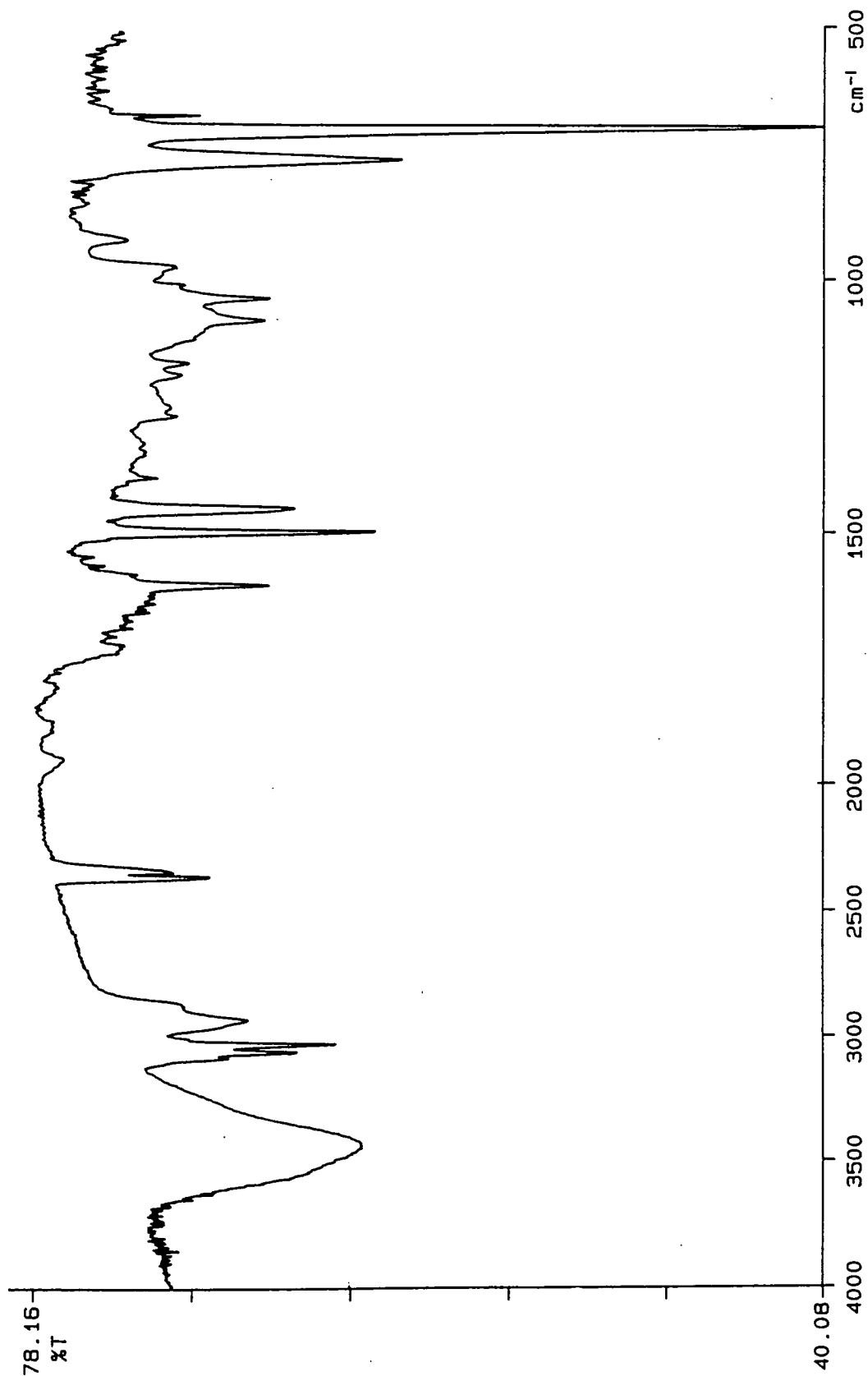
Appendix 1.21 IR spectrum of the products from the attempted polymerisation of trans-1,2-dibenzoylethylene
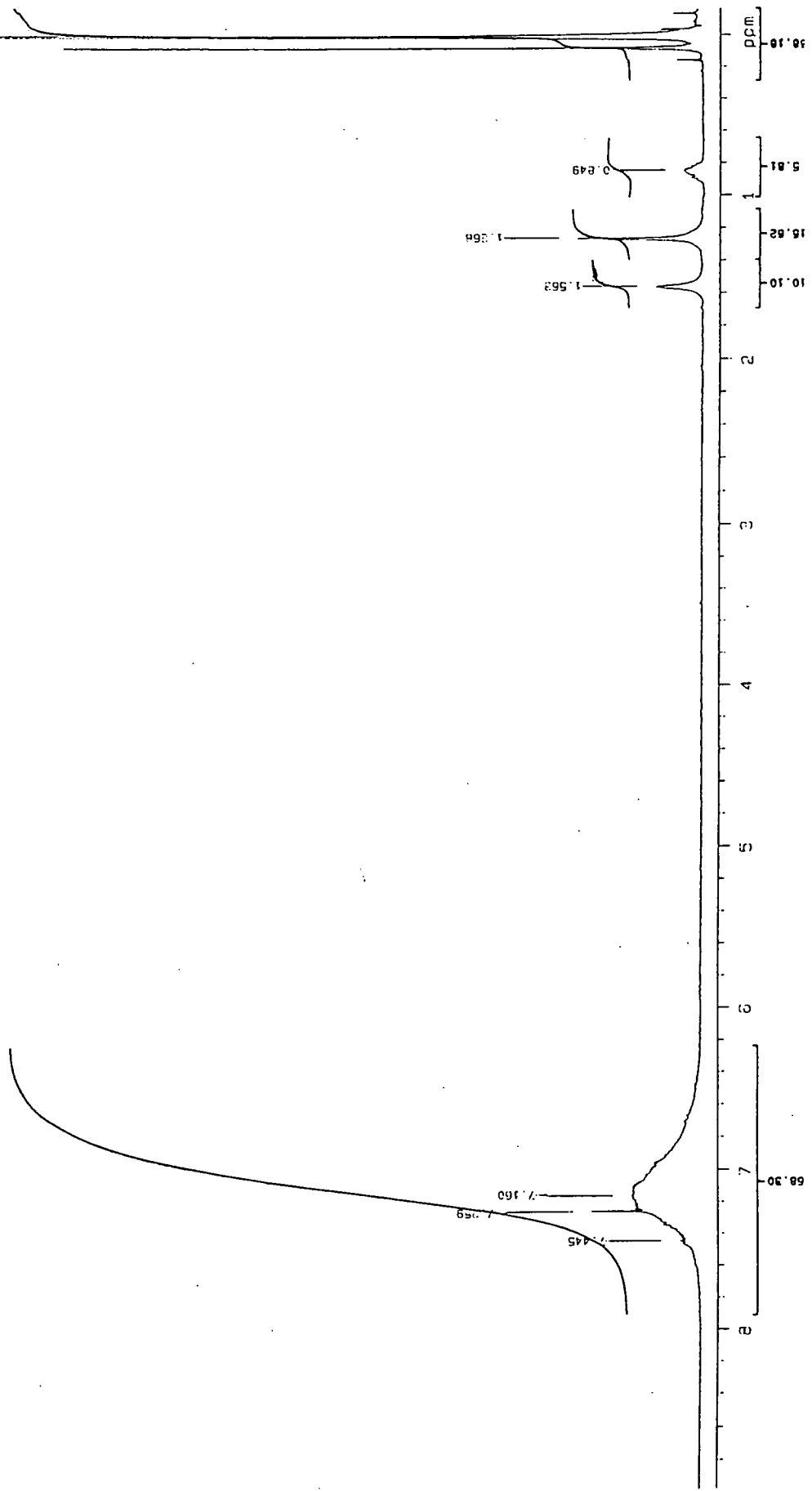
Appendix 1.22 ¹H nmr spectrum of the products from the attempted polymerisation of trans-1,2-dibenzoylethylene
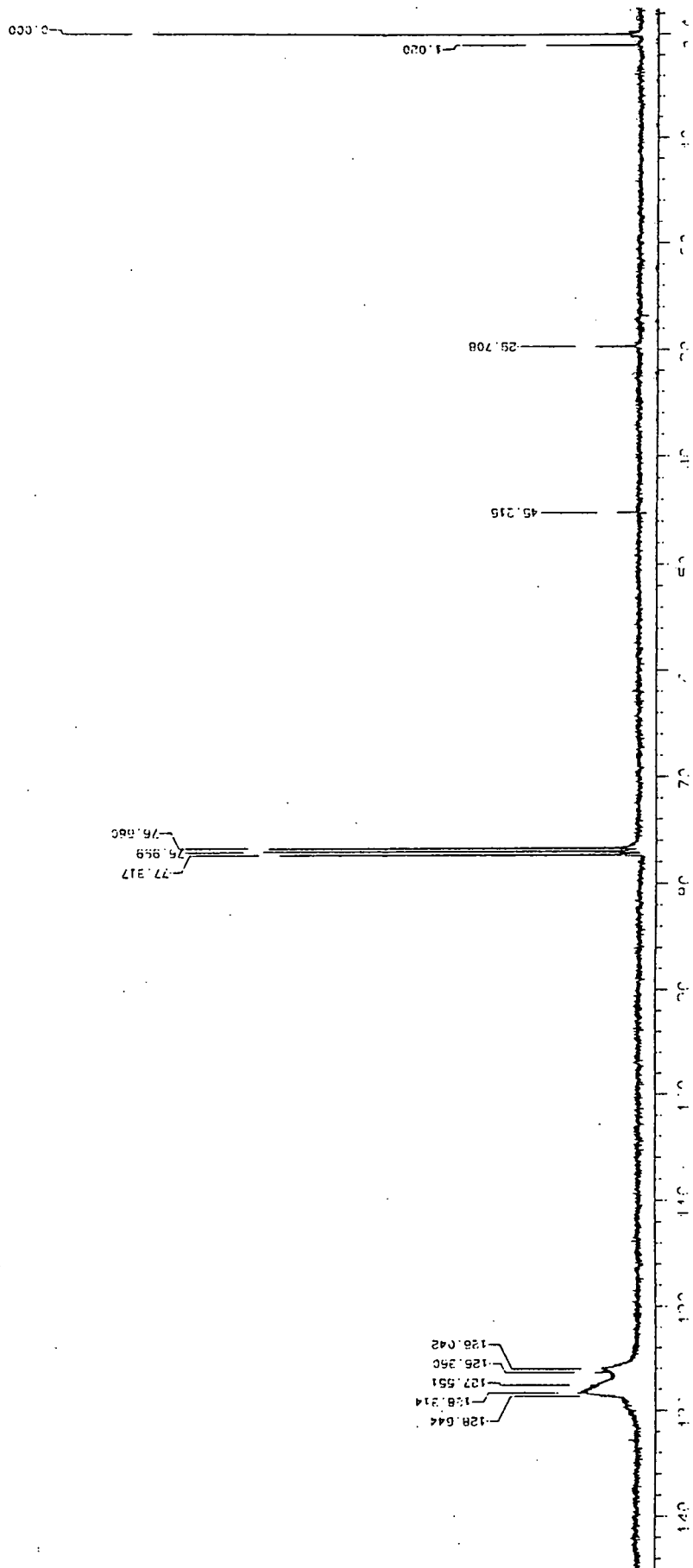
Appendix 1.23 ^{13}C nmr spectrum of the products from the attempted polymerisation of trans-1,2-dibenzoylethylene

APPENDIX 2

Spectra From Chapter 3
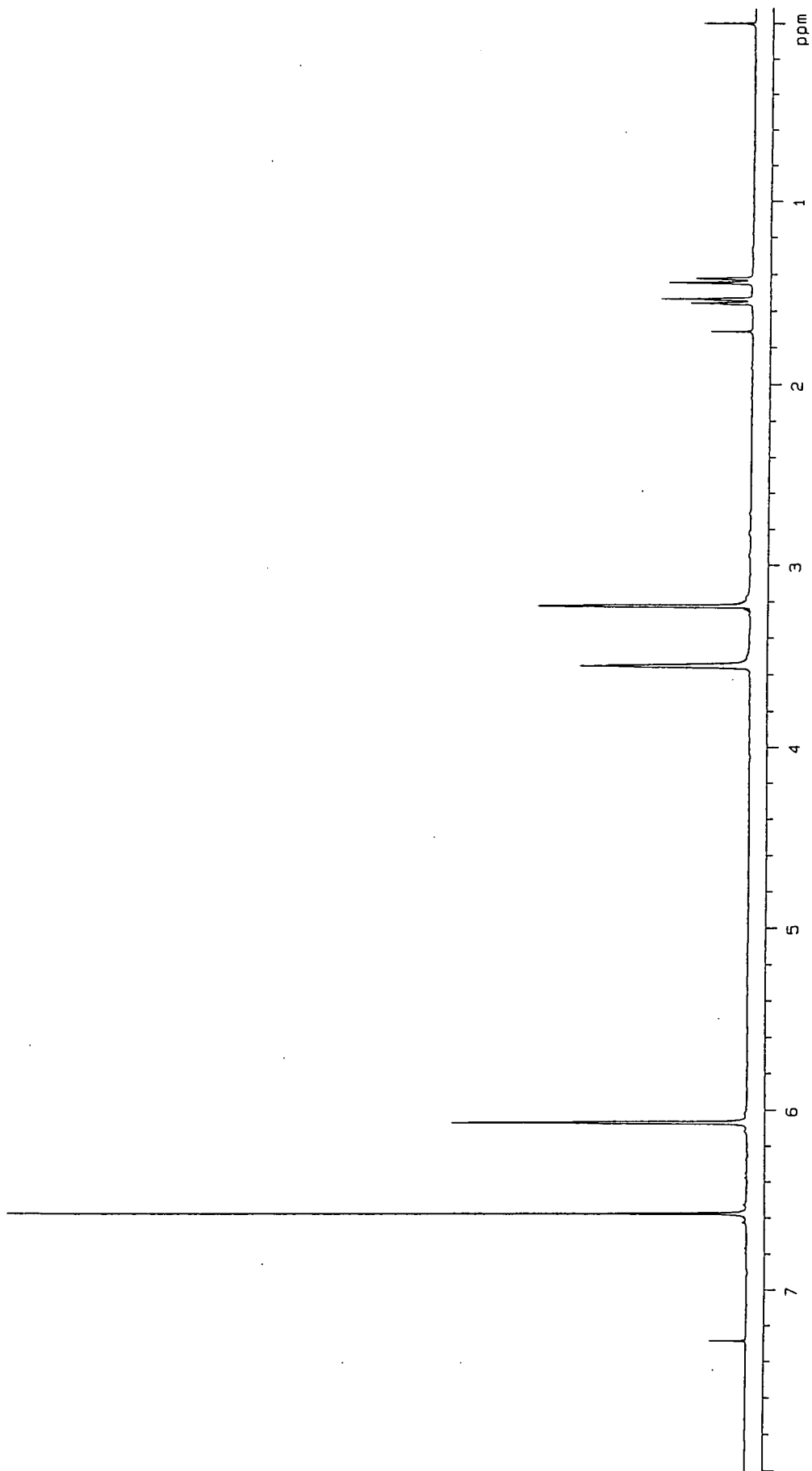
Appendix 2.1 ^{1}H nmr spectrum of endo - 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (I)
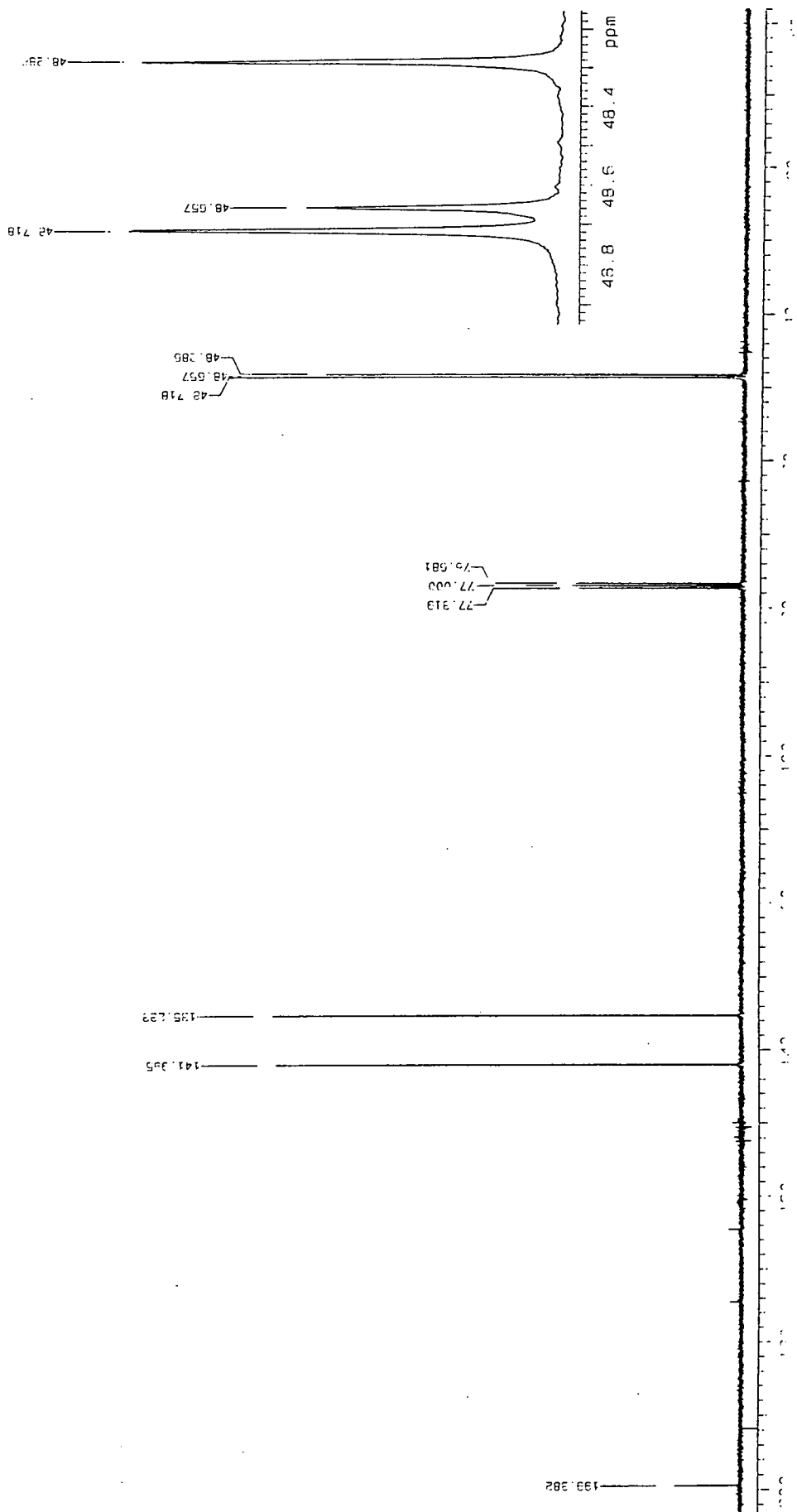
Appendix 2.2 ^{13}C nmr spectrum of endo - 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (I)
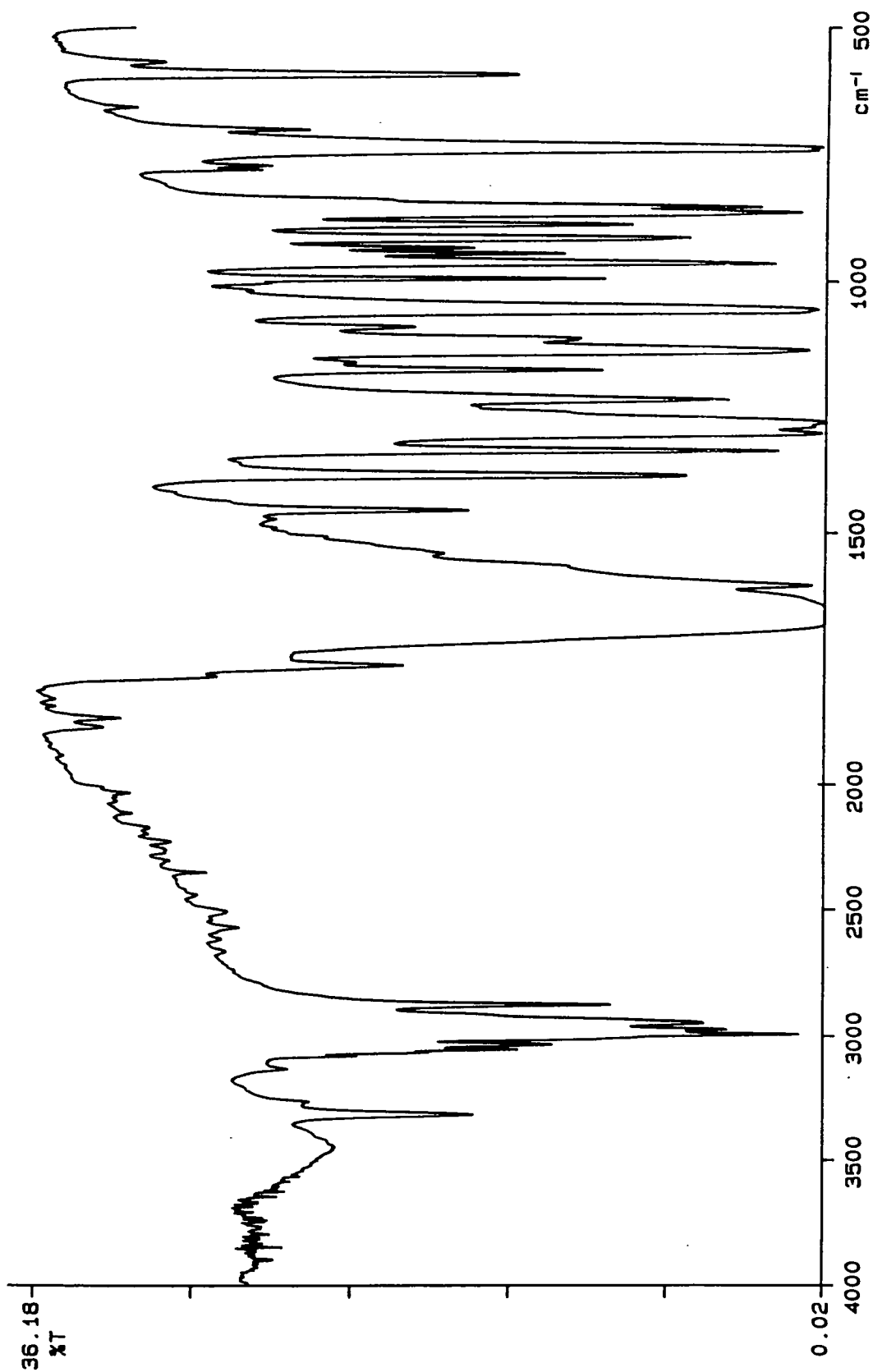
Appendix 2.3 IR spectrum of endo - 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (I)
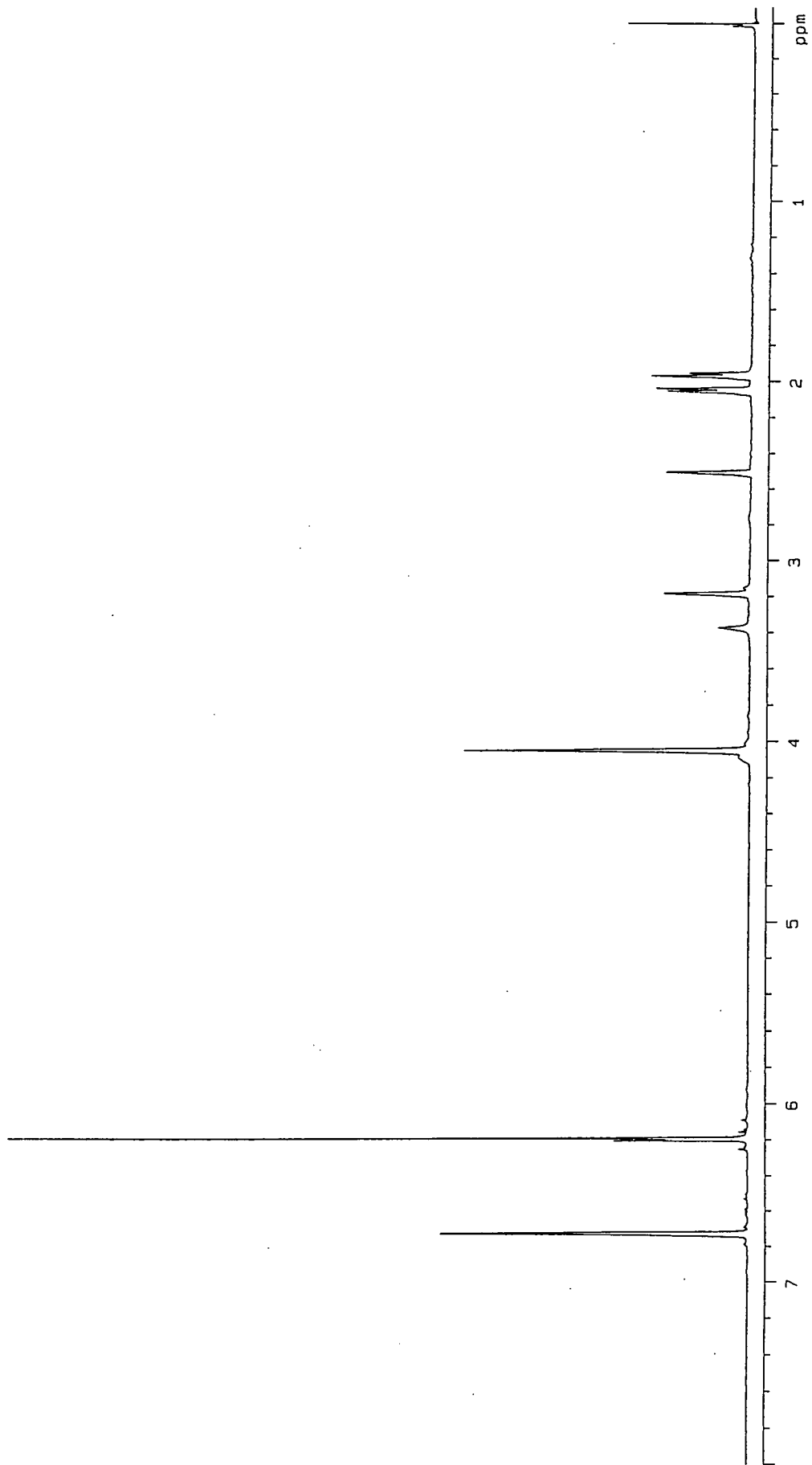
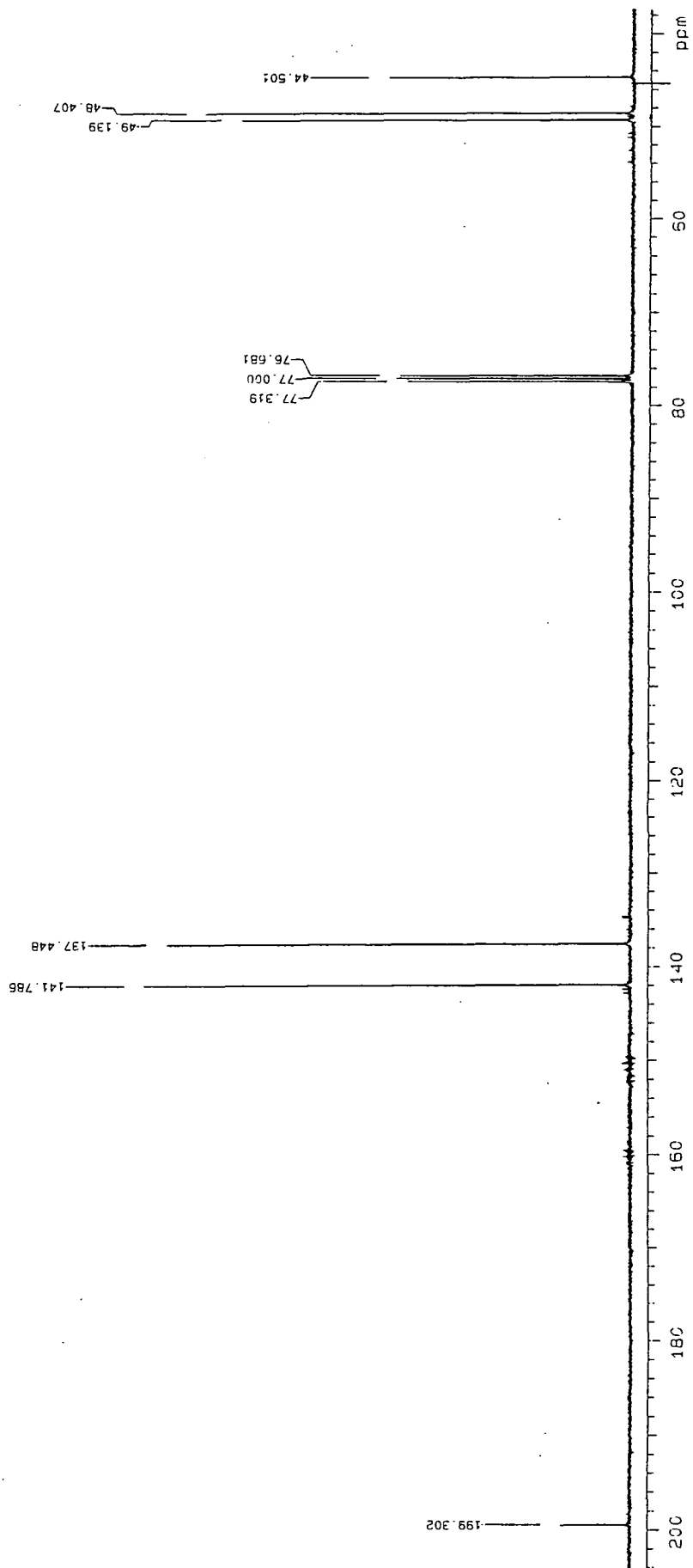**Appendix 2.4** ^{1}H nmr spectrum of 1,4-dihydro-1,4-methanonaphthalene-5,8-diol (II)
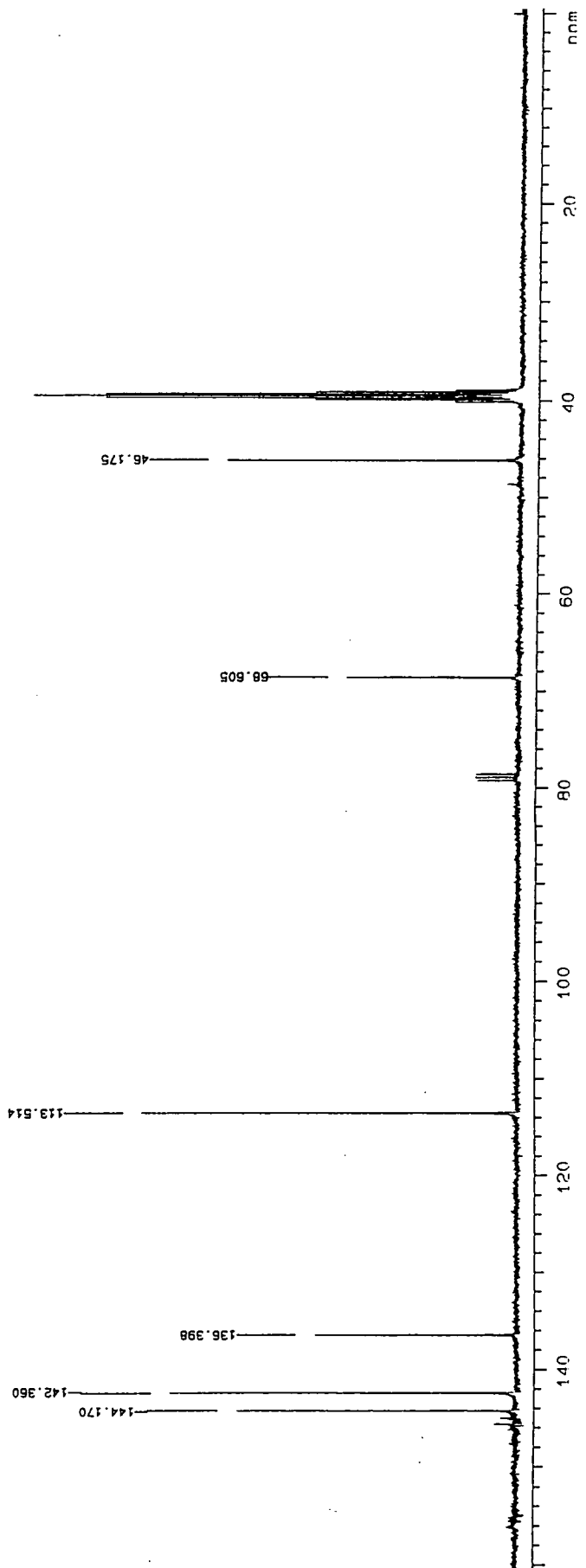
Appendix 2.5 ^{13}C nmr spectrum of 1,4-dihydro-1,4-methanonaphthalene-5,8-diol (II)
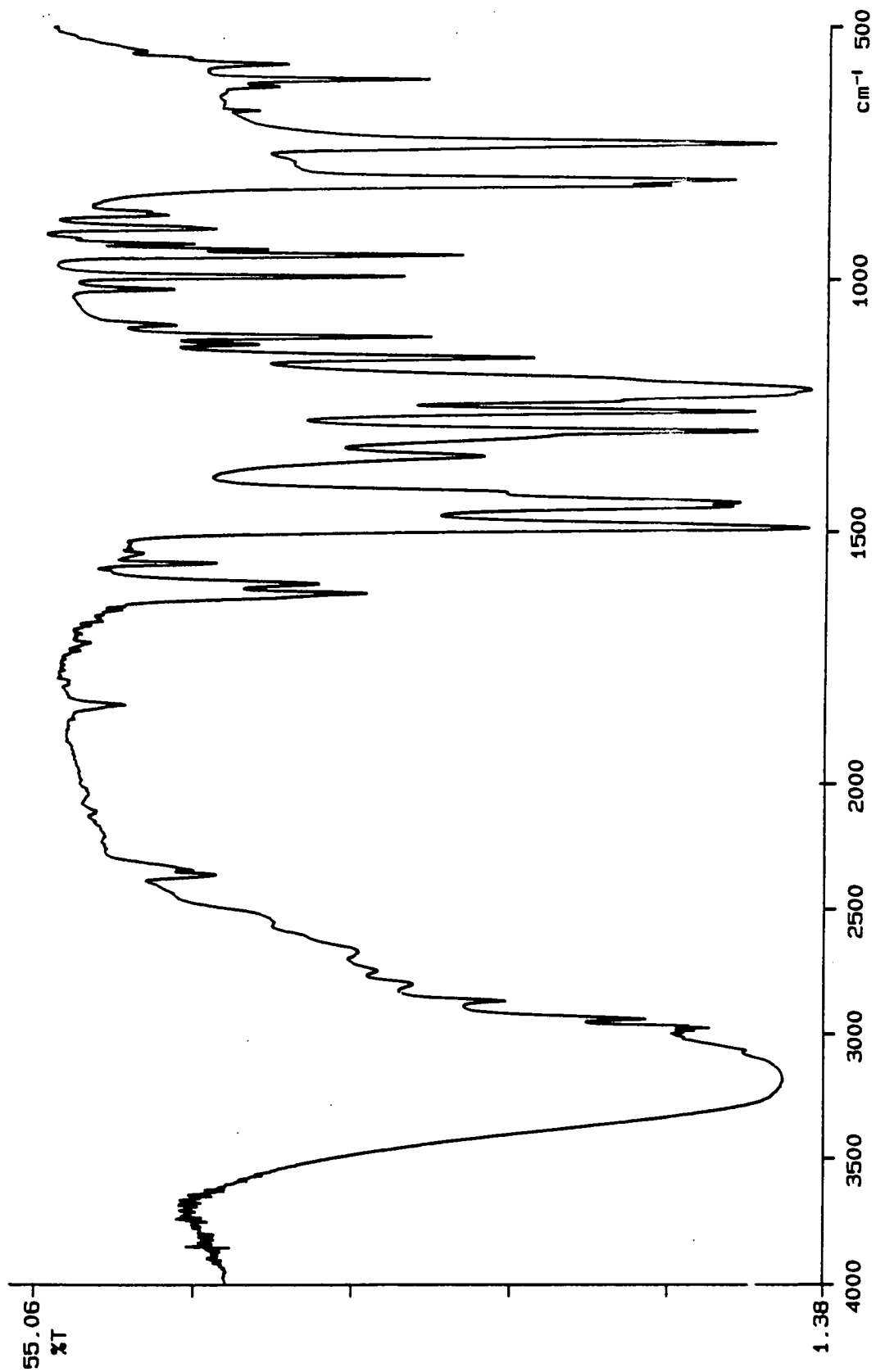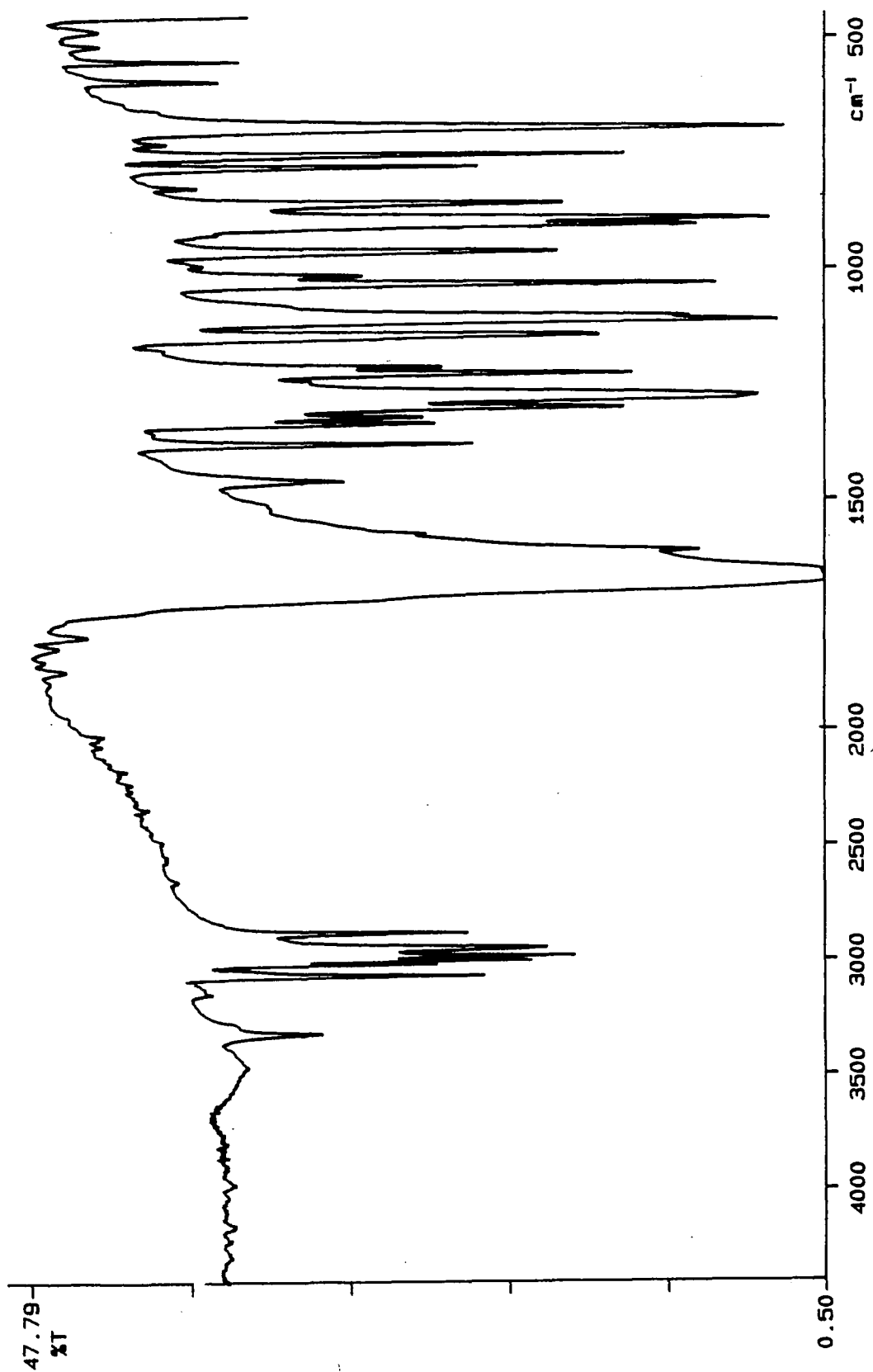
Appendix 2.6 IR spectrum of 1,4-dihydro-1,4-methanonaphthalene-5,8-diol (II)
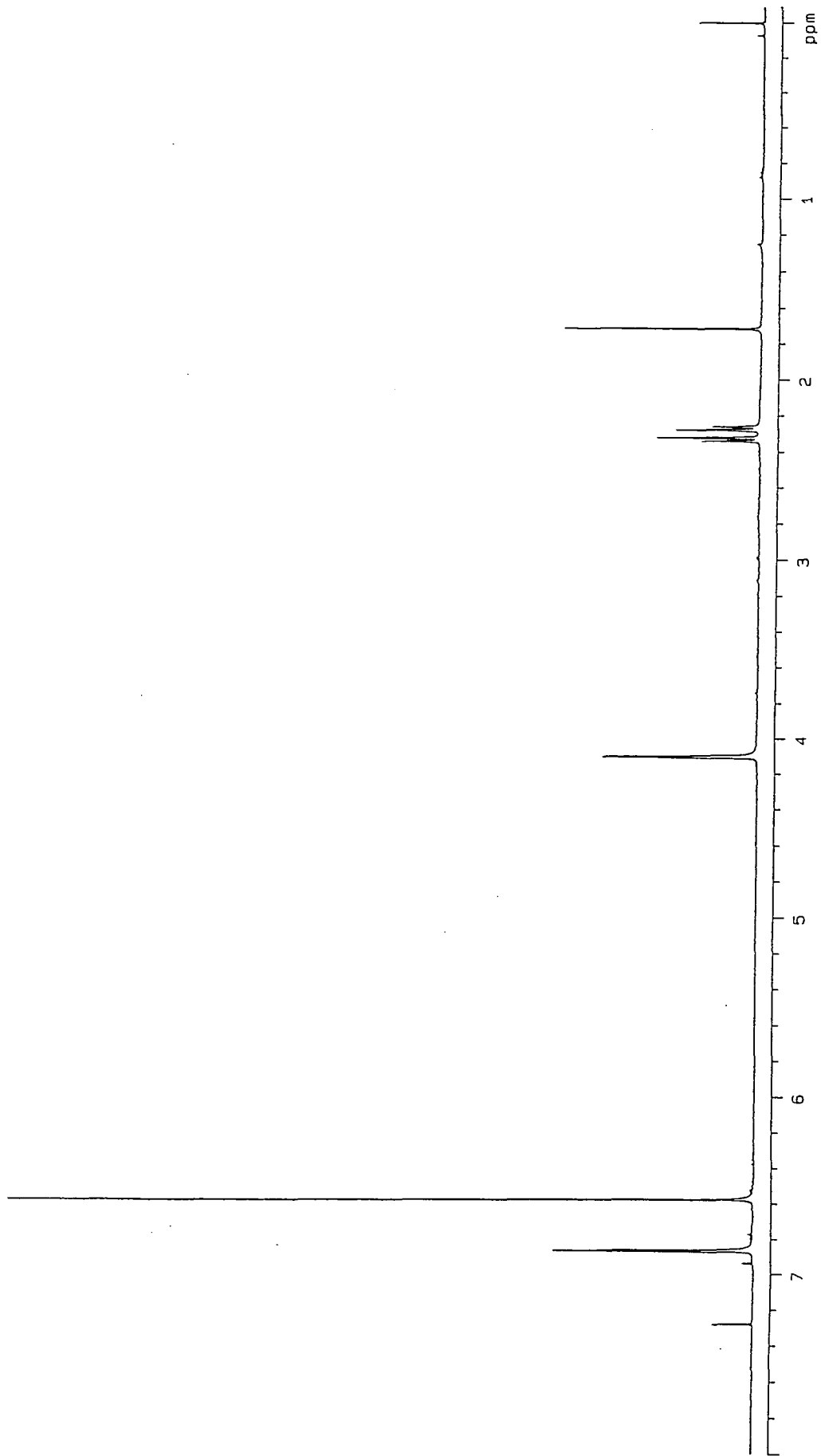
Appendix 2.7 ^{1}H nmr spectrum of 1,4-dihydro-1,4-methanonaphthalene-5,8-dione (III)
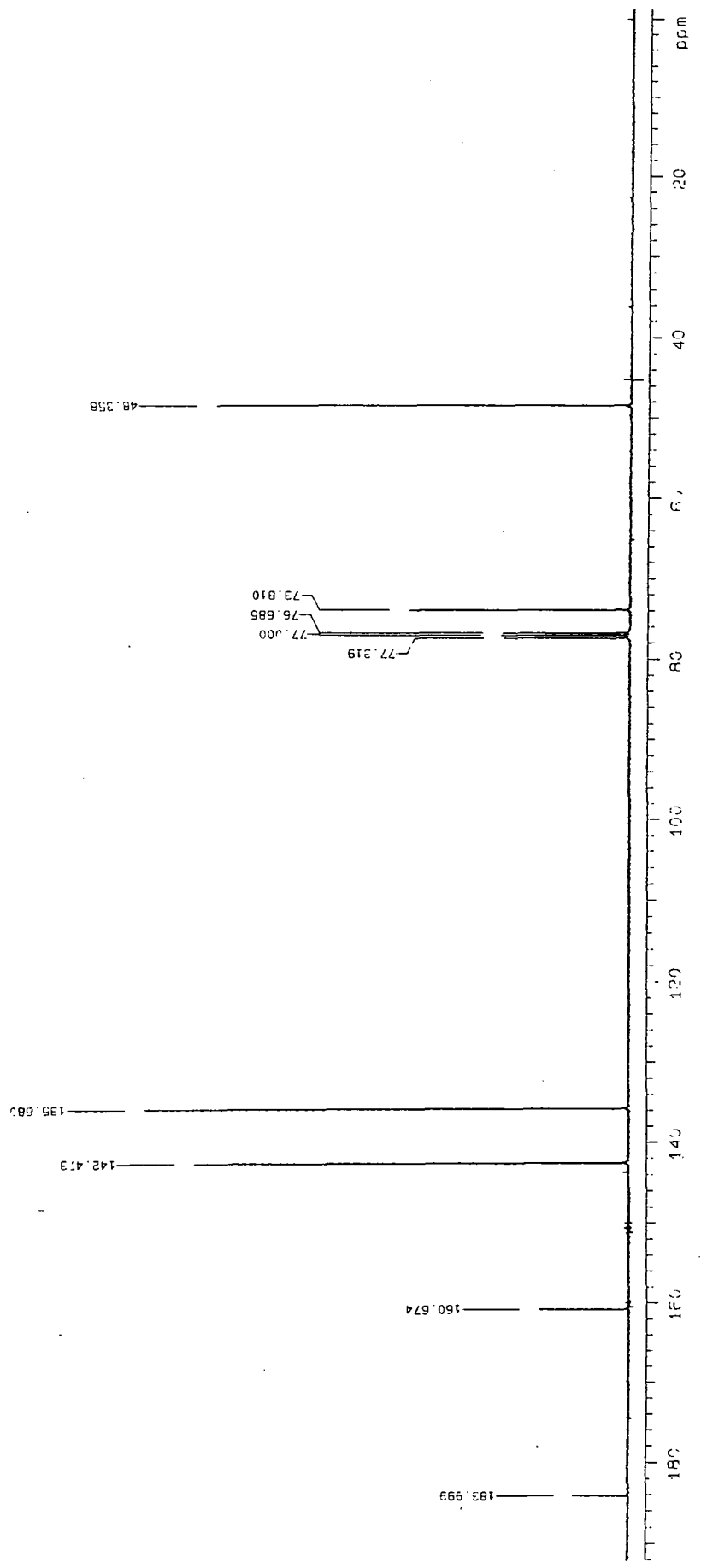
Appendix 2.8 ^{13}C nmr spectrum of 1,4-dihydro-1,4-methanonaphthalene-5,8-dione (III)
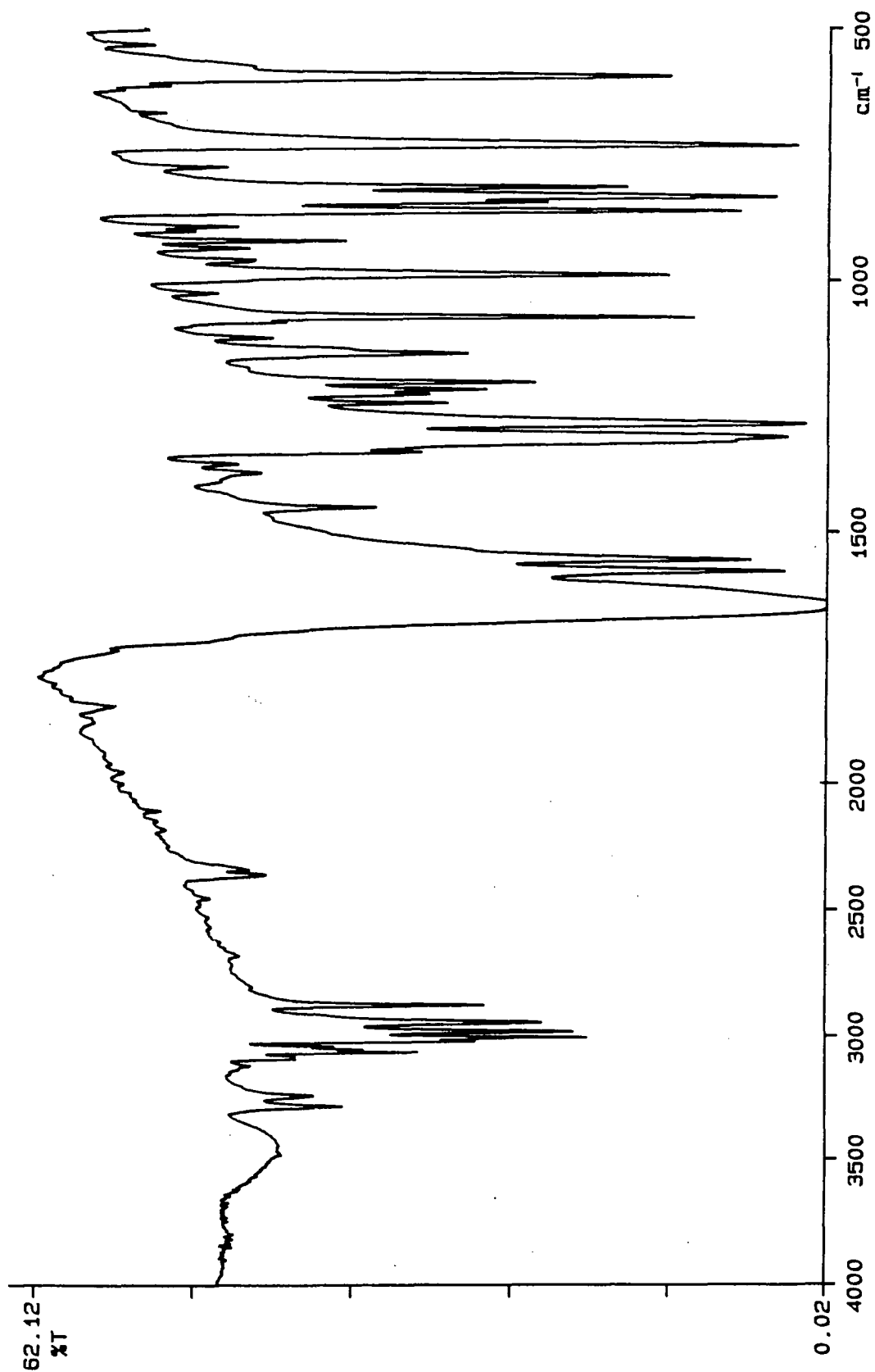
Appendix 2.9 IR spectrum of 1,4-dihydro-1,4-methanonaphthalene-5,8-dione (III)
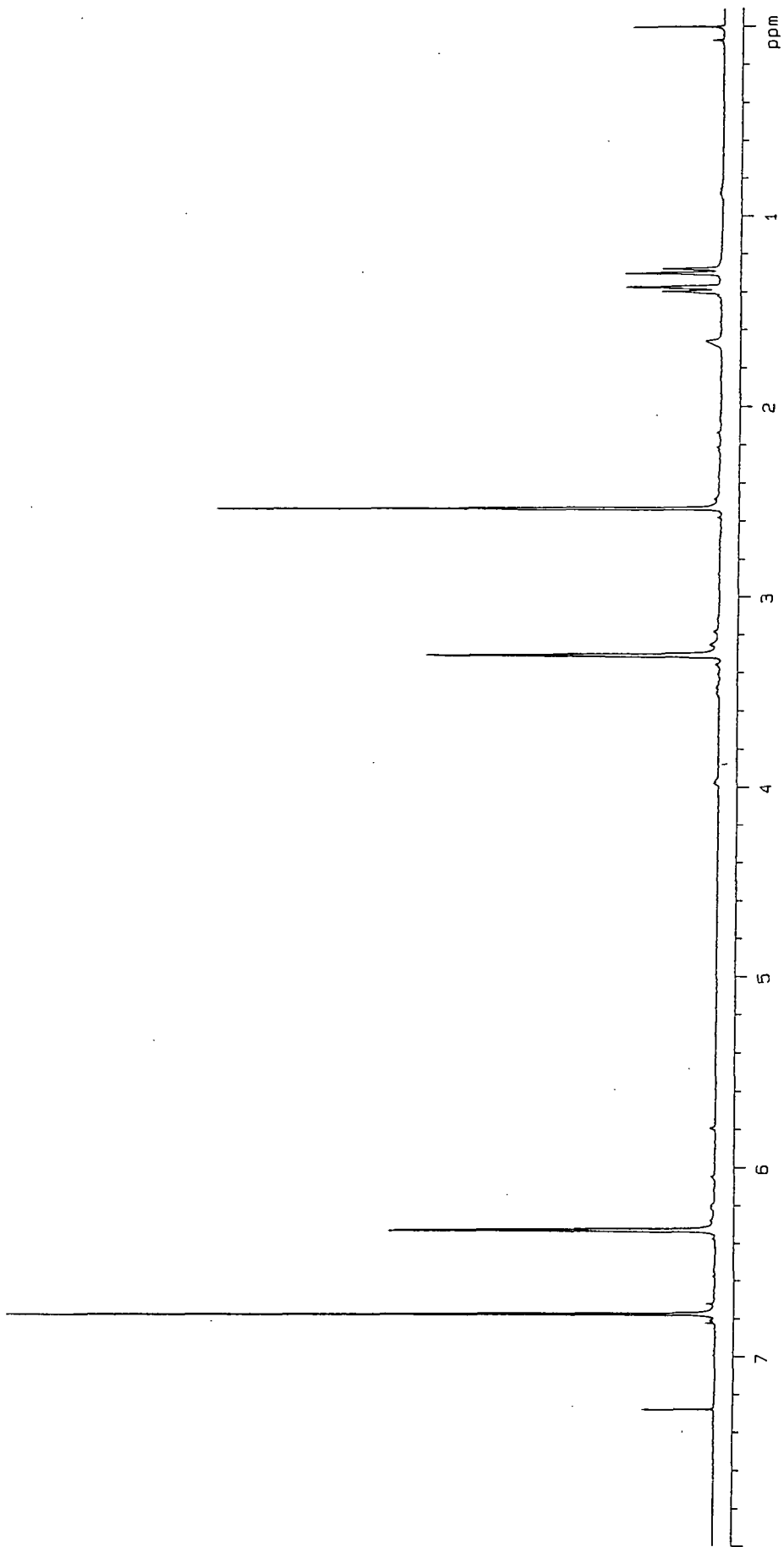
Appendix 2.10 ^{1}H nmr spectrum of exo - 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (IV)
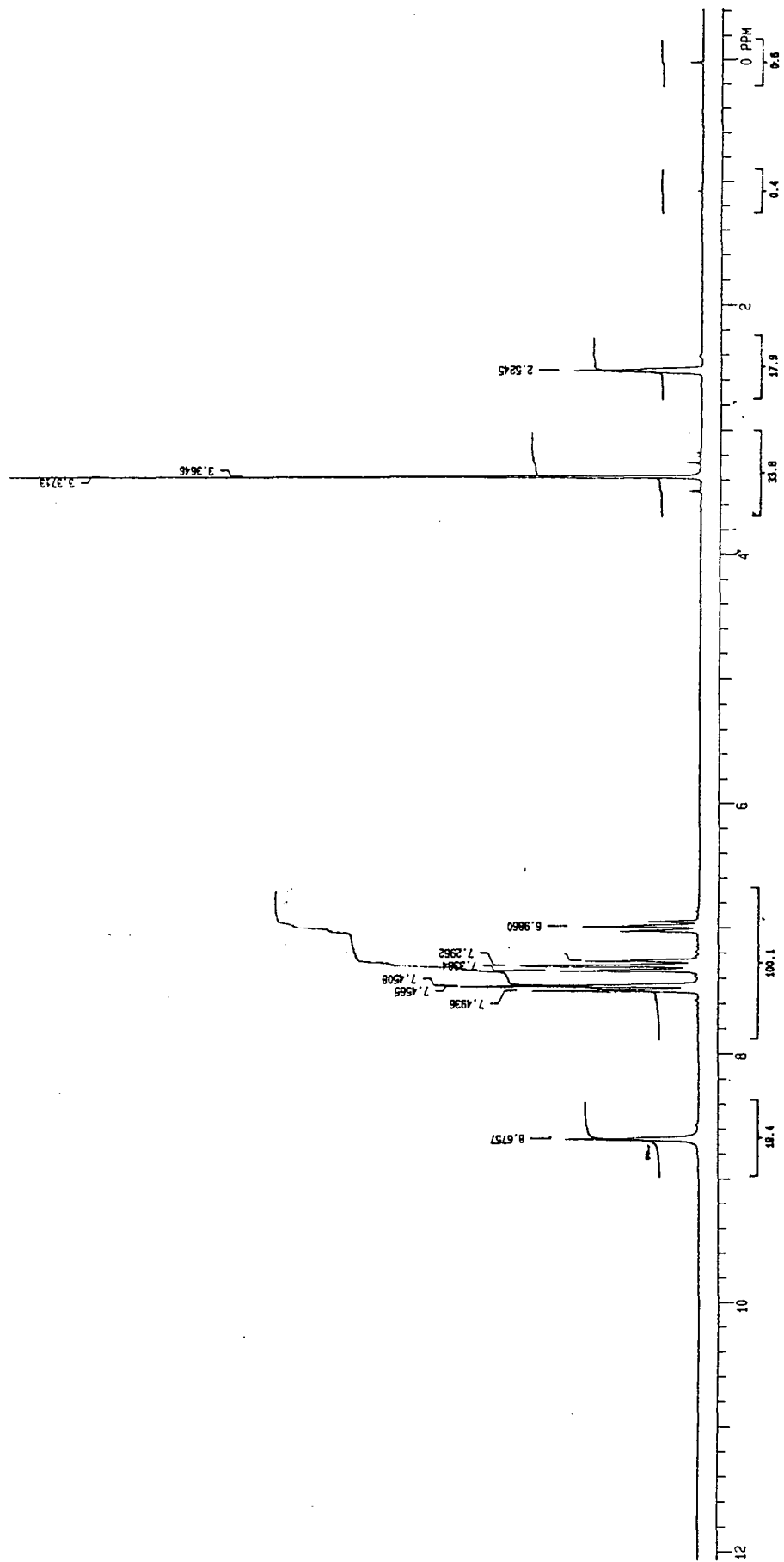
44.501

48.407
49.139

50

76.681
77.000
77.319

80

100

120

137.448

140

141.786

160

180

199.305

200

Appendix 2.11 ^{13}C nmr spectrum of exo - 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (IV)

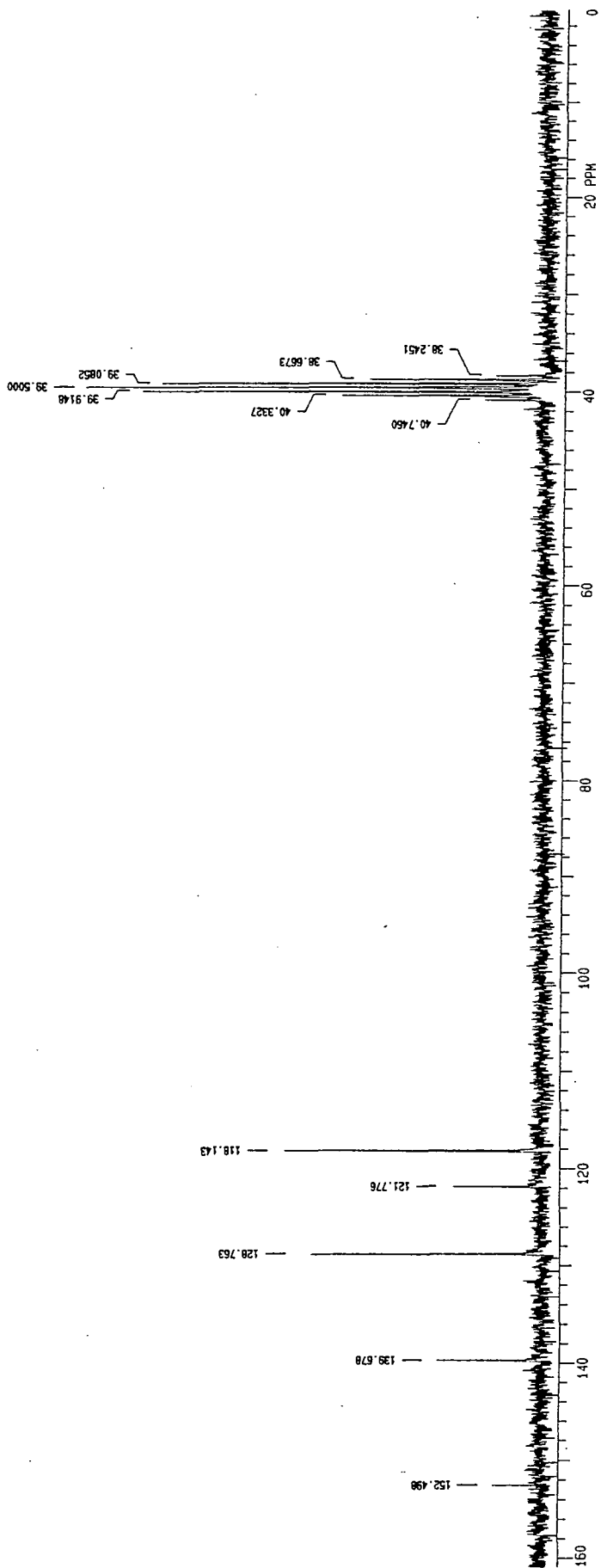**Appendix 2.12** IR spectrum of exo - 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (IV)
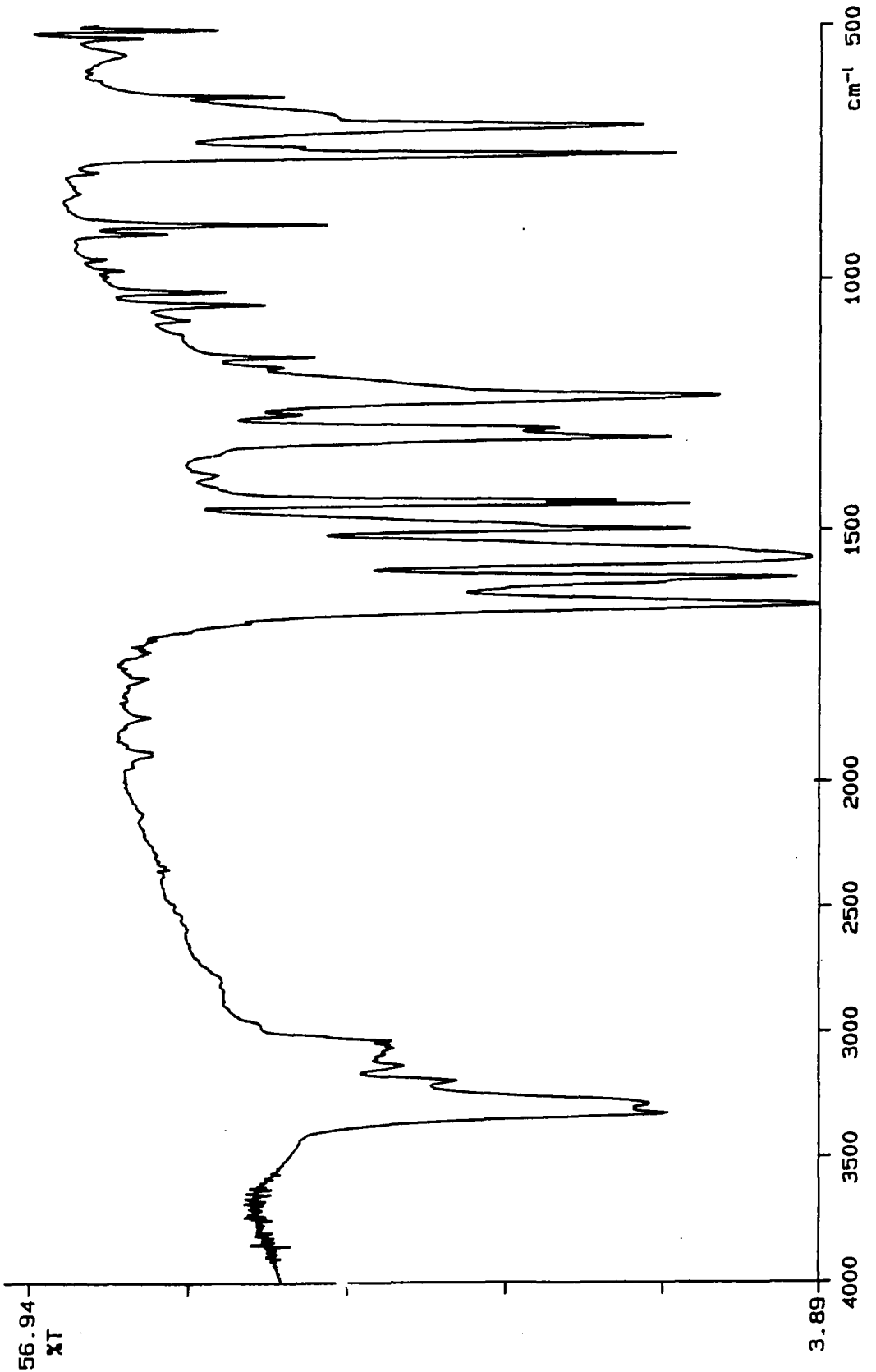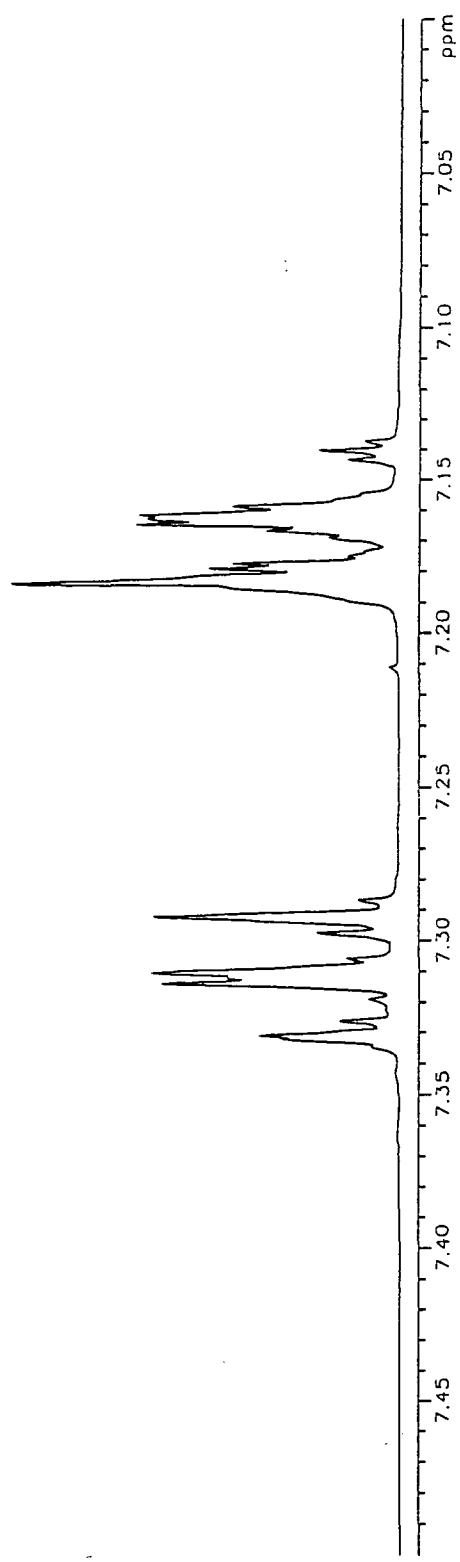
APPENDIX 3

Spectra from Chapter 4

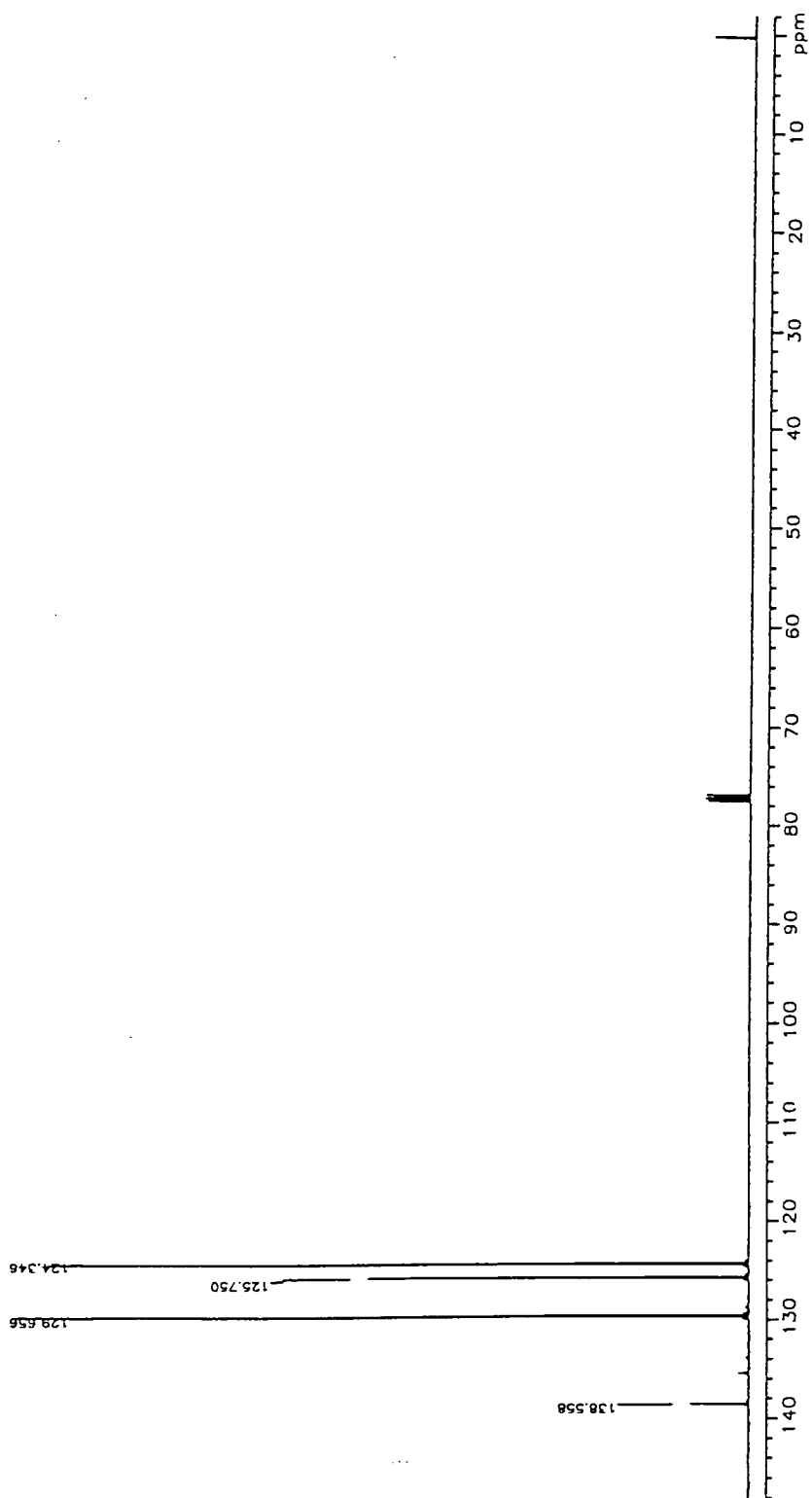**Appendix 3.1** ^{1}H nmr spectrum of diphenylurea

Appendix 3.2 ^{13}C nmr sprectrum of diphenylurea
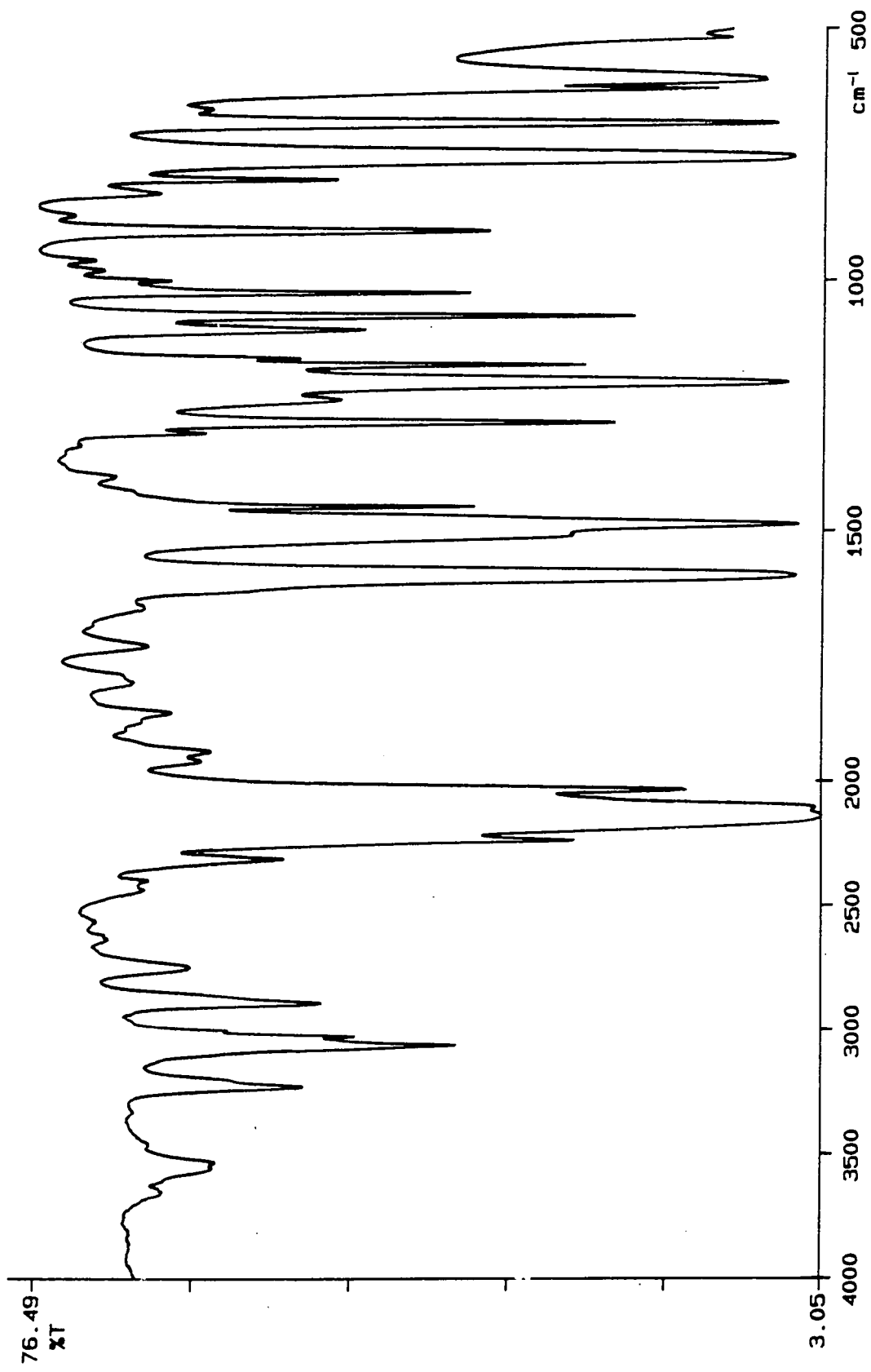
Appendix 3.3 IR spectrum of diphenylurea

Appendix 3.4 ^{1}H nmr spectrum of diphenyl carbodiimide

Appendix 3.5 ^{13}C nmr spectrum of diphenyl carbodiimide

Appendix 3.6 IR spectrum of diphenyl carbodiimide

A3 - 7
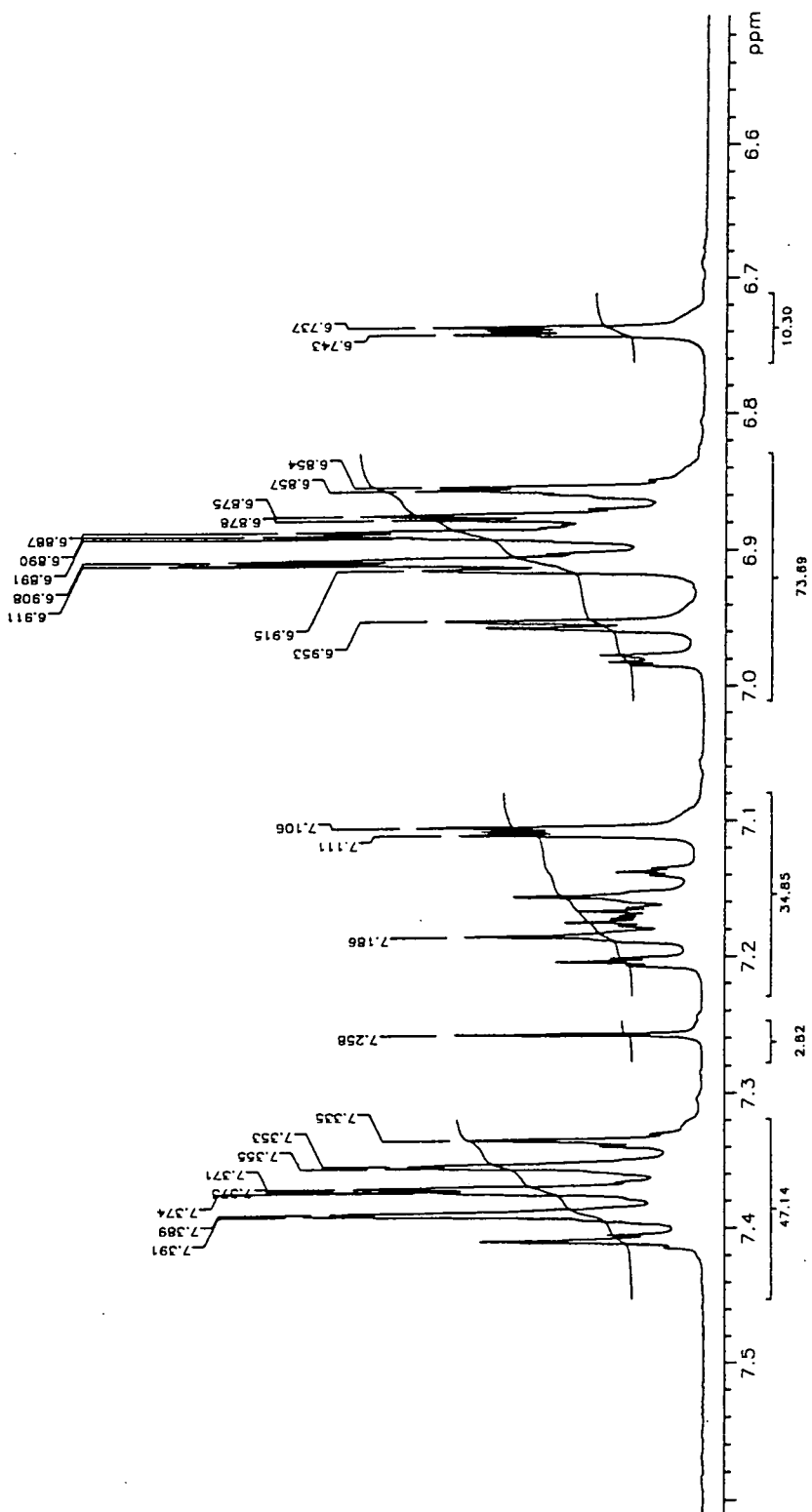
Appendix 3.7 ^{1}H nmr spectrum of N,N′-diphenyl-2,5-dicyclohexadiene-1,4-diimine
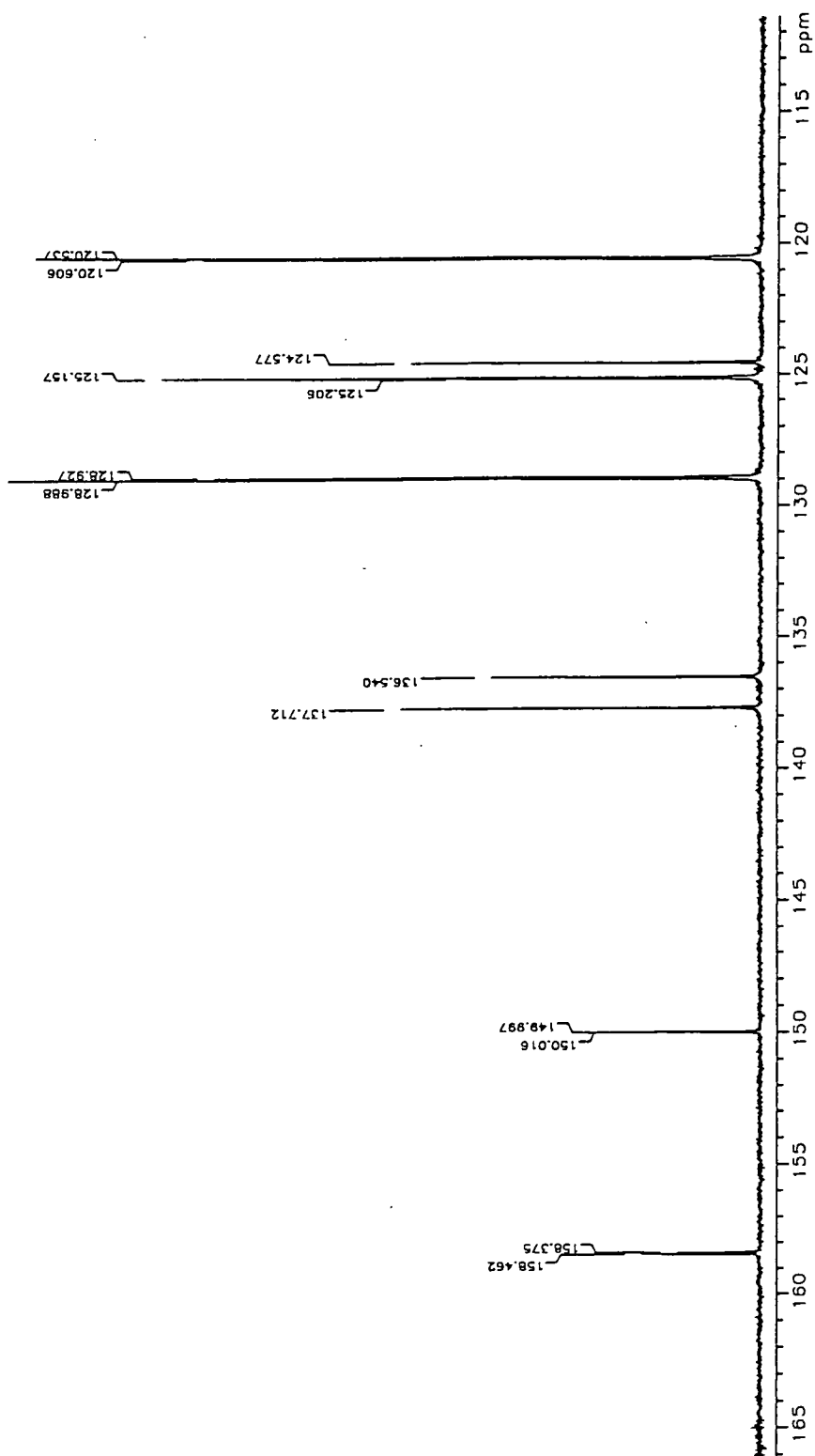
Appendix 3.8 ^{13}C nmr spectrum of N,N'-diphenyl-2,5-dicyclohexadiene-1,4-diimine
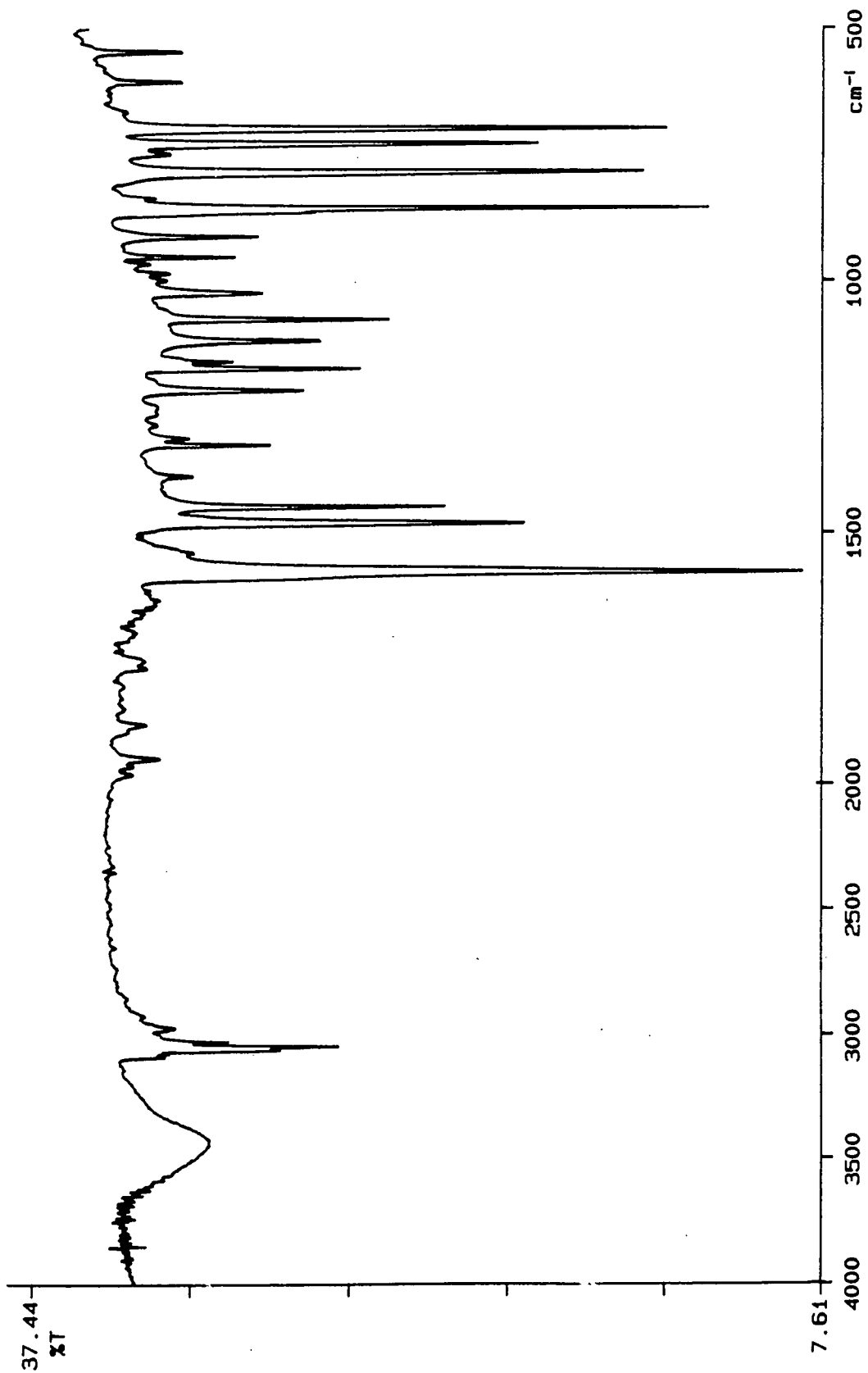
Appendix 3.9 IR spectrum of N,N′-diphenyl-2,5-dicyclohexadiene-1,4-diimine
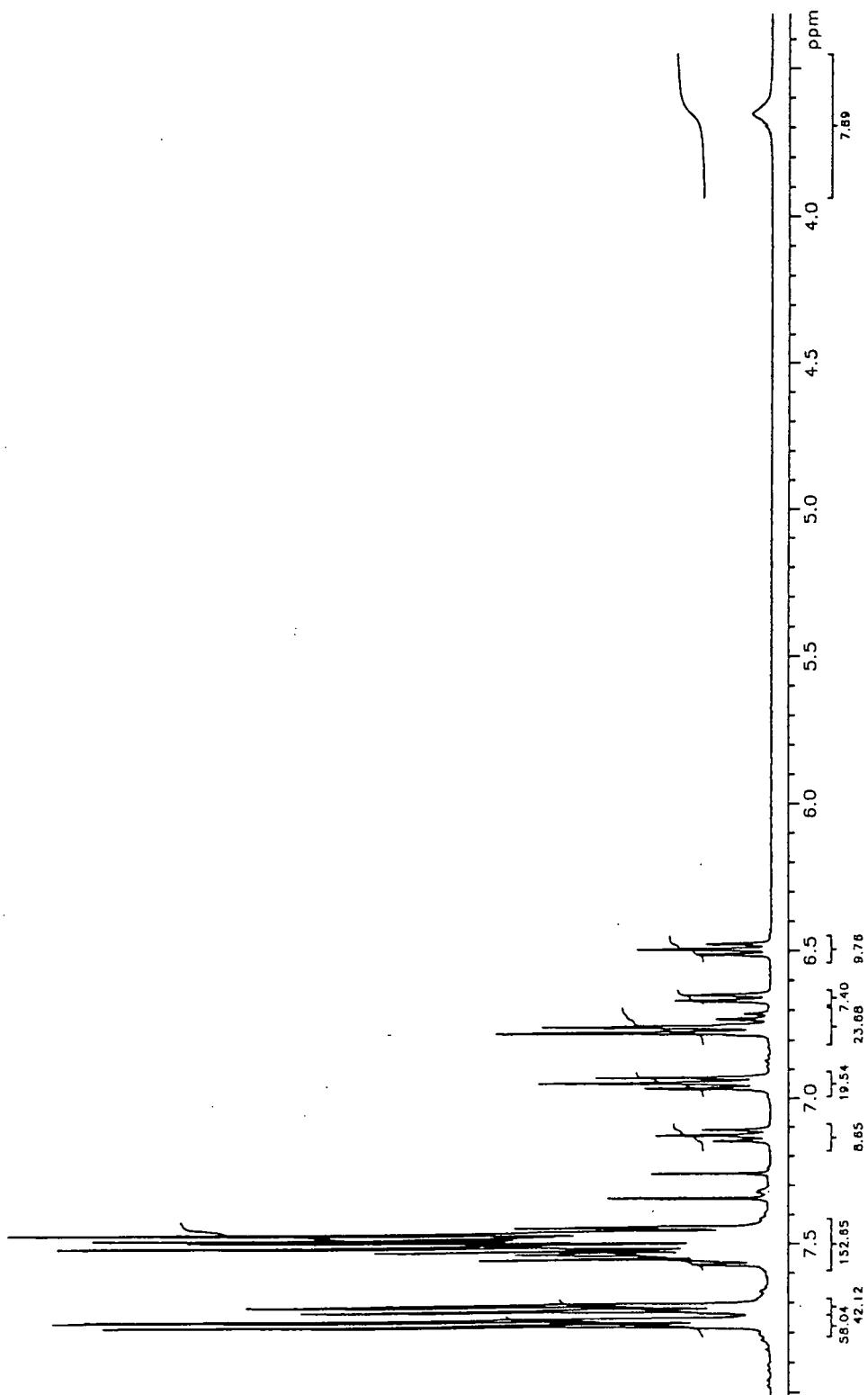
Appendix 3.10 ¹H nmr spectrum of the reaction products from a typical preparation of triphenylarsine phenylimine
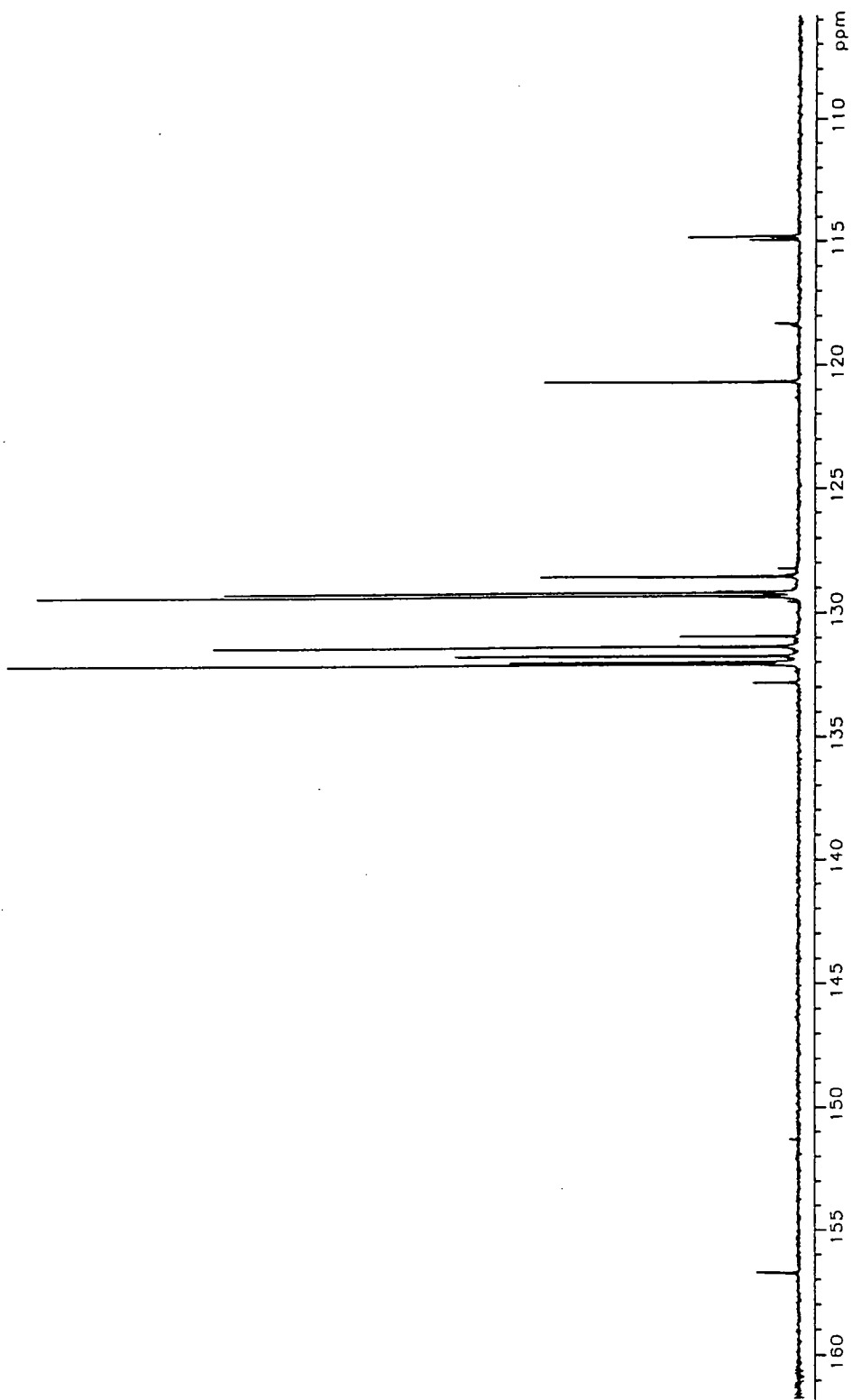
Appendix 3.11 ^{13}C nmr spectrum of the reaction products from a typical preparation of triphenylarsine phenylimine
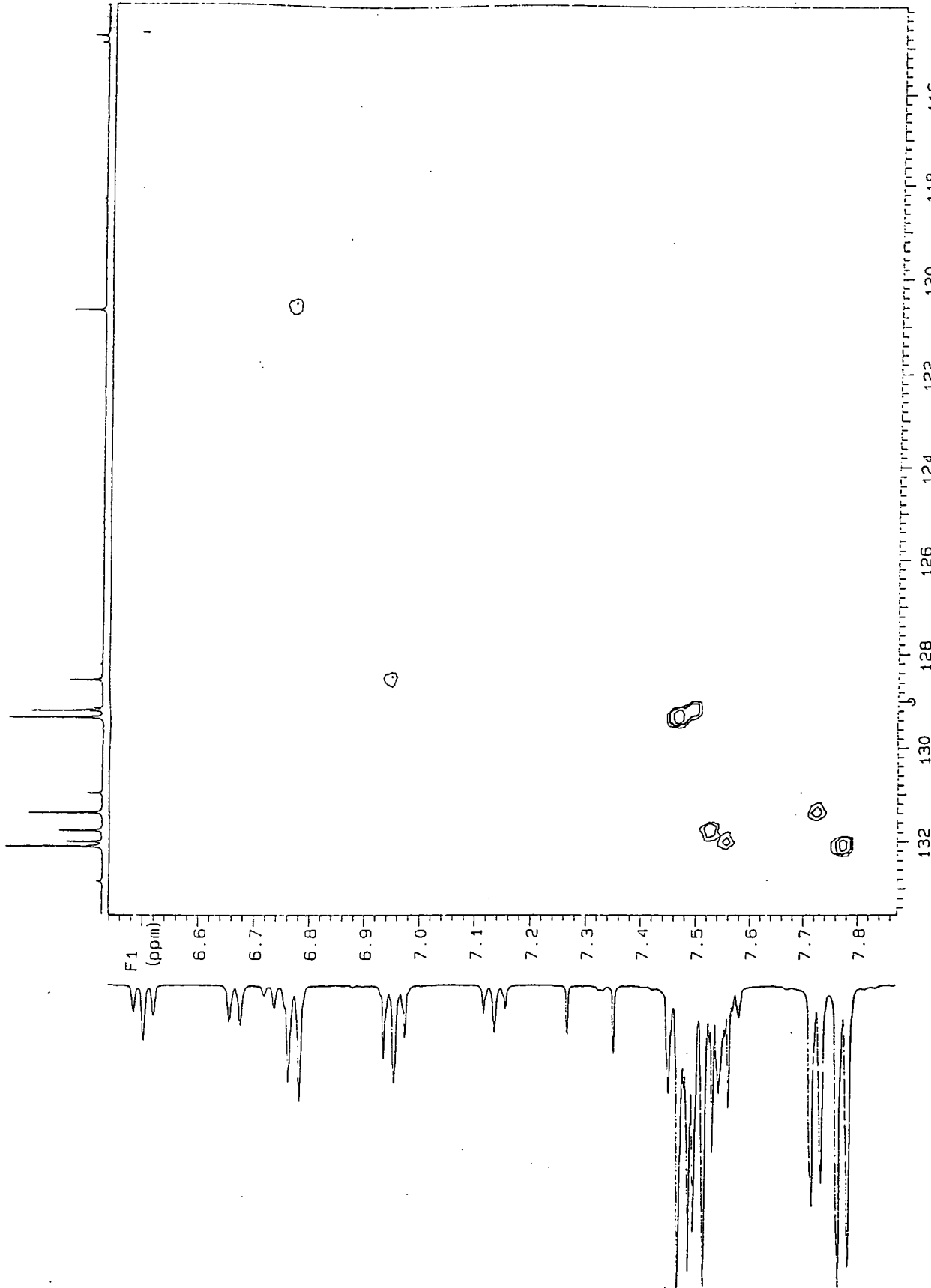
Appendix 3.12 HETCOR spectrum of the reaction products from a typical preparation of triphenylarsine phenylimine
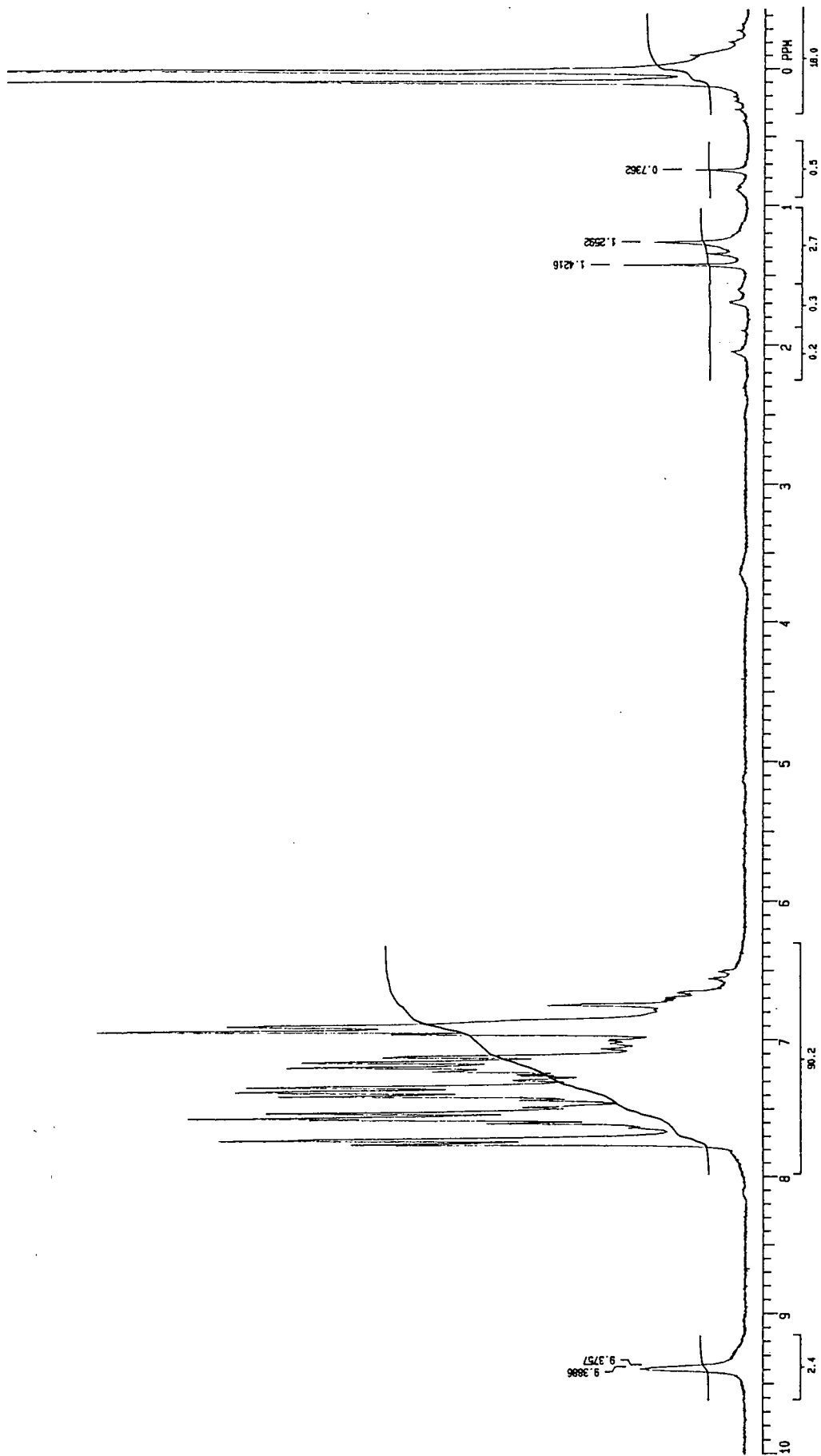
Appendix 3.13 ^{1}H nmr spectrum of the reaction products from the preparation of N,N′-diphenyl-2,5-dicyclohexadiene-1,4-diimine using triphenylarsine phenylimine
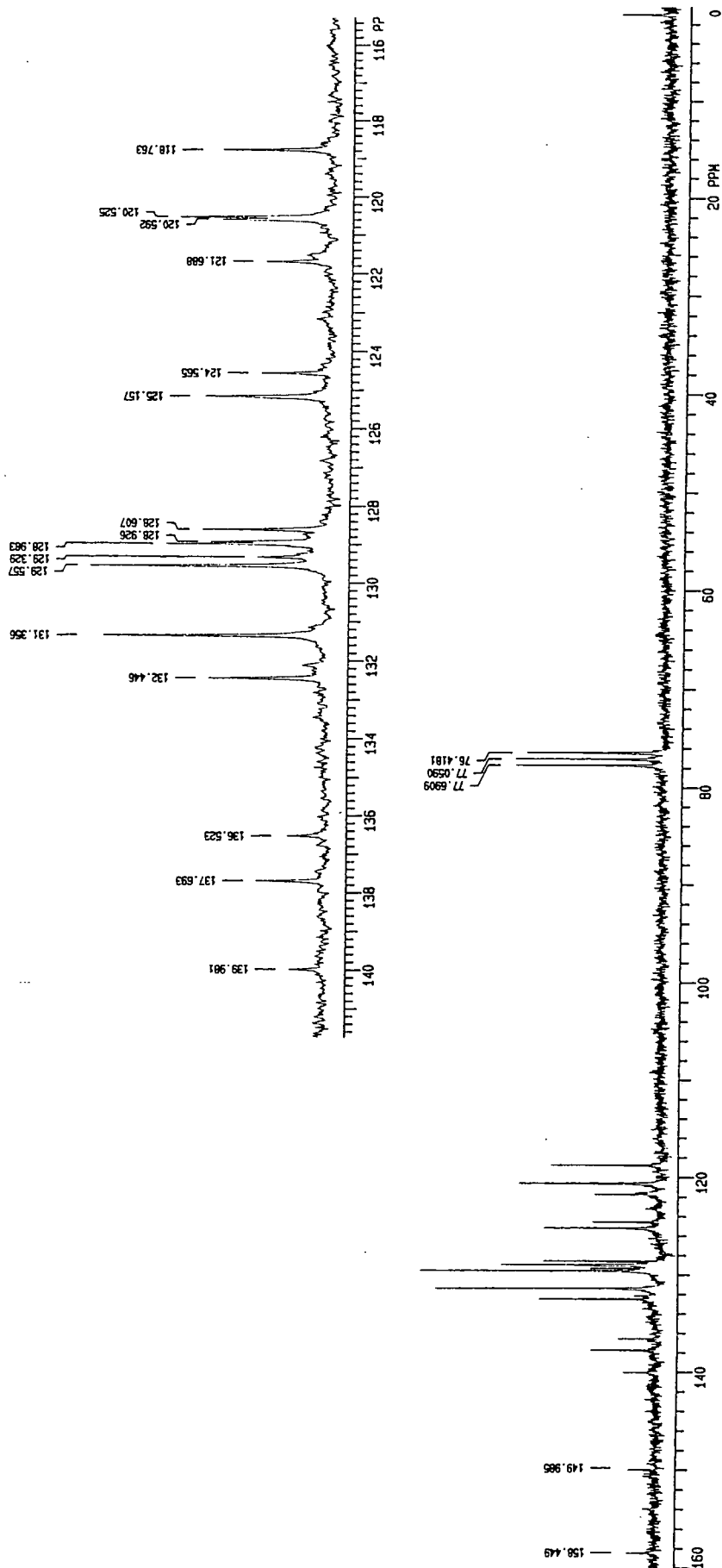
Appendix 3.14 ^{13}C nmr spectrum of the reaction products from the preparation of N,N′-diphenyl-2,5-dicyclohexadiene-1,4-diimine using triphenylarsine phenylimine
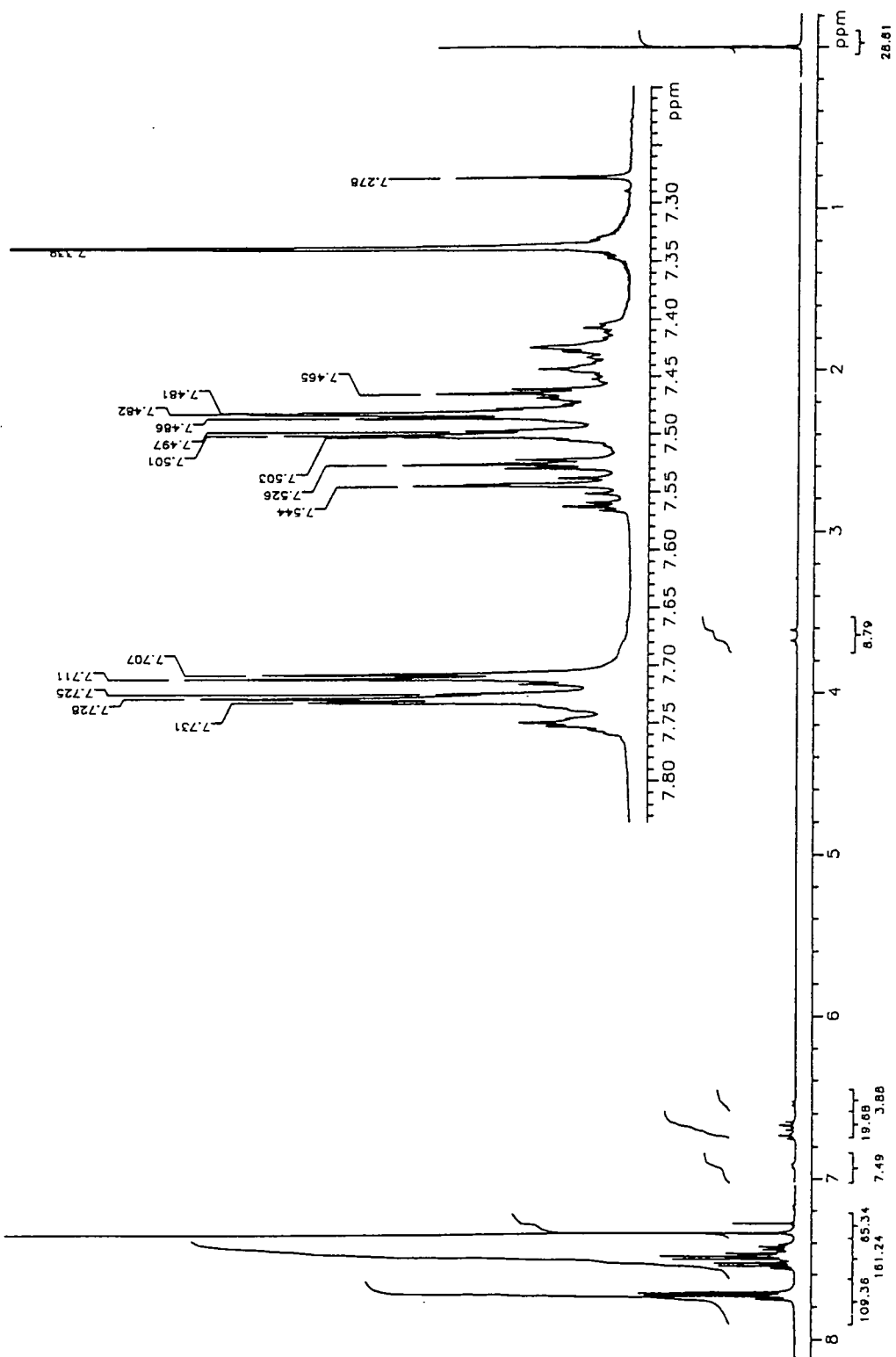
Appendix 3.15 ^{1}H nmr spectrum of the reaction products from a typical preparation of 4,4′-methylene bis(triphenylarsine phenylimine)
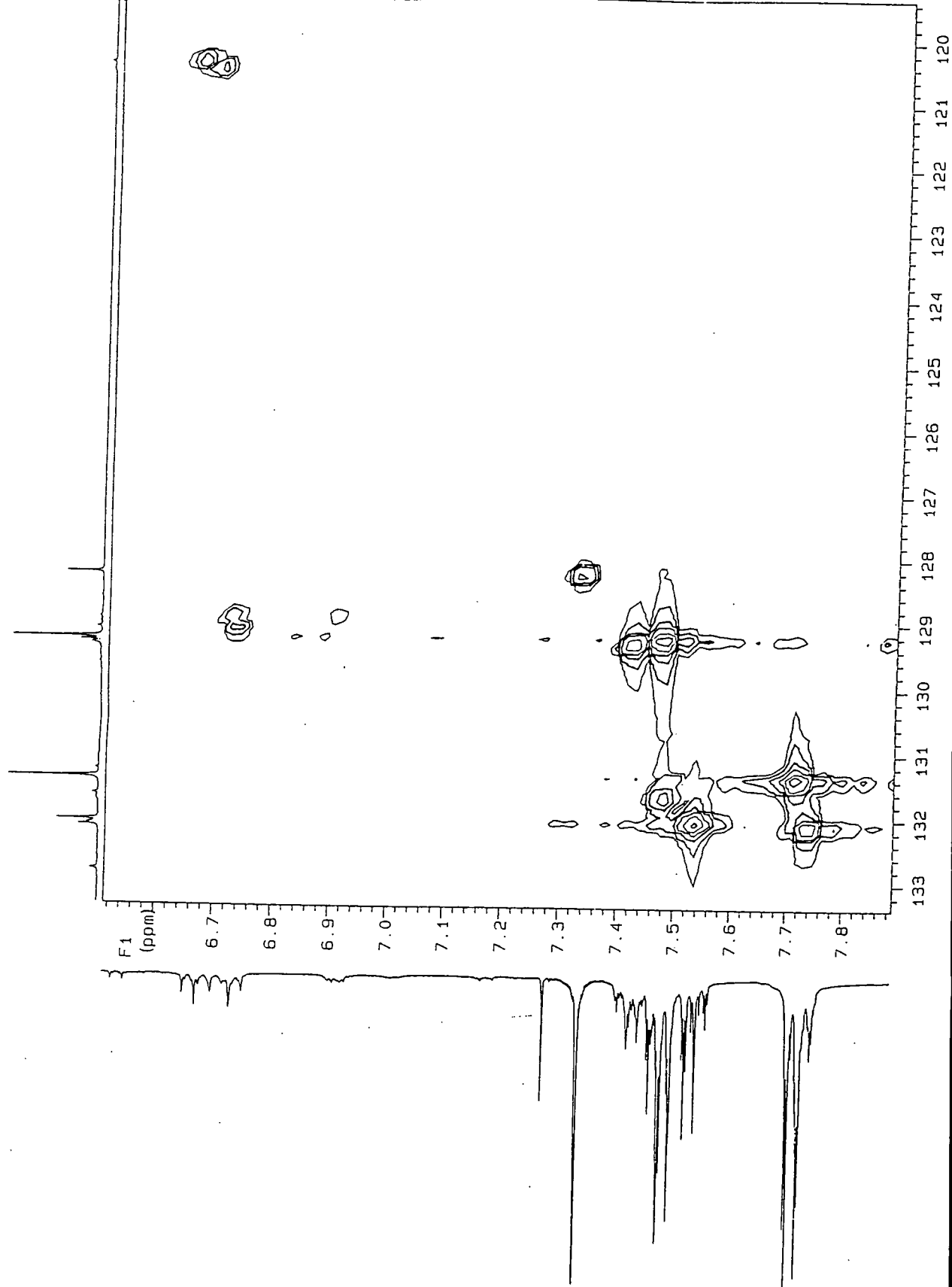
Appendix 3.16 HETCOR spectrum of the reaction products from a typical preparation of 4,4′-methylene bis(triphenylarsine phenylimine)
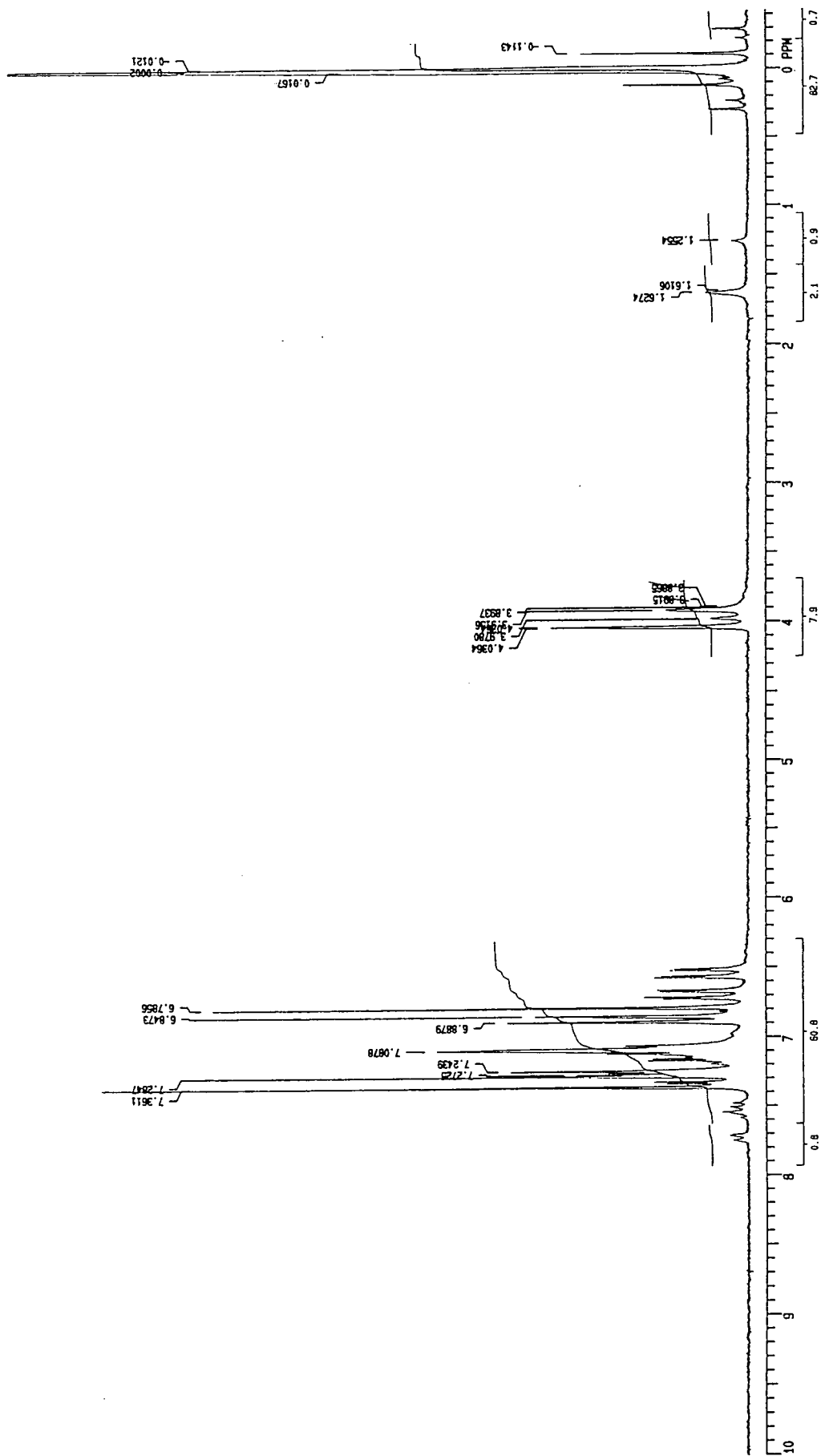
Appendix 3.17 ¹H nmr spectrum of the reaction products from the attempted polymerisation of 4,4′-methylene bis(phenylisocyanate) and p-benzoquinone - method 1
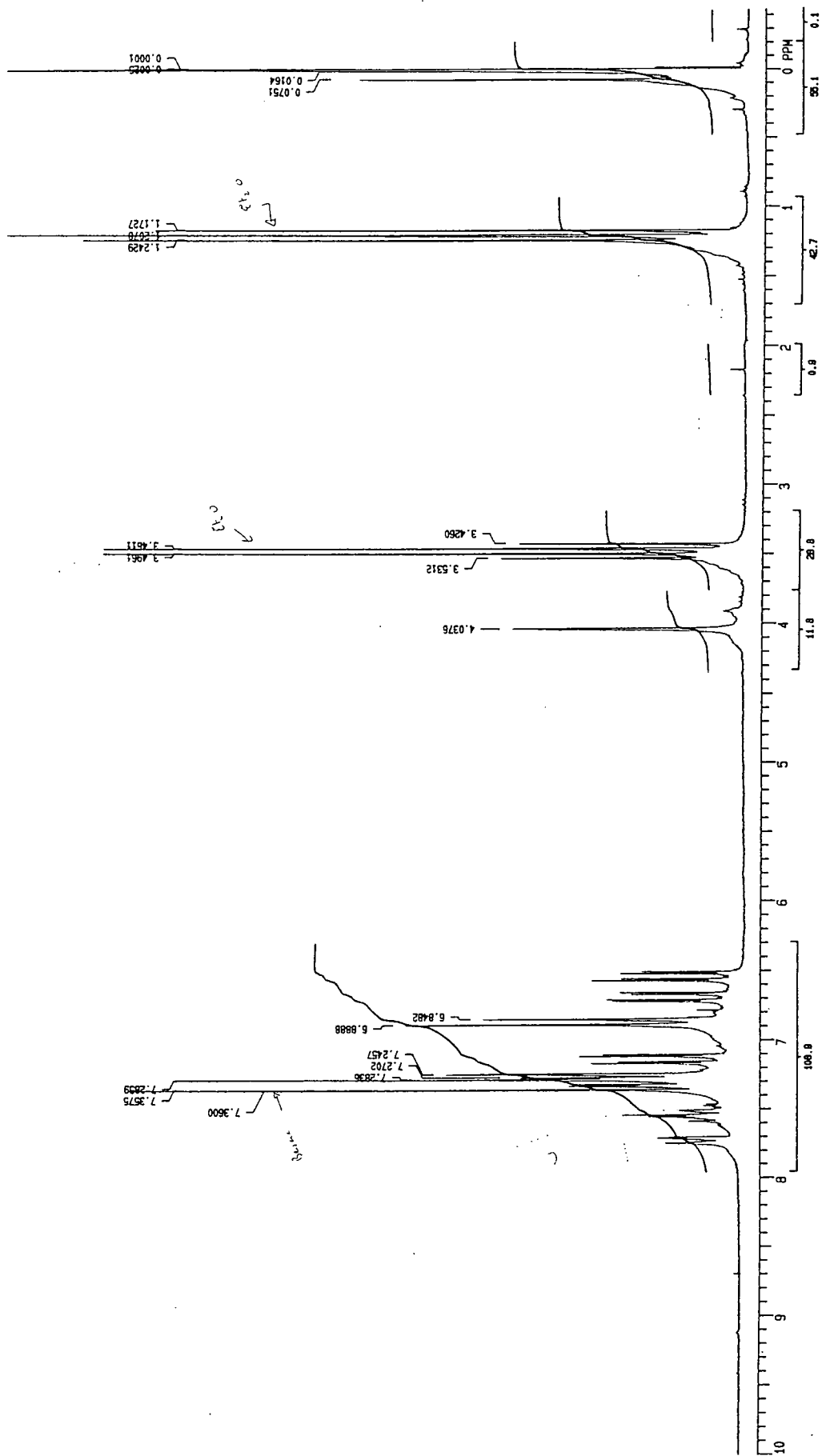
Appendix 3.18 ^{1}H nmr spectrum of the reaction products from the attempted polymerisation of 4,4'-methylene bis(phenylisocyanate) and p-benzoquinone - method 2

NH006GJ
EXP2 PULSE SEQUENCE S2PUL
DATE 02-16-93
SOLVENT CDCL3
FILE C

c-13 — 15.2811

30.6332

40.9642

c-13 — 65.8578

76.4059
76.5040
77.0422
77.6742
77.7783

123.313

128.206
128.325
129.381
129.589
131.483
132.513
132.731
133.396

141.889

20 40 60 80 100 120 140 160 PPM

Appendix 3.19 ^{13}C nmr spectrum of the reaction products from the attempted polymerisation of 4,4′-methylene bis(phenylisocyanate) and p-benzoquinone - method 2
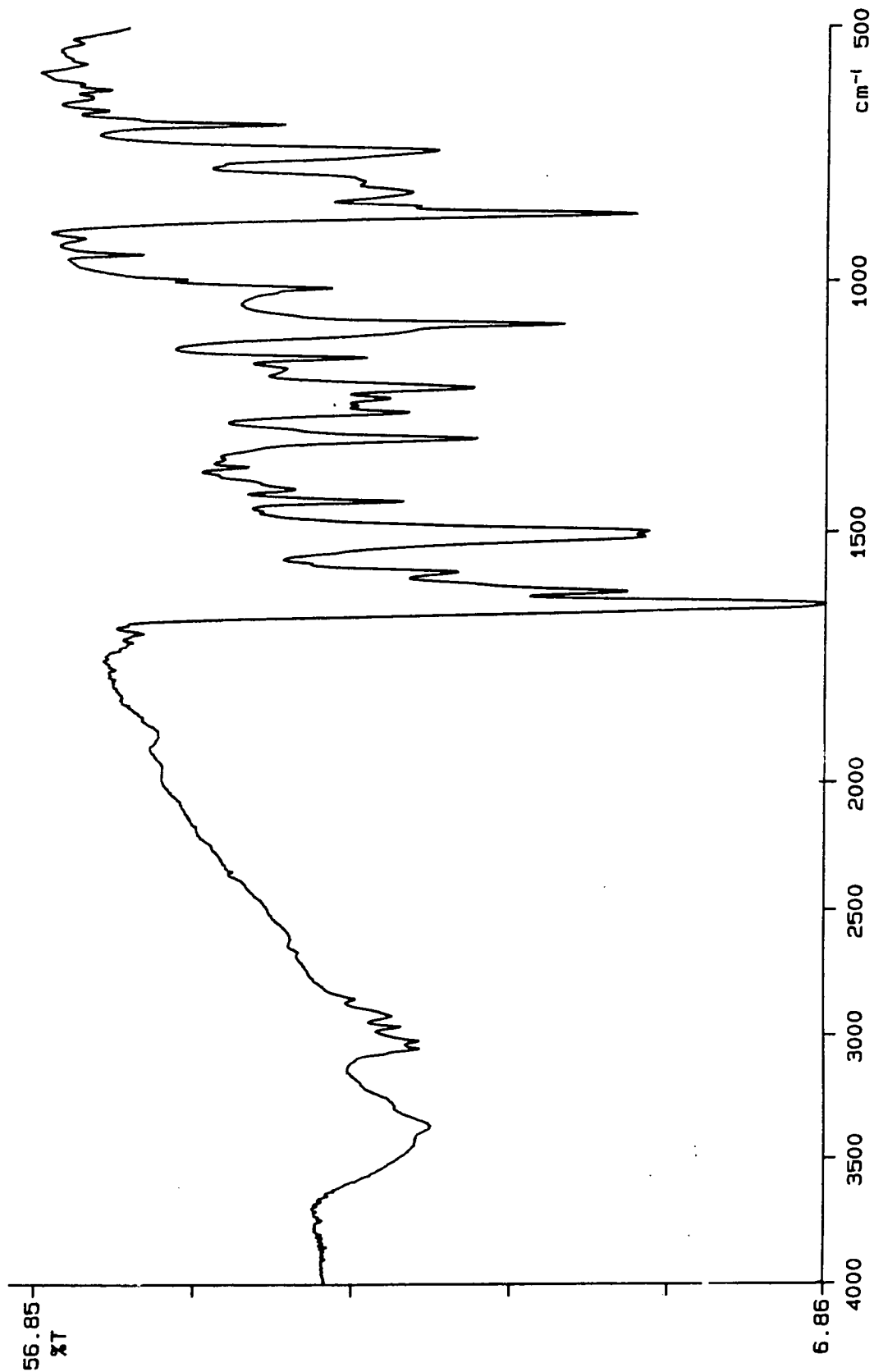
Appendix 3.20 IR spectrum of the reaction products from the attempted polymerisation of 4,4′-methylene bis(phenylisocyanate) and p-benzoquinone - method 2

APPENDIX 4

Lectures, Meetings and Conferences Attended

University of Durham - Borad of Studies in Chemistry

Colloquia, seminars and lectures given by invited speakers

<u>1992</u>

October 15   Dr. M. Glazer, Oxford University, & Dr. S. Tarling, Birkbeck College, London
It Pays To Be Brittish! The Chemists Role as an Expert Witness in Patent Litigation.

October 20   Dr. H.E. Bryndza, Du Pomt Central Research
Syntheseis, Reactions and Thermochemistry of Metal (Alkyl) Cyanide Complexes and Their impact on Olefin Hydrocyanation Catalysis

October 22   Prof. A. Davies, University College London
The Ingold-Albert Lecture. The Behaviour of Hydrogen as a Pseudometal

October 28   Dr. J. K. Cockcroft, University of Durham
Recent Developments in Powder Diffraction

October 29   Dr. J. Emsley, Imperial College London
The Shocking History of Phosphorus

November 4   Dr. T. P. Kee, University of Leeds
Synthesis and Co-ordination Chemistry of Silylated Phosphites

November 5   Dr. C. J. Ludman, University of Durham
Explosions, A Demonstration Lecture

November 11   Prof. D. Robins, Glasgow University
Pyrrolizidine Alkaloids: Biological Activity, Biosynthesis and Benefits

November 12   Prof. M. R. Truter, University college, London
Luck and Logic in Host-Guest Chemistry

November 18   Dr. R Nix, Queen Mary College, London
Characterisation of Heterogeneous Catalysts

November 25   Prof. Y. Vallee, Univerity of Caen
Reactive tiocarbonyl Compounds

November 25   Prof. L. D. Quin, University of Massachusetts, Amherst
Fragmentation of Phosphorus Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding

November 26   Dr. D. Humber, Glaxo Greenford
AIDS- The Development of a Novel Series of Inhibitors of HIV

December 2   Prof. A. F. Hegarty, University College Dublin
              Highly Reactive Enols Stabilised by Steric Protection

December 2   Dr. R. A. Aitken, University of St. Andrews
              The Versatile Cycloaddition of $Bu_3P.CS_2$

December 3   Prof. P Edwards, Birmingham University
              The SCI Lecture: What is Metal?

December 9   Dr. A. N. Burgess, ICI Runcorn
              The structure of Perfluorinated Inonomer Membranes

1993

January 20   Dr. D. C. Clary, University of Cambridge
              Energy Flow in Chemical Reactions

January 21   Prof. L. Hall, Cambridge
              NMR- Window to the Human Body

January 27   Dr. W. Kerr, University of Strathclyde
              Development of the Pauson-Khand Annulation Reaction:
              Organocobalt Mediated Synthesis of Natural and Unnatural Products

January 28   Prof. J. Mann, University of Reading
              Murder, Magic and Medicine

February 3   Prof. M. S. Roberts, University of Exeter
              Enzymes in Organic Synthesis

February 10   Dr. D. Gillies, University of Surrey
              NMR and Molecular Motion in Solution

February 11   Prof. S. Knox, Bristol University
              The Tiden Lecture: Organic Chemistry at Polynuclear Metal Centres

February 17   Dr. W. R. Kemmitt, University of Leicester
              Oxatrimethylenemethane Metal Complexes

February 18   Dr. I. Fraser, ICI Wilton
              Reactive Processing of Composite Materials

February 22   Prof. D. M. Grant, Universityof Utah
              Single Crystals, Molecular Structure and Chemical-Shift Anisotropy

February 24   Prof. C. J. M. Stirling, University of Sheffield
              Chemistry on the Flat Reactivity of Ordered Systems

March 10   Dr. P. K. Baker, University College of North Wales, Bangor
           'Chemistry of Highly Versatile 7-Coordinate Complexes

March 11   Dr. R. A. Y. Jones, University of East Anglia
           The Chemistry of Wine Making

March 17   Dr. R. J. K. Taylor, University of East Anglia
           Adventures in Natural Product Synthesis

March 24   Prof. I. O. Sutherland, University of Liverpool
           Chromogenic Reagents for Cations

May 13   Prof. J. A. Pople, Carnegie-Mellon University, Pittsburgh, USA
           The Boys-Rahman Lcture: Applications of Molecular Orbital Theory

May 21   Prof. L. Weber, University of Bielefeld
           Metallo-phospha Alkenes as Synthons in Organometallic Chemistry

June 1   Prof. J. P. Konopelski, University of California Santa Cruz
           Synthetic Adventures with Enantiomerically Pure Acetals

June 2   Prof. F. Ciardelli, University of Pisa
           Chiral Discrimination in the Stereospecific Polymerisation of Alpha
           Olefins

June 7   Prof. R. S. Stein, University of Massachusetts
           Scattering Studies of Crystaline and Liquid Crystalline Polymers

June 16   Prof A. K. Covington, University of Newcastle
           Use of Ion Selective Electrodes as Detectors in Ion Chromatography

June 17   Prof. O. F. Nielsen, H. C. Ørsted Institute, University of Copenhagen
           Low-Frequency IR- and Raman Studies of Hydrogen Bonded Liquids

September 13 Dr A. D. Schluter, Freie Universitat, Berlin, Germany
           Synthesis and Characterisation of Molecular Rods and Ribbons

September 13 Dr. K. J. Wynne, Office of Naval Research, Washington, USA
           Polymer Surface Design for Minimal Adhesion

September 14 Prof. J. M. DeSimone, University of North Carolina, Chapel Hill, USA
           Homogeneous and Heterogeneous Polymerisations in Environmentally
           Responsible Carbon Dioxide

September 28 Prof. H. Ila, North Eastern Hill University, India
           Synthetic Strategies for Cyclopentanoids via Oxoketene Duithioacetals

October 4 Prof. F. J. Feher, University of California, Irvine, USA
           Bridging the Gap Between Surfaces and Solution with Sessilquioxanes

October 14   Dr. P. Hubberstey, University of Nottingham
              Alkali Metals: Alchemist's Nightmare, Biochemist's Puzzle and
              Technologist's Dream

October 20   Dr. P. Quayle, University of Manchester
              Aspects of aqueous ROMP Chemistry

October 21   Prof. R. Adams, University of South Carolina, USA
              Chemistry of Metal Carbonyl Cluster Complexes: Development of
              Cluster Based Alkyne Hydrogenation Catalysts

October 27   Dr. R. A. L. Jones, Cavendish Laboratory, Cambridge
              Perambulating Polymers

November 10   Prof. M. N. R. Ashfold, University of Bristol
              High Rsolution Photofragment Translational Spectroscopy: A New
              Way to Watch Photodissociation

November 17   Dr. A. Parker, Rutherford Appleton Laboratory, Didcot
              Applications of Time Ressolved Resonance Raman Spectroscopy to
              Chemical and Biochemical Problems

November 24   Dr P. G. Bruce, University of St. Andrews
              Structure and Properties of Inorganic Solids and Polymers

November 25   Dr. R. P. Wayne, University of Oxford
              The Origin and Evolution of the Atmosphere

December 1   Prof. M. A. McKervey, Queen's University, Belfast
              Synthesis and Applications of Chemically Modified Calixarenes

December 8   Prof. O. Meth-Cohn, University of Sunderland
              Friedel's Folly Revisited- A Super Way to Fused Pyridines

December 16   Prof. R. F. Hudson, University of Kent
              Close Encounters of the Second Kind

1994

January 26   Prof. J. Evans, University of Southampton
              Shining Light on Catalysts

February 2   Dr. A. Masters, University of Manchester
              Modelling Water Without Using Pair Potentials

February 9   Prof. D. Young, University of Sussex
              Chemical and Biological Studies on the Coenzyme Tetrahydrofolic
              Acid

| February 16 | Prof. K. P. Theopold, University of Delaware, USA
Paramagnetic Chromium Alkyls: Synthesis and Reactivity |

February 16   Prof. K. P. Theopold, University of Delaware, USA
Paramagnetic Chromium Alkyls: Synthesis and Reactivity

February 23   Prof. P. M. Maitlis, University of Sheffield
Across the Border: From Homogeneous to Heterogeneous Catalysis

March 2   Dr. C. Hunter, University of Sheffield
Noncovalent Interaction between Aromatic Molecules

March 9   Prof. R. Wilkinson, Loughborough University of Technology
Nanosecond and Pecosecond Laser Flash Photolysis

March 10   Prof. S. V. Ley, University of Cambridge
New Methods for Organic Synthesis

March 25   Dr. J. Dilworth, University of Essex
Technetium and Rhenium Compounds with Applications as Imaging
Agents

April 28   Prof. R. J. Gillespie, McMaster University, Canada
The Molecular Structure of some Metal Fluorides and Oxofluorides:
Apparent Exceptions to the VSEPR Model

May 12   Prof. D. A. Humphreys, McMaster University, Canada
Bringing Knowledge to Life

October 5   Prof N. L. Owen, Brigham Young University, Utah, USA
Determining Molecular Stuctrure-The INADEQUATE NMR Way

October 19   Professor N. Bartlett, University of California
Some Aspects of (AgII) and (AgIII) Chemistry.

October 26   Dr. G. Rumbles, Imperial College
Real or Imaginary 3rd Order Non-Linear Optical Materials.

November 2   Dr. P. G. Edwards, University of Wales, Cardiff
The Manipulation of Electronic and Structural Diversity in Metal
Complexes - New Ligands for New Properties.

November 9   Dr. G. Hogarth, University College, London
New Vistas in Metal Imido Chemistry.

November 16   Professor M. Page, University of Huddersfield
Four Membered Rings and β-Lactamase.

November 23   Dr. J. Williams, University of Loughborough
New Approaches to Asymmetric Catalysis.

November 30   Professor P. Parsons, University of Reading
              Applications of Tandem Reactions in Organic Synthesis.

<u>1995</u>

January 25   Dr. D. A. Roberts, Zeneca Pharmaceuticals
              The Design and Synthesis of Inhibitors of the Renin-Angiotensin
              System.

February 1   Dr. T. Cosgrove, Bristol University
              Polymers do it at Interfaces.

February 8   Dr. D. O'Hare, Oxford University
              Synthesis and Solid State Properties of Poly- Oligo- and Multidecker
              Metallocenes.

February 15   Professor W. Motherwell, University College, London
              New Reactions for Organic Synthesis.

March 1   Dr. M. Rosseinsky, Oxford University
              Fullerene Intercalation Chemistry.

April 26   Dr. M. Schroder, University of Edinburgh
              Redox Active Macrocyclic Complexes: Rings, Stacks and Liquid
              Crystals.

May 3   Professor E. W. Randall, Queen Mary and Westfield College
              New Perspectives in NMR imaging.

May 24   Dr. P. Beer, Oxford University
              Anion Complexation Chemistry.

The author has also attended the following lectures in the IRC in Polymer Science and Technology International Seminar Series.

1993

March 16   Prof. J.M.G. Cowie (Heriot-Watt University), at Bradford University
High Technology in Chains : The Role of Polymers in Electronic
Applications and Data Processing

April 1   Prof. H. W. Speiss (Max-Planck Institut for Polymerforschung, Mainz),
at Durham University.
Multidimensional NMR Studies of Structure and Dynamics of Polymers.

June 2   Prof. F. Ciardelli (University of Pisa), at Durham University
Chiral Discrimination in the Stereospecific Polymerisation of ∝-olefins.

June 8   Prof. B. E.Eichinger (BIOSYM Technologies Inc. San Diego),
at Leeds University.
Recent Polymer Modeling Results and a look into the Future.

Conferences, meeting and courses attended by the author

January 1993   IRC Polymer Engineering Course, University of Bradford

March 1993   IRC Polymer Physics Course, University of Leeds

April 1993   Macro Group (U.K) Family Meeting, University of Lancaster

September 1993   IRC Club Meeting, University of Durham

April 1994   Macro Group (UK) Family Meeting, University of Birmingham

April 1994   New Electronic Materials, Royal Society of Chemistry, London

June 1994   SERC Graduate School, University of Stirling

February 1995   †SELMAT Meeting, University of Marburg, Germany

April 1995   †Macro Group (UK) Family Meeting, Loughborough University
                    of Technology

June 1995   *PAT 95, University of Pisa, Italy

July 1995   ISOM 95, University of Durham

September 1995   †IRC Club Meeting, University of Durham

† Oral Presentation by the author
* Poster presentation by the author