Synthesis and characterisation of poly(arylene vinylene)s

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SYNTHESIS AND CHARACTERISATION OF POLY(ARYLENE VINYLENE)S

Rusli Daik

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Abstract

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Rusli Daik Ph D Thesis September 1997

The synthesis of a series of poly(arylene vinylene)s via transition metals catalysed polycondensation with a view to producing well defined and clean samples for study , particularly for the incorporation of the material in light emitting devices has been described. Initially the McMurry reaction was applied in the synthesis of poly(4,4'-diphenylene diphenylvinylene). The reaction conditions have been optimised and relatively high molecular weight polymers with narrow molecular weight distributions were produced by fractionating the polymer. The feasibility of the McMurry reaction was established in the synthesis of related polymers; including poly(1,3-phenylene diphenylvinylene), poly(1,3-phenylene dimesitoylvinylene) and poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene). In other attempts the Yamamoto and Suzuki polycondensations were applied in the synthesis of structurally defined poly(arylene vinylene)s which could not be made via the route used earlier. Studies on UV-visible absorption, photoluminescence and electroluminescence properties of polymers produced were carried out and correlation between polymer structure and electro-optical properties of the polymer, particularly photoluminescence has been established.

Acknowledgements

This thesis would not have been possible without the great help of my supervisor, Professor W. James Feast. I am deeply indebted for his willingness and unfailing guidance and support during the supervision of this work, and without his assistance the bits and pieces of this thesis would not have been pulled together. Secondly I must thank Professor Ibrahim Abdullah who gave me the chance to further my study in the first place.

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Memorandum

The work reported in this thesis has been carried out at the Durham site of the Interdisciplinary Research Centre in Polymer Science and Technology between October 1994 and September 1997. This work has not been submitted for any other degree either in Durham or elsewhere and is the original work of the author except where acknowledge by means of appropriate reference.

Statement of Copyright

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Contents

page

Abstract ii

Acknowledgements iii

Memorandum iv

Statement of Copyright iv

Financial Support iv

Chapter 1 A review of poly(arylene vinylene)s 1

1.1 Introduction 2

1.2 What are poly(arylene vinylene)s? 3

1.3 Synthetic methods utilised in the preparation of poly(arylene vinylene)s 4

1.3.1 Precursor routes to poly(arylene vinylene)s 4

1.3.2 Application of Wittig reaction to poly(arylene vinylene)s synthesis 10

1.3.3 Application of dehalogenation and dehydrohalogenation reactions to poly(arylene vinylene)s synthesis 10

1.3.4 Application of the Knoevenagel condensation to poly(arylene vinylene)s synthesis 12

1.3.5 Application of the Heck reaction to poly(arylene vinylene)s synthesis 13

1.3.6 Application of ring opening metathesis polymerisation (ROMP) to synthesis of poly(arylene vinylene)s 14

1.3.7 Acyclic diene metathesis (ADMET) polymerisation route to poly(arylene vinylene)s 15

1.4 PAVs synthesised via transition metals catalysed polycondensation 16

1.4.1 Application of the McMurry reaction to poly(arylene vinylene)s synthesis 16

1.4.2 Suzuki reaction route to poly(arylene vinylene)s 18

1.4.3 Yamamoto reaction route to poly(arylene vinylene)s 20

1.5 Reasons for interest in poly(arylene vinylene)s 22

1.6 Aims of the project 24

1.7 References 26

Chapter 2 The McMurry approach to poly(arylene vinylene)s 30

2.1 Introduction 31

2.2 The McMurry reaction 31

2.2.1 Low-valent titanium reagent 32

2.2.2 Mechanism 34

2.2.3 Scope and limitations 37

2.3 The synthesis of aromatic diketone monomers 39

2.4 Results and Discussion 41

2.4.1 Aromatic diketone monomers 41

2.4.1.1 4,4'-Dibenzoylbiphenyl 41

2.4.1.2 1,3-Dibenzoylbenzene 43

2.4.1.3 1,3-Dimesitoylbenzene 45

2.4.1.4 4,4'-Di(4-nitrobenzoyl)biphenyl 46

2.4.1.5 4,4'-Bis(pentafluorobenzoyl)biphenyl 50

2.4.1.6 Attempted synthesis of 3-pentafluorobenzoylbenzophenone 51

2.4.1.7 Attempted synthesis of 1,3-bis(pentafluorobenzoyl)benzene 51

2.4.2 Poly(4,4'-diphenylene diphenylvinylene) 52

2.4.2.1 Preliminary experiments 52

2.4.2.2 Influence of reaction time 56

2.4.2.3 Recoupling of poly(4,4'-diphenylene diphenylvinylene) 57

2.4.2.4 Influence of $TiCl_3/LiAlH_4$ molar ratio 58

2.4.2.5 Influence of monomer concentration 60

2.4.2.6 Fractionation of poly(4,4'-diphenylene diphenylvinylene) 61

2.4.2.7 Thermal properties of poly(4,4'-diphenylene diphenylvinylene) 65

2.4.3 Poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene 65

2.4.4 Poly(1,3-phenylene diphenylvinylene) 68

2.4.5 Poly(1,3-phenylene dimesitylvinylene) 71

2.4.6 Coupling reaction of 4-nitrobenzoylbiphenyl 73

2.5 Conclusions 73

2.6 Experimental 75

2.6.1 Synthesis of 4,4'-dibenzoylbiphenyl 75

2.6.2 Synthesis of 1,3-dibenzoylbenzene 76

2.6.3 Synthesis of 1,3-dimesitoylbenzene 77

2.6.4 Synthesis of 4-nitrobenzoylbiphenyl 78

2.6.5 Synthesis of 4,4'-di(4-nitrobenzoyl)biphenyl 79

2.6.6 Synthesis of 4,4'-bis(pentafluorobenzoyl)biphenyl 80

2.6.7 Attempted synthesis of 3-pentafluorobenzoylbenzophenone 81

2.6.8 Attempted synthesis of 1,3-bis(pentafluorobenzoyl)benzene 82

2.6.9 Synthesis of poly(arylene vinylene)s via McMurry reaction 82

2.6.10 Polymer fractionation 83

2.7 References 85

Chapter 3 The Yamamoto polycondensation route to poly(arylene vinylene)s 87

3.1 Introduction 88

3.2 The Kumada reaction 89

3.2.1 Reaction conditions involved in the Kumada reaction 89

3.2.2 Mechanism 91

3.2.3 Scope and limitations 92

3.3 Results and Discussion 96

3.3.1 Aryl dibromide monomers 96

3.3.1.1 2,3-Di(4-bromophenyl)-2-butenes 96

3.3.1.2 1,2-Di(4-bromophenyl)-1,2-diphenylethenes 101

3.3.2 Polymers 104

3.3.2.1 Poly(4,4'-diphenylene dimethylvinylene)s 104

3.3.2.2 Poly(4,4'-diphenylene diphenylvinylene)s 106

3.4 Conclusions 109

3.5 Experimental 110

3.5.1 Synthesis of 2,3-di(4-bromophenyl)-2-butenes 111

3.5.2 Synthesis of 1,2-di(4-bromophenyl)-1,2-diphenylethenes 112

3.5.3 Synthesis of poly(4,4'-diphenylene dimethylvinylene)s 114

3.5.4 Synthesis of poly(4,4'-diphenylene diphenylvinylene)s 114

3.6 References 116

Chapter 4 The Suzuki coupling approach to poly(arylene vinylene)s 118

4.1 Introduction 119

4.2 The Suzuki cross-coupling reaction 119

4.2.1 Palladium catalysed cross-coupling reaction of aryl boronic acids with aryl bromides 119

4.2.2 Mechanism 121

4.2.3 Scope and limitations 125

4.3 Results and Discussion 131

4.3.1 Monomers 131

4.3.2 Polymers 132

4.3.2.1 Preliminary experiments 134

4.3.2.2 Poly(tri-*p*-phenylene diphenylvinylene)s 136

4.3.2.3 Poly(tri-*p*-phenylene dimethylvinylene)s 139

4.3.2.4 Poly(tetra-*p*-phenylene diphenylvinylene)s 140

4.3.2.5 Poly(tetra-*p*-phenylene dimethylvinylene)s 144

4.4 Conclusions 145

4.5 Experimental 147

4.5.1 Synthesis of poly(tetra-*p*-phenylene diphenylvinylene) 148

4.5.2 Synthesis of poly(tri-*p*-phenylene diphenylvinylene) 149

4.5.3 Synthesis of poly(tetra-*p*-phenylene dimethylvinylene) 150

4.5.4 Synthesis of poly(tri-*p*-phenylene dimethylvinylene) 150

4.6 References 152

Chapter 5 The optical and electro-optical properties of poly(arylene vinylene)s 154

5.1 Introduction 155

5.2 Application of UV-visible absorption study in poly(arylene vinylene)s 155

5.3 Photoluminescence and electroluminescence of poly(arylene vinylene)s 156

5.4 Organic polymer light emitting diodes 157

5.4.1 What is an organic polymer light emitting diode? 157

5.4.2 How does an organic polymer light emitting diode work? 158

5.4.3 Challenges in developing organic light emitting diodes 160

5.4.3.1 Colour tuning 160

5.4.3.2 Emission efficiency 165

5.5 Results and Discussion 166

5.5.1 UV-visible studies of poly(arylene vinylene)s 166

5.5.1.1 Poly(4,4'-diphenylene diphenylvinylene)s 166

5.5.1.2 Poly(1,3-phenylene diphenylvinylene)s 169

5.5.1.3 Poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)-vinylene)s 171

5.5.1.4 Poly(tetra-*p*-phenylene diphenylvinylene)s 173

5.5.1.5 Summary of UV-visible studies of poly(arylene vinylene)s 176

5.5.2 Photoluminescence studies of poly(arylene vinylene)s 177

5.5.2.1 Poly(4,4'-diphenylene diphenylvinylene)s 177

5.5.2.2 Poly(4,4'-diphenylene-1,2-bis(pentafluoropheny)-vinylene)s 180

5.5.2.3 Poly(1,3-phenylene diphenylvinylene)s 182

5.5.2.4 Poly(tetra-*p*-phenylene diphenylvinylene)s 183

5.5.3 Electroluminescence studies of poly(arylene vinylene)s 186

5.6 Conclusions 188

5.7 References 189

Chapter 6 Overall conclusions and proposals for future work 191

6.1 Overall conclusions 192

6.2 Proposals for future work 193

6.3 References 195

Appendix 1 Analytical data for Chapter 2

Appendix 2 Analytical data for Chapter 3

Appendix 3 Analytical data for Chapter 4

Appendix 4 Analytical data and instrumentation for Chapter 5

Colloquia, Lectures and Seminars Attended

Conferences and Courses Attended

Chapter 1

A review of poly(arylene vinylene)s

1.1 Introduction

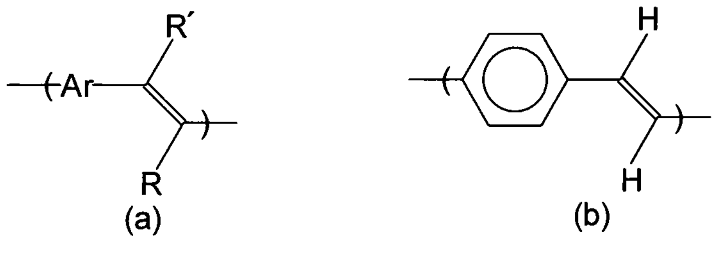
Conjugated polymers are the basis of an important class of electronically conducting organic materials. The electrical properties arise from the delocalised π-electrons along the conjugated backbone.[1] Thus they offer the possibility of combining the desirable properties of a polymer, such as processability, with electrical properties varying from insulator, through semiconductor to metallic conductor. Polymers with conjugated backbones display unusual electronic properties such as low ionisation potentials and high electron affinities. As a result, these polymers can be oxidised or reduced much more easily than conventional saturated polymers. Although most conjugated polymers in their pure state are best described as electrical insulators, they can be converted into conducting materials when they are reduced or oxidised. The best known exception to this generalisation is poly(sulphur nitride), $(SN)_x$, which is a metallic conductor in its pristine state.[2]

The discovery of electroluminescence from poly(*p*-phenylene vinylene)[3] has given a new drive to research activities in the area of conjugated polymers generally, and particularly in the area of poly(arylene vinylene)s, (PAVs). Although at the time of its discovery, the electroluminescence efficiency of the first device structure was only about 0.01%, tremendous efforts have been made since then, not only to improve the efficiency[4,5,6] but also to enhance other aspects of device performance, such as lifetime and stability[7] as well as the ability to control the emission colour.[8,9]

This chapter provides a brief introduction to poly(arylene vinylene)s, (PAVs). This includes an account of the common understanding of what PAVs are, the accessible synthetic approaches to PAVs which have been established and the various reasons for interest in PAVs.

1.2 What are poly(arylene vinylene)s?

In recent years there has been a dramatic growth in interest in the development of organic materials for use in electronic devices. Organic materials and especially polymers present many advantages over inorganic materials, such as good mechanical properties, ease of processability, and almost an unlimited number of accessible chemical structures.[10] Poly(arylene vinylene)s, (PAVs), polymers with an alternating sequence of arylene and vinylene segments, have aroused significant interest due to their optoelectronic properties. Poly(*p*-phenylene vinylene), (PPV), is the simplest example of this class. It is electrically conductive upon redox modification, photoconductive and it also shows promising features as a non-linear optical material.[11] The general structure of a poly(arylene vinylene) and the structure of poly(*p*-phenylene vinylene) are shown in *Figure 1.1*.



R′, R = H, Aryl, Alkyl, or substituted group
Ar = arylene

Figure 1.1. (a) Poly(arylene vinylene) and (b) poly(*p*-phenylene vinylene).

The recent development of PPV has concentrated on its behaviour, particularly since it was established that it can be used as the emissive layer in light emitting diodes (LEDs).[3] Since then a great number of poly(arylene vinylene)s suitable for use in LEDs have been developed.

1.3 Synthetic methods utilised in the preparation of poly(arylene vinylene)s

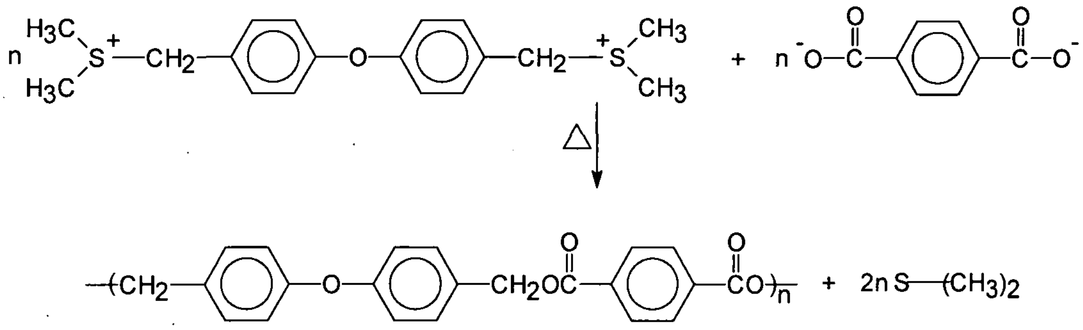
The synthesis, analysis and processing of PAVs have been inhibited by the insolubility and infusibility displayed by many polymers of this type. PAVs have been prepared by a variety of polycondensation reactions, often this work resulted only in oligomeric materials with limited processability. Different strategies have been developed in order to prepare processable materials containing arylenevinylene sequences.

1.3.1 Precursor routes to poly(arylene vinylene)*s*

Greiner reported that derivatives of PPV with substituents on the phenylene unit showed improved solubility as compared to their unsubstituted analogues, but the synthesis employed gave products with molecular weights below 10,000g/mol.[11] Great attention has been paid to PPV prepared by the precursor method. In this approach, a water soluble precursor polymer is converted to PPV by thermal treatment. The advantages of this method are clear: thus, high molecular weight processable precursor polymers can form free standing films or fibres, which can be oriented in the conventional manner. Disadvantages, that are often neglected, include the limited post-synthesis processing possibilities, the high temperature treatment required for the conversion to PPV, the possibility of trapping of low molecular weight elimination products in the final film and the limited possibilities for the formation of blends with water soluble polymers.[11]

The most commonly used precursor routes to PPV, and many PAVs, are based on the method of Wessling and Zimmerman.[12] 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 films, fibres or coatings.

Research on the polymerisation of bis-sulfonium salts was initiated by Turner Alfrey in 1964.[12] They made the key observation that sulfonium intermediates could be used to make hydrophilic polymers that converted easily to hydrophobic products on mild heating. Alfrey and co-workers used this approach to prepare a series of condensation polymers from chloromethylated diphenyloxide via sulfonium intermediates. The bulk of the work was carried out with the difunctional monomer, *p,p'*-dichloromethyldiphenyloxide. It reacts readily with dimethylsulfide to form a bis-sulfonium salt, *p,p*'-oxydiphenylenedimethylene-bis-dimethylsulfonium chloride. Linear condensation polymers were prepared by reacting the bis-sulfonium salt with a difunctional anionic nucleophilic, such as terephthalate ion, see *Scheme 1.1*.[12]



Scheme 1.1 Linear saturated polymer prepared via sulfonium precursor route.

Polymerisation is made possible by the fact that displacement reactions are reasonably selective on the benzyl carbons. Polymerisation is induced by mild heating. The unique behaviour of *p*-xylylene sulfoniums was discovered when this method was applied to make polymers of other bischloromethylated aromatics.[12] When *p*-xylylene bisdimethylsulfonium chloride was passed through an ion exchange column, a viscous yellow-green syrup was eluted. The latter thickened, gelled, and finally deposited as a yellow-orange precipitate. Based on appearance, physical properties, and IR spectra, it appeared to be poly-*p*-xylylidene (PXD)[12], later known as poly(*p*-phenylene vinylene), PPV.

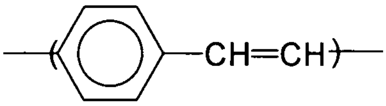


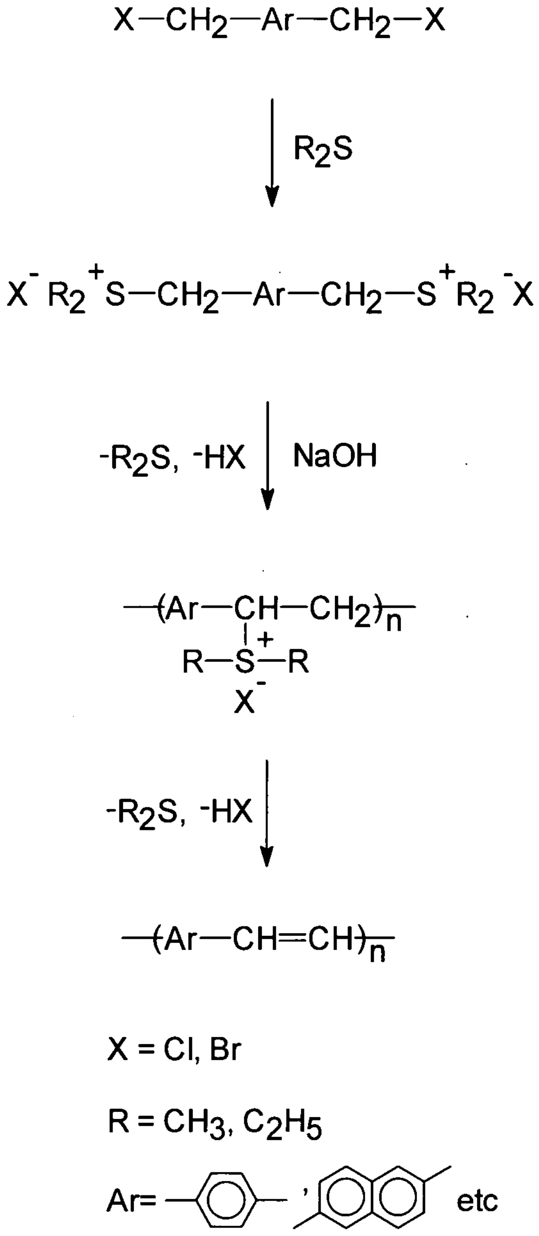
Figure 1.2 Poly(*p*-xylylidene), (PXD), now usually known as poly(*p*-phenylene vinylene), (PPV).

Work on original condensation polymerisation theme was soon abandoned because of the generally disappointing results and synthesis of PXD became the new target of the research instead. Interest in this polymer was high because of the belief that the fully conjugated structure would impart high temperature stability and unusual electrical properties. However, the PXD produced by other methods was an intractable powder that could not be fabricated into useful products. The sulfonium precursor route presented an opportunity to develop some novel fabrication techniques.[12]

The Wessling precursor route for the synthesis of PPV is of much interest, since it is the most convenient method at present to obtain processable, high quality films of high molecular weight PPVs, and analogous polymers.[13] The precursor route involves the synthesis of water soluble sulfonium salt polyelectrolytes which are subsequently converted to linear π-conjugated structures by thermal elimination.

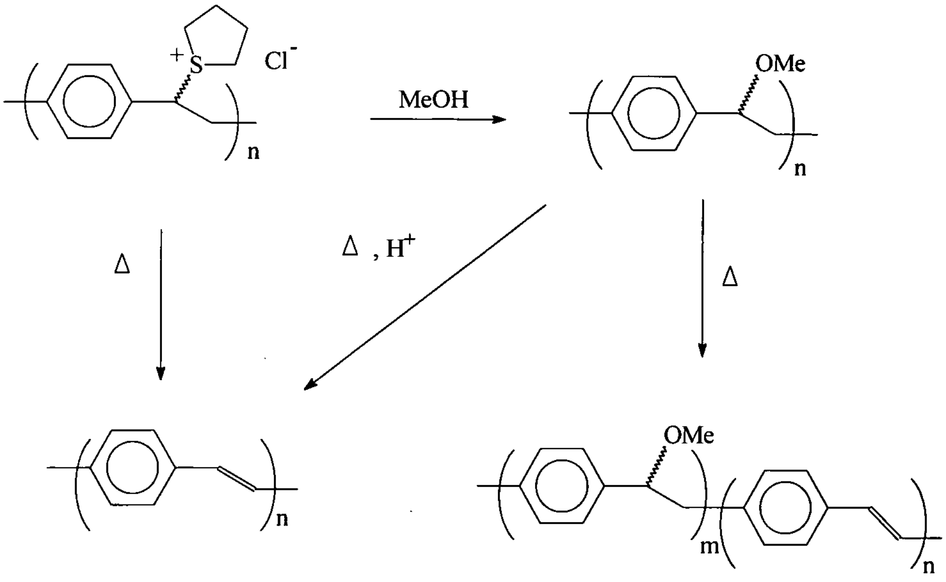
This synthesis of poly(arylene vinylene)s through the precursor route is undoubtedly one of the most important methods for obtaining insoluble polymer films with extended π-conjugated structures.[15] This procedure has been applied to the preparation of the parent polymer PPV and other poly(arylene vinylene)s such as poly(2,5-dimethoxy-*p*-phenylene vinylene), poly(2,5-naphthalene vinylene) and poly(2-methoxy-5-nitro-1,4-phenylene vinylene).[16] The general scheme of synthesis is shown below and, in principle, it is possible to prepare an almost unlimited number of polymers by using various bis(halomethyl) aromatic derivatives as starting materials.[17]

Gagnon *et al.* used essentially the same method to prepare poly(*p*-phenylene vinylene) which was produced and simultaneously doped from soluble precursor polymers by trapping the eliminated acid as a doping agent.[14]



Scheme 1.2 General route to poly(arylene vinylene)s via sulphonium precursors.

Recently, Murase[18] and the Cambridge group[3,19,20], amongst others, have all successfully used this route to produce high molecular weight PPV and its derivatives. Replacing the sulphonium ion with methoxy (*Scheme 1.3*) produces methoxy leaving group precursor polymer which, unlike the sulphonium precursor polymer, is soluble in organic solvents, such as chloroform, dichloromethane and THF, which conveys some processing advantage.



Scheme 1.3 Modified sulfonium precursor route to PPV and its derivatives.

Although the sulphonium leaving group polymer requires a temperature of approximately 300°C to fully complete the elimination, the polymer is slightly unstable at room temperature and some spontaneous elimination may occur, giving segments of conjugated polymer which tend to decrease the solubility and hence the processability of the precursor. 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 methoxy group. These different properties of the precursor polymers allow selective elimination. If complete elimination is required fresh sulphonium precursor polymer is used.[3] However if partial elimination is required, for example in the synthesis of a polymer with breaks in the conjugation,[20,21] methoxy polymer is synthesised and then partial elimination can be effected by heating without acid. In this way some degree of control of conjugation length can be obtained.

1.3.2 Application of Wittig reaction to poly(arylene vinylene)s synthesis

The Wittig reaction, which is widely used in organic chemistry to obtain alkenes, was used as early as 1960 to prepare poly(arylene vinylene)s.[22] The application of the Wittig reaction in the synthesis of PPV was reported by McDonald, *p*-xylylene-bis(triphenylphosphonium chloride) and terephthaldehyde were used as starting materials.[22] In general, the Wittig reaction involves the use of aldehydes and quaternary phosphonium salts and oligomers and polymers can be synthesised according to the following scheme.[17]

$$\text{OCH-Ar-CHO} + [\text{Ph}_3\text{P}^+\text{-CH}_2\text{-Ar}'\text{-CH}_2\text{-P}^+\text{Ph}_3]2\text{X}^- \rightarrow (\text{-Ar-CH=CH-Ar}'\text{-CH=CH-})_n$$

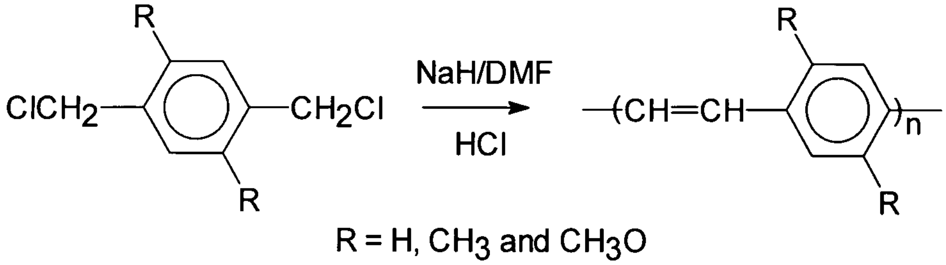
X=halogen
Ar and Ar′ can be a variety of arylenes.

Scheme 1.4 General route using the Wittig reaction for synthesis of poly(arylene vinylene)s.

This method has been used by Kossmehl to make a great number of polymers, however, all of them were obtained as insoluble and infusible powders which were shown to display semiconducting behaviour.[17] Even though it is not widely used at present to synthesis PPV or PAVs, the Wittig method is still used to synthesis PAVs oligomers via controlled step growth reactions.[23]

1.3.3 Application of dehalogenation and dehydrohalogenation reactions to poly(arylene vinylene)s synthesis

Poly(arylene vinylene)s can be synthesised via dehydrohalogenation reactions. Horhold synthesised a wide range of PAVs and substituted PPVs by this method, see *Scheme 1.5.*[24,25]



Scheme 1.5 Substituted PPVs prepared via dehydrohalogenation reactions.

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 1.3*. 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.

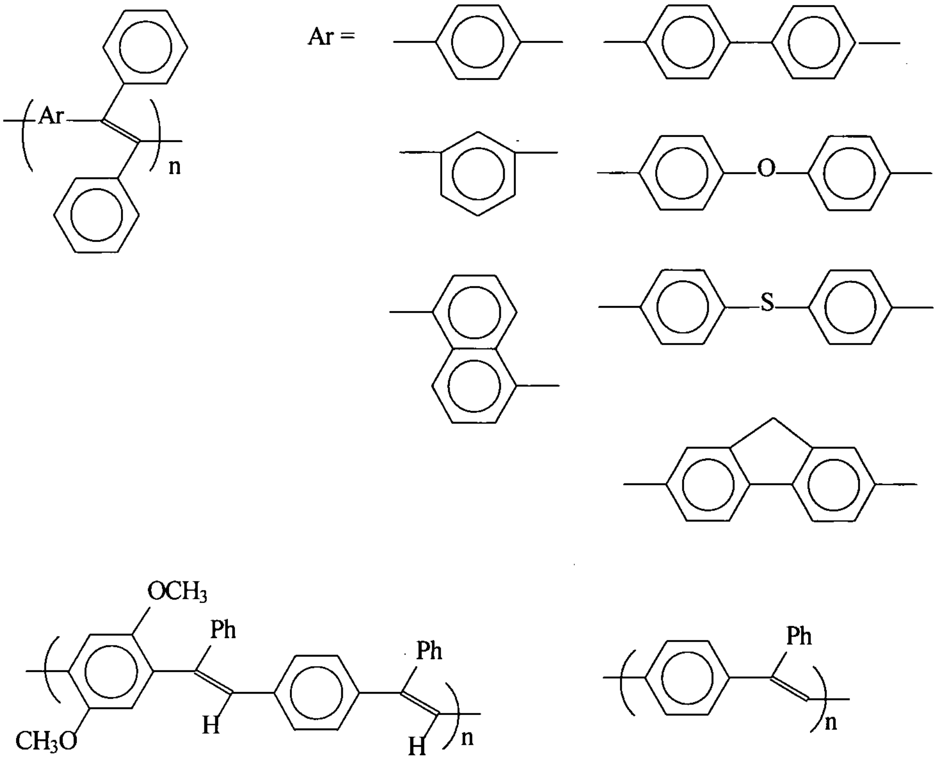


Figure 1.3 Examples of polymers synthesised via dehydrohalogenation.

Another example is the synthesis poly(2,5-dibromo-1,4-phenylene bis(4-tert-butylphenyl)-vinylene) by using 2,5-dibromo-1,4-bis(4-tert-butyl-α,α-dichlorobenzyl)benzene in a reductive dehalogenation polycondensation with chromium(II) acetate as reducing agent, see *Figure 1.4.*[26]

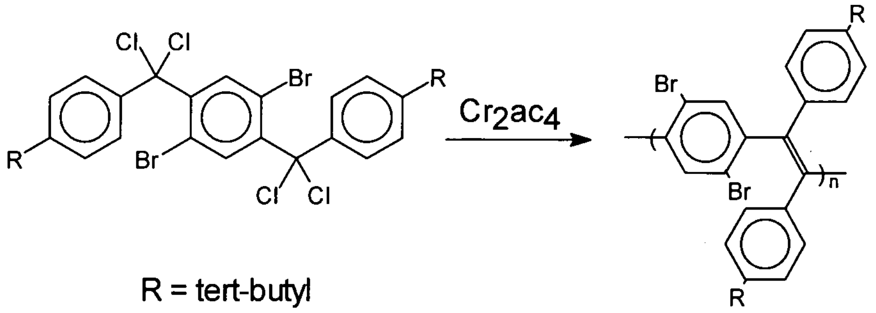
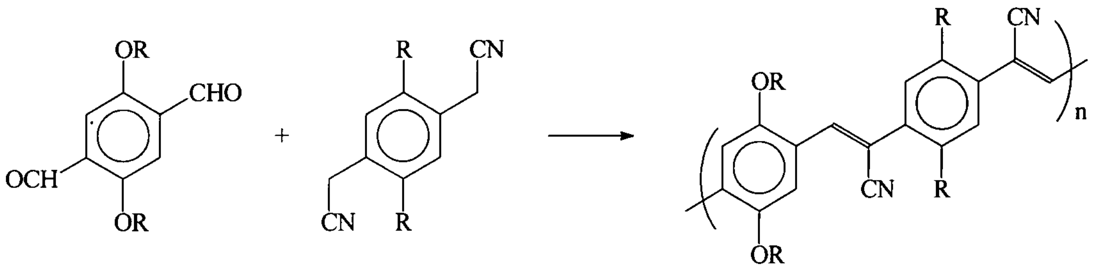


Figure 1.4 Poly(*p*-phenylene vinylene) derivative prepared via dehalogenation reaction.

1.3.4 Application of the Knoevenagel condensation to poly(arylene vinylene)s synthesis

Holmes and co-workers have reported the use of Knoevenagel condensation in the synthesis of a series of soluble cyano substituted polymers based on PAVs.[27,28] One of the advantages of the Knoevenagel condensation is that a wide range of monomer units can be used. The synthetic route and examples of polymers prepared via this method are presented in *Figure 1.5.*



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

Figure 1.5 Example of PAVs prepared via Knoevenagel condensation.

However, the reaction conditions need careful control in order to avoid side reactions such as Michael addition by various nucleophiles to the newly formed cyano vinylene linkage or direct attack on the nitrile.

A similar procedure was also applied to prepare the heteroaromatic polymer, poly(2,5-furylene vinylene), from 5-methylfuran-2-carbaldehyde.[17]

1.3.5 Application of the Heck reaction to poly(arylene vinylene)s synthesis

The coupling reaction between organic halides and vinyl derivatives in the presence of palladium catalysts, generally known as the Heck reaction, has been shown to have great potential for the synthesis of PAVs and leads to the formation of predominantly *trans* double bonds.[29] It was first utilised by Heitz *et al.* to prepare substituted poly(*p*-phenylene vinylene)s from ethylene and aryl dihalides, mainly dibromides as exemplified in *Figure 1.6.* Aromatic diiodides generally give a higher molecular weight than the corresponding dibromides.

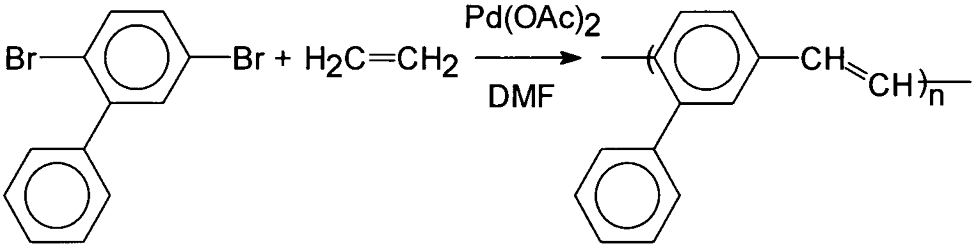


Figure 1.6 PPV derivative prepared via the Heck reaction.

In another example, a PPV based co-polymer was prepared, consisting of regularly alternating terphenylene and phenylenebisvinylene blocks see *Figure 1.7.*[10]

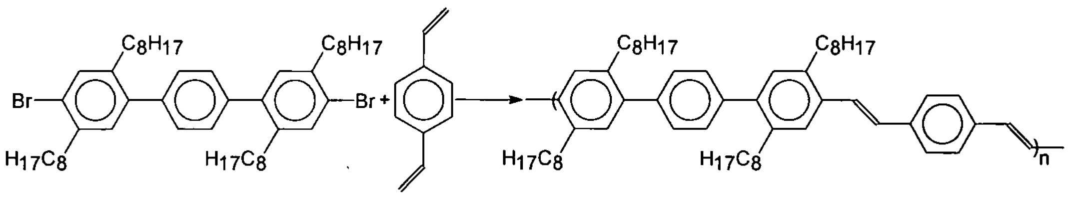
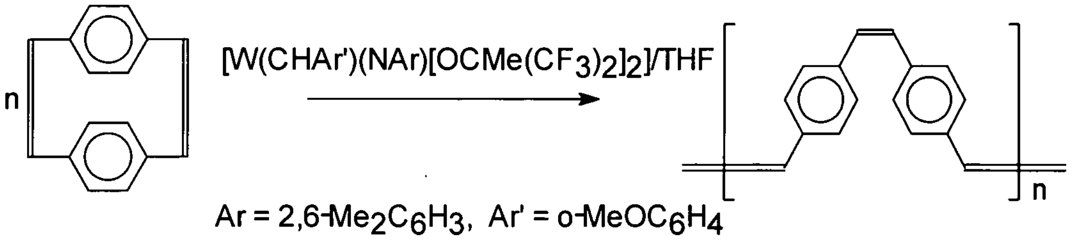


Figure 1.7 PPV based co-polymer prepared via the Heck reaction.

1.3.6 Application of ring opening metathesis polymerisation (ROMP) to synthesis of poly(arylene vinylene)s

Some very attractive reports on the preparation of PPV by ring opening metathesis polymerisation (ROMP) have appeared recently.[11] All of these new routes to PAVs are useful for the preparation of high molecular weight PAVs even though monomers which are rather difficult to make are required. Thorn-Csanyi and Hohnk have prepared PPV by ring opening metathesis polymerisation of an olefinic paracyclophane derivative using a tungsten carbene initiator as shown in *Figure 1.8*.[30]



$[W(CHAr')(NAr)[OCMe(CF_3)_2]_2]/THF$

$Ar = 2,6\text{-}Me_2C_6H_3$, $Ar' = o\text{-}MeOC_6H_4$

Figure 1.8 PPV prepared via ring opening metathesis polymerisation (ROMP).

Grubbs and co-workers have developed a new soluble precursor polymer for PPV which uses living ROMP of a bicyclooctadiene biscarboxylate derivative in the presence of a molybdenum carbene initiator, see *Figure 1.9*.[31] The precursors have narrow molecular weight distributions and free standing films of PPV are obtained by pyrolysis of the precursor film at 200°C.

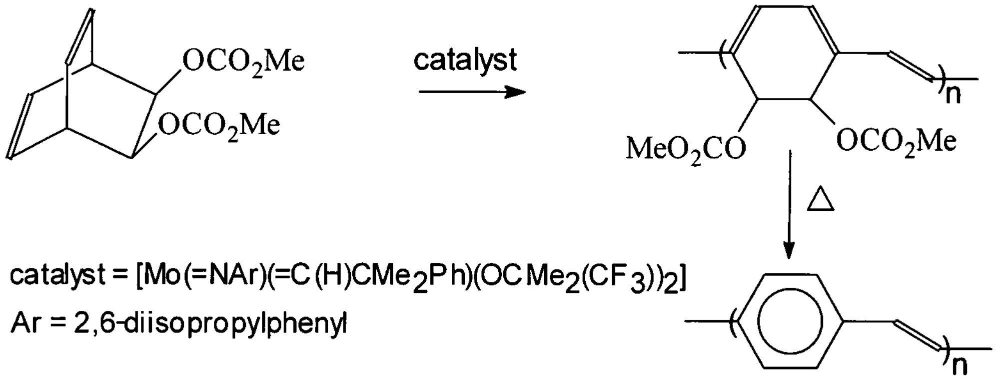


Figure 1.9 PPV prepared via a precursor obtained by living ROMP.

The potential of this route lies in the solubility of the precursor in organic solvents, the control of molecular weight and end groups, and relatively low elimination temperatures.

Another application of ROMP is in the synthesis of side chain PPVs. Monodisperse PPV oligomers are synthesised and attached to a norbornene monomer which can be polymerised by ROMP to generate a soluble graft co-polymer.[32] This method allows, of course, perfect control over the conjugation lengths of the side chain oligomers and attachment to a polynorbornene back bone renders the oligomers processable via solution methods.

1.3.7 Acyclic diene metathesis (ADMET) polymerisation route to poly(arylene vinylene)s

Acyclic diene metathesis (ADMET) polymerisation has also been used in the synthesis of PAVs. As an example, Thorn-Csanyi and co-workers reported that ADMET polymerisation has been used in the preparation of a series of soluble poly(2,5-dialkyl-*p*-phenylenevinylene)s, see *Figure 1.10*[33] In another report, ADMET polymerisation was used by Kumar and Eichinger to prepare PPV from

1,4-divinylbenzene,[11] since the polymer is insoluble and intractable it seems likely that this was a low molecular weight product.

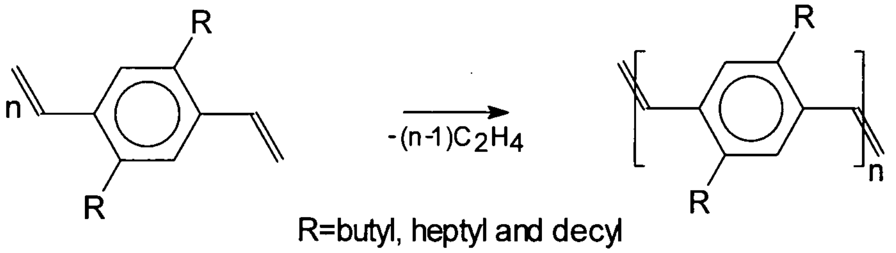


Figure 1.10 Substituted PPV prepared via ADMET polymerisation.

1.4 PAVs synthesised via transition metals catalysed polycondensation

Many of the synthetic approaches to PAVs involve condensation polymerisations. This section presents a brief review of condensation polymerisation routes to PAVs catalysed by transition metals, namely titanium, nickel and palladium.

1.4.1 Application of the McMurry reaction to poly(arylene vinylene)s synthesis

The reductive coupling of aldehydes and ketones by low-valent titanium species to form alkenes was first reported in early 1970s.[34,35] The reaction has been extensively elaborated by McMurry and co-workers and is now generally referred to as the McMurry reaction. The application of this system has been extended to the preparation of poly(arylene vinylene)s via polycondensation of diketone[36] or dialdehyde[37] monomers. Details of the McMurry reaction are reviewed in Chapter 2.

Reductive coupling of a diketone or a dialdehyde 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.[37]

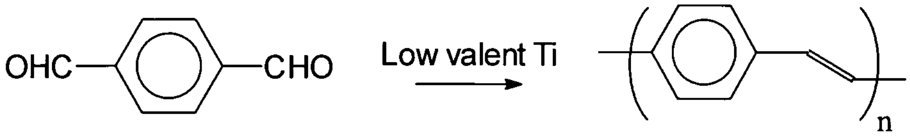


Figure 1.11 PPV synthesised via the McMurry reaction.

Cooke and Wagener repeated the experiment using low valent titanium generated from titanium trichloride and zinc and results similar to those previously reported were obtained.[38] The same reagent was also applied in the synthesis of poly(2,5-furylene vinylene) from furan-2,5-dicarboxyldehyde, see *Figure 1.12*.[39]

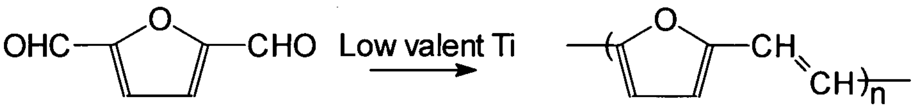


Figure 1.12 Poly(2,5-furylene vinylene) synthesised via the McMurry reaction.

Rehahn and Schluter,[11] reported the preparation of the soluble poly(2,5-dihexyl-1,4-phenylene vinylene) by coupling of the corresponding dialdehyde in the presence of an excess of a Ti reagent ($TiCl_3$/Zn/Cu) in dimethoxyethane.

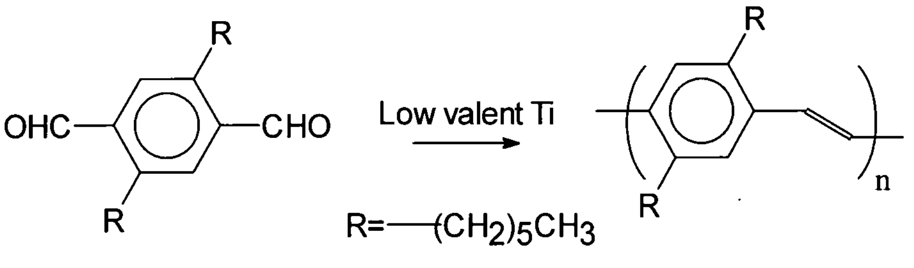


Figure 1.13 Substituted PPV synthesised via the McMurry reaction.

Low valent titanium reagent generated by the reaction of titanium trichloride and Zn dust can also be used in the polymerisation of isophthaldehyde to poly(*m*-phenylene vinylene).[40]

However, the first effective use of the McMurry reaction in the synthesis of PAVs was demonstrated by Feast and Millichamp.[36] They reported, soluble poly(4,4'-diphenylene diphenylvinylene) was obtained with a degree of polymerisation of more than 100 via reductive coupling of the corresponding diketone. This route to PAVs has been repeated by the author in order to optimise the reaction conditions. The author has also been able to establish a practical purification procedure with a view to producing well defined materials for study, particularly the incorporation of the material in light emitting diodes by workers in Professor Friend's group in the Cavendish Laboratory, Cambridge. This approach has been also extended by the author to the synthesis of other PAV polymers which will be discussed later in this thesis.

1.4.2 **Suzuki reaction route to poly(arylene vinylene)s**

In 1981, Suzuki and his co-workers first reported that benzene boronic acid could be coupled with aryl halides, catalysed by a palladium phosphine complex and in the presence of sodium carbonate.[41] This cross-coupling reaction, now generally referred to as the Suzuki reaction, turned out to be a useful method for synthesis of polymers.[42,43] Although reports of the use of the Suzuki reaction in the synthesis of substituted poly(*p*-phenylene)s appeared in 1989[44], this condensation polymerisation route has been used to prepare PAVs only very recently and up to now only a few reports have emerged in the literature.[42,43] The synthesis proceeds under mild conditions and tolerates functional groups. The polymers are structurally pure and show a degree of polymerisation of 100 and more.

Figure 1.14 presents an example of the applications of the Suzuki reaction in the synthesis of PAVs. In this example, the polymer was found to be photoluminescent, emitting in the blue region of the spectrum.[43]

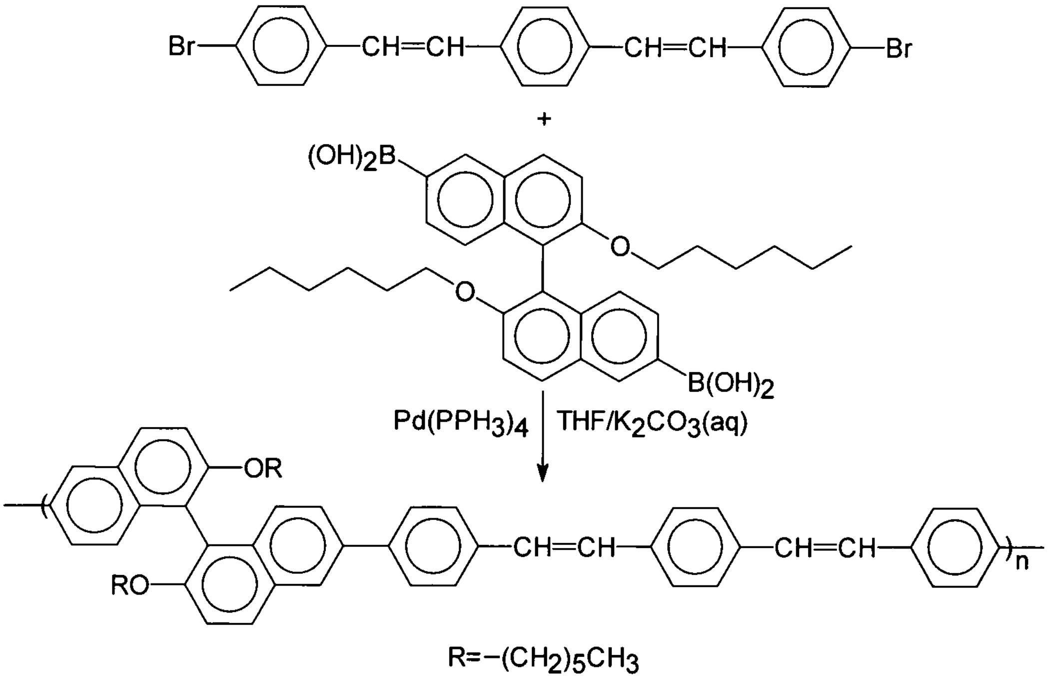


Figure 1.14 An example of a PAV synthesised via the Suzuki reaction.

In another recent example, which was published during the course of this work, the preparation of a series of PAVs, including poly(diphenylene vinylene), poly(terphenylene vinylene) and poly(pentaphenylene vinylene) has been reported.[42] Aromatic diboronic esters were used in these preparations rather than aromatic diboronic acids which are commonly used in the Suzuki reaction. The preparation of poly(terphenylene vinylene) is shown in *Figure 1.15*.[42]

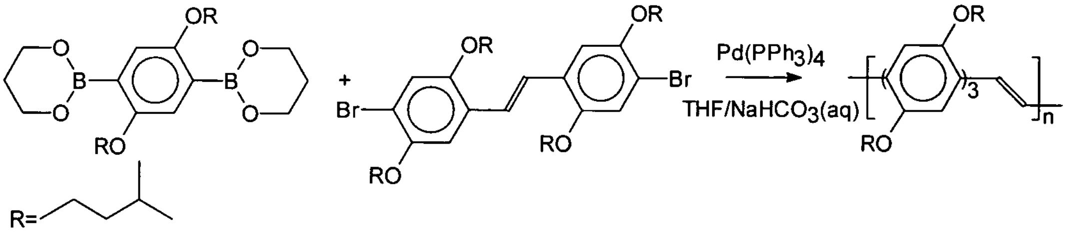


Figure 1.15 Substituted poly(terphenylene vinylene) prepared via the Suzuki reaction.

Although this route to PAVs is not widely used currently, it has been extensively applied in the synthesis of substituted poly(*p*-phenylene)s during the last ten years. This condensation reaction has been proved to be regioselective[44] and its versatility has been shown not only in the synthesis of small compounds but also in the preparation of polymers. In addition, it shows good tolerance towards a variety of functionalities including; carbonyl, ethers, carboxylic acids, imides, aldehydes, nitro and alkoxy.[45] Thus, the Suzuki reaction offers promising potential as a versatile synthetic approach to PAVs carrying functionalities, especially those associated with electron withdrawing or electron donating groups. As a preliminary step, the author has applied this route to synthesis a series of PAVs with a view to establishing an approach in which the *cis/trans* vinylene composition in the polymer chains can be controlled. This becomes possible by controlling the *cis/trans* composition of the vinylene segment incorporated in the dibromide monomers. This approach allows studies of how the *cis/trans* vinylene composition affects the properties of the resultant polymers, particularly the electrooptical properties.

1.4.3 Yamamoto reaction route to poly(arylene vinylene)s

The coupling reaction between Grignard reagents and aryl halides has been reported to be catalysed by nickel compounds as shown in *Figure 1.16*.[46]

$$\mathrm{ArMgX} + \mathrm{Ar'X} \xrightarrow{\text{Ni catalysts}} \mathrm{Ar{-}Ar'} + \mathrm{MgX_2}$$

Figure 1.16 General scheme for Ni catalysed aromatic coupling reactions.

This reaction was extended to the preparation of unsubstituted poly(*p*-phenylene)-type polymers, for the first time, by Yamamoto *et al.* (*Figure 1.17*).[47] The route was then applied by Feast *et al.*, to the synthesis of poly(*p*-phenylene)s carrying flexible side chains in the polymer repeat units, thus polymers with improved solubility were obtained (*Figure 1.18*).[48]

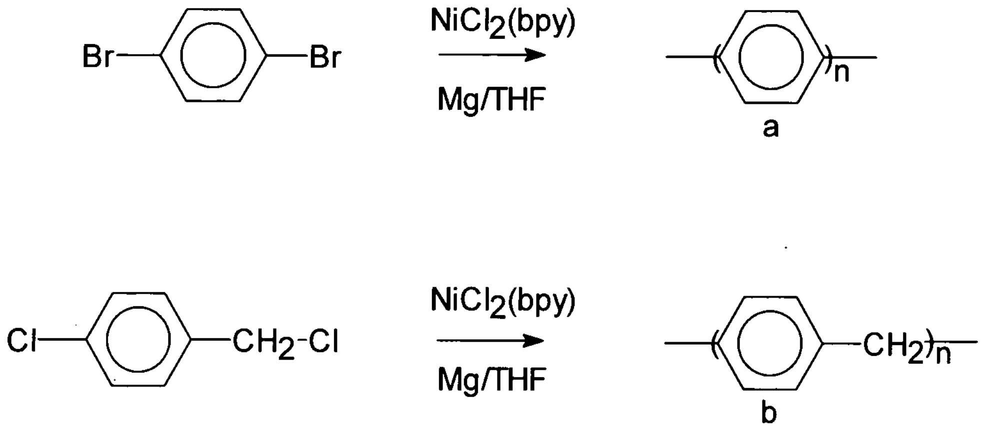


Figure 1.17 a) Poly(*p*-phenylene) and b) poly(*p*-phenylene methylene) prepared via the Yamamoto reaction.

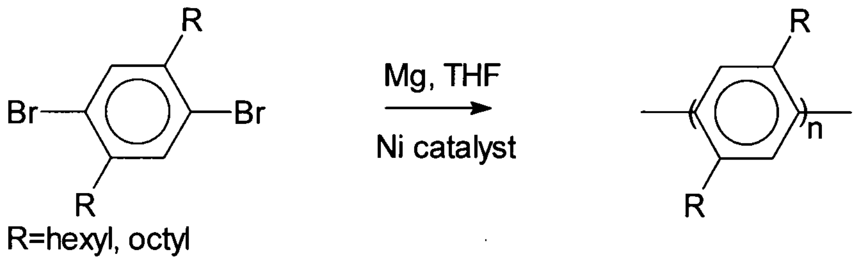


Figure 1.18 Alkyl substituted poly(*p*-phenylene)s prepared via the Yamamoto reaction.

Up to now, the application of this condensation polymerisation, commonly referred to as Yamamoto reaction, has been limited to the synthesis of poly(*p*-phenylene) and its derivatives.

However, since the Yamamoto reaction proceeds under mild conditions and tolerates a large range of substituents, including ester, keto, formyl and also alkoxy groups[29], the author sees it as a potential route to PAVs. Additionally, it offers an alternative approach to some of the PAVs prepared previously via the McMurry reaction. Thus comparison between polymers synthesised via both routes can be made. This is especially useful in terms of the effect of *cis/trans* vinylene composition on the properties of the polymers synthesised by both the McMurry and Yamamoto reactions, whereby, only the latter route offers the possibility to control the *cis/trans* vinylene composition.

1.5 Reasons for interest in poly(arylene vinylene)s

There is a strong possibility that poly(arylene vinylene) will find commercial use in a variety of display applications.[5] This arises from the novel property of electroluminescence, the emission produced when charge carriers are injected into and travel through the polymer film under the influence of an applied electric field to recombine with the formation of an electronically excited species which can decay with emission of light in the visible region.[49] It has been found that poly(*p*-phenylene vinylene), the simplest member of poly(arylene vinylene)s, is electroluminescent and can be incorporated in light emitting diodes (LEDs) as an emissive layer.[3]

Commercial products available so far are based on inorganic semiconductor light emitting diodes, fluorescent ion doped inorganic semiconductor thin film diodes and inorganic semiconductor powder diodes, but there are drawbacks with all three systems.[5] Light emitting diodes based on inorganic semiconductors find widespread use in many electronic machines, but are limited to small area devices. Other problems include difficulties in finding materials to form good p-n junction with high radiative recombination yields and the colours are limited to the green and longer wavelengths. The second system, the fluorescent ion doped inorganic semiconductor requires high fields to accelerate electrons or holes to ionise the fluorescent ion centres, which increases the cost of drive circuitry for displays. The problems associated with inorganic semiconductor powder diodes include high voltage a.c. drive, poor stability and little colour tunability.

Electroluminescent poly(arylene vinylene)s with relatively impressive emission efficiency, brightness and uniformity, exhibit advantages over their inorganic counterparts in LED applications.[50] They offer potential in large flat-panel display technologies since they are soluble either as the final material or as a precursor, thus can be fabricated over large areas using solution processing techniques.[51] The solubility of poly(arylene vinylene)s also brings the possibility to construct an elecroluminescent polymer film on a flexible substrate to form LEDs in a variety of unusual shapes. In fact, Heeger and co-workers have developed such LEDs by using poly(ethylene terephthalate) as the substrate.[52]

The colour of the emission can also be tuned.[53] A variety of colours has already been achieved, including the three colours (red, green and blue) required for full colour displays. Some example are presented in *Figure 1.19.*

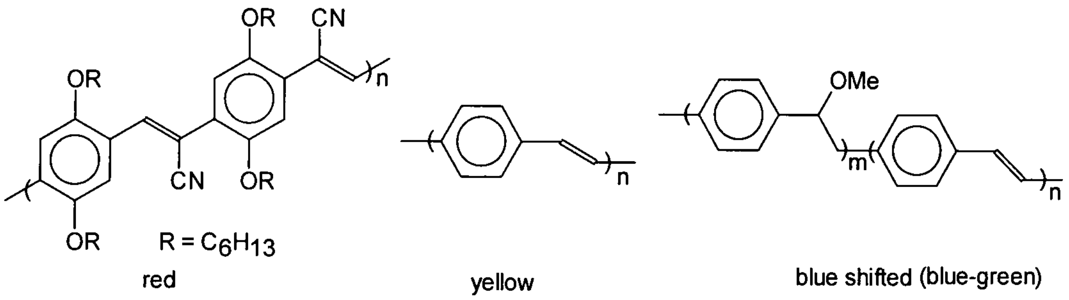


Figure 1.19 Examples of electroluminescence colours.

In addition to this they show superior chemical stability compared to their inorganic counterparts against moisture and oxygen at room temperature.[54]

1.6 Aims of the project

The aim of the project was the synthesis and characterisation of a series of poly(arylene vinylene)s of high molecular weight, initially via the McMurry coupling outlined by Feast and Millichamp.[36] Previous reports had shown that the reaction is feasible but yields and molecular weights were somewhat erratic. In this study, the aim was to explore the experimental parameters which control the outcome of the reaction and expand the number and structural varieties of polymers accessible. The properties of the characterised products were to be explored particularly with a view to their possible exploitation in organic polymer light emitting diodes. This part of the programme involved collaboration with Professor Friend's group in Cambridge.

Materials for use in electooptics devices should ideally be well defined structurally and of high purity. In the case of poly(arylene vinylene)s prepared via the McMurry reaction, the frequency and distribution of *cis* and *trans* vinylenes along the polymer backbone was not known. Thus, it was also intended to investigate other routes to poly(arylene vinylene)s which allowed control over the distribution of *cis* and *trans* vinylenes along the polymer backbone in an effort to obtain structurally well defined polymers. In this way it would be possible to study the effects of the polymer's structure on its electrooptical properties.

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Chapter 2

The McMurry approach to poly(arylene vinylene)s

2.1 Introduction

Two classes of reductive carbonyl coupling reactions have been observed.[1] The reduction of carbonyls to pinacols is a well-established reaction, particularly for aromatic ketones. The use of carbonyl coupling in the synthesis of olefins is much more recent, the first report of coupling two carbonyls to give an olefin being produced by Schreibmann who obtained tetraphenylethene, *trans*-αα'-dimethylstilbene and *trans*-stilbene from the corresponding carbonyl compounds using aluminium amalgam in dichloromethane.[2] A large number and variety of low-valent titanium reagents has been applied to olefin synthesis via carbonyl coupling since their initial use in 1973.[3] These systems have been used for the synthesis of a variety of alkenes and extended to the preparation of poly(arylene vinylene)s via polycondensation of diketone[4] or dialdehyde monomers.[5]

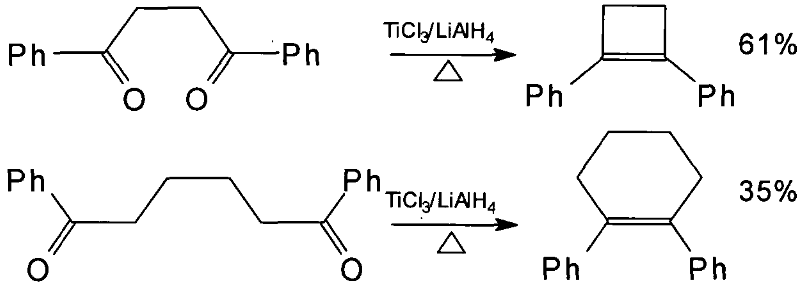
The first part of this chapter presents a review of the McMurry reaction, including a discussion of the reactive species involved, the reaction mechanism and the scope and limitations of the reaction. The bulk of the chapter is concerned with the author's work on the exploitation of the McMurry reaction in the synthesis of a series of poly(arylene vinylene)s. The optimisation of the reaction condition with a view to producing high molecular weight polymers as well as polymer purification in order to obtain clean samples with relatively narrow molecular weight distributions is discussed in detail.

2.2 The McMurry Reaction

The reductive coupling of aldehydes and ketones by low-valent titanium species was first reported independently between 1973 and 1974 by Tyrlik *et al.*[6], Mukaiyama *et al.*[3] and McMurry *et al.*[7] The latter used titanium trichloride and lithium aluminium hydride to generate the low-valent titanium species, this method has been further elaborated by McMurry and co-workers and is now generally referred to as "The McMurry reaction".[8]

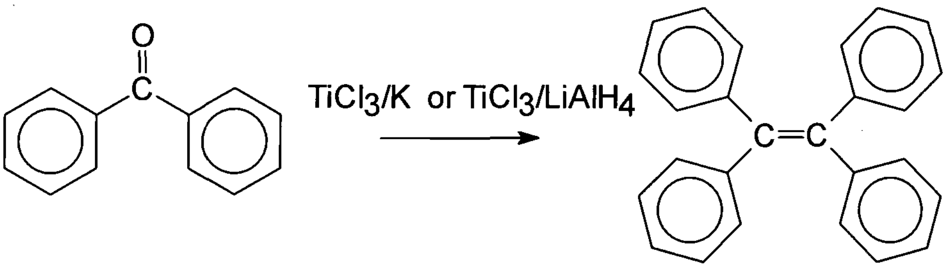
2.2.1 Low-valent titanium reagents

The ability to couple all manner of ketones and aldehydes to give olefins in high yield is unique to titanium.[1] The application of other metals (Al, Si, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Sn, W, Hf, and Ta) in this reaction has been examined and deoxygenation was observed only with tungsten, and then only in low yield.[9] The original low-valent titanium reagent system was prepared by reduction of $TiCl_3$ with $LiAlH_4$.[7] McMurry reported that addition of a THF solution of benzophenone to a slurry of $TiCl_3$ and $LiAlH_4$ in THF gave tetraphenylethene in 95% isolated yield.[7] The same reagent system was used by Baumstark *et al.* who reported that 1,2-diphenylcyclobutene and 1,2-diphenylcyclohexene were obtained from 1,2-dibenzoylethane and 1,4-dibenzoylbutane respectively (*Scheme 2.1*).[10]



Scheme 2.1 The synthesis of 1,2-diphenylcyclobutene (top) and 1,2-diphenylcyclohexene (bottom) via McMurry reaction.

On the whole the $TiCl_3/LiAlH_4$ system was found to give reasonably reproducible reductions. However, one drawback of the $TiCl_3/LiAlH_4$ system was that it was said to give "capricious results" sometimes, apparently depending on the quality of the reagents used.[11] Owing to this minor problem associated with reagent irreproducibility, other preparations of low-valent titanium were examined in an attempt to improve on the original procedure. In 1976, it was reported that a highly active Ti(0) reagent could be prepared by reduction of $TiCl_3$ with three equivalent of potassium in THF[12], and soon thereafter $TiCl_3$/Li and $TiCl_3$/Zn-Cu systems were introduced.[13] However, the $TiCl_3$/K system has a tendency to give poorer yields compared to the $TiCl_3/LiAlH_4$. As an example, tetraphenylethene (*Scheme 2.2*), was isolated in 95% and 80% yields when benzophenone was treated with $TiCl_3/LiAlH_4$[7] and $TiCl_3$/K[12] respectively.



Scheme 2.2 The application of the McMurry reaction in the synthesis of tetraphenylethene from benzophenone.

Improved reproducibility has been claimed for the reagent systems $TiCl_4$/Zn/pyridine and $TiCl_3$/K/graphite. McMurry and co-workers reported that treatment of $TiCl_3$ with refluxing dimethoxyethane (DME) prior to reaction with a reducing agent can give excellent yields of coupled products.[9] Sodium, magnesium and zinc have also been applied as reducing agents for titanium trichloride.[8] Low-valent titanium reagents could also be prepared from titanium tetrachloride with either zinc, a zinc-copper couple, a magnesium/mercury amalgam, an aluminium/aluminium trichloride mixture or lithium aluminium hydride as the reducing agents.[8] Despite all these investigations the combination of $TiCl_3$ and $LiAlH_4$ is still the most convenient, effective and widely used reagent for McMurry coupling.[11]

The combination of reducing agent and solvent turned out to be critical in producing active coupling species. Dams *et al.* reported that Na and Mg only worked in THF, while Li, K and $LiAlH_4$ functioned in glyme, diglyme and diethyl ether as well as THF.[14] Of all solvents tested, THF performed best in all instances.[14]

Temperature influences the coupling reactions as well; lower temperatures result in the formation of pinacol only, whilst elevated temperatures, usually the reflux temperature of the solvents, are used in the synthesis of olefins.[14]

2.2.2 **Mechanism**

The detailed mechanism of this reductive coupling process is still a matter of discussion. However, it is generally agreed that the actual process proceeds in two steps, namely :-

1. reductive dimerisation of the starting ketone or aldehyde to form the carbon-carbon bond, followed by
2. deoxygenation of the 1,2 diolate intermediate to yield the alkene.

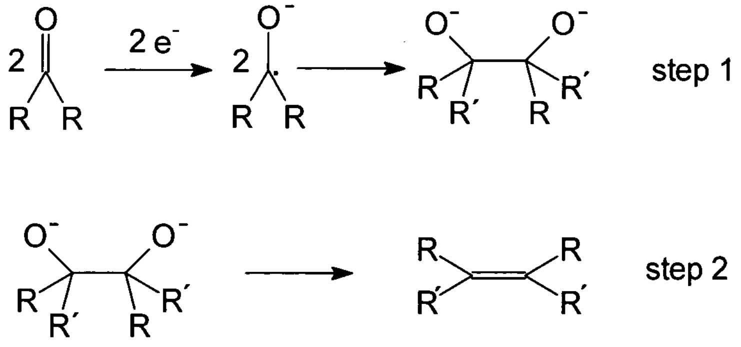


Figure 2.1 General steps involved in the McMurry reaction mechanism.

It is known that reducing agents are capable of donating an electron to a ketone or aldehyde carbonyl group, yielding a radical anion that dimerises. The possibility of isolating intermediate pinacols in high yield, in the presence of protonating agents, supports this proposal for the first step in the reaction. Initially McMurry suggested that the five membered ring structure, shown below, was the intermediate involved.[7]

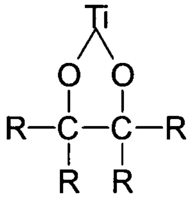


Figure 2.2 The five membered ring intermediate suggested by McMurry.[7]

Later he found that cyclic 1,2-diols gave approximately equal yields of alkenes from both the *cis* and *trans* isomers at the same rate whereas the rate would be expected to be different if a five membered ring was involved.[9,11] As a result of this observation he proposed the mechanism shown in *Figure 2.3*. In this proposal the pincol formed two bonds to active titanium **particles**, such titanium particles as components of the mixture were identified by scanning electron microscopy.

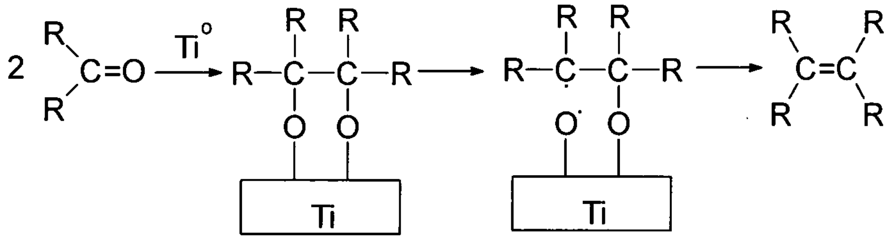


Figure 2.3 The mechanism of low valent titanium catalysed carbonyl coupling as proposed by McMurry.[9,11]

A more detailed mechanism has been proposed by Dams *et al.* and they provided support for McMurry's suggestion by ESR studies.[14] Dams *et al.* noted that the active species, [M], according to the following equations (2.1 and 2.2), was ESR inactive as would be expected for zero valent titanium.

$$TiCl_3 + \text{reducing agent} + \text{solvent} \rightarrow [M] \qquad (2.1)$$

$$[M] + \text{ketone} \rightarrow [M,O] + \text{coupling products} \qquad (2.2)$$

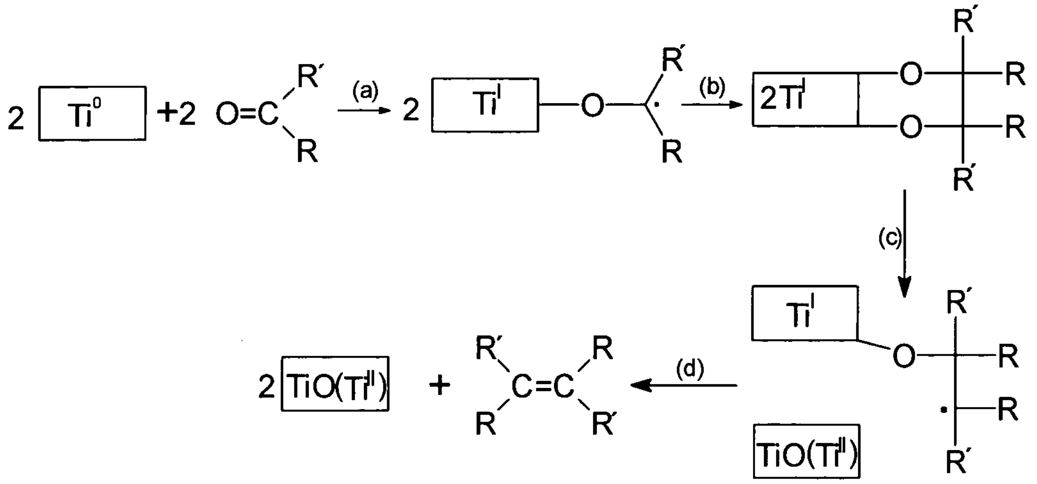


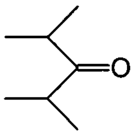
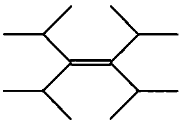
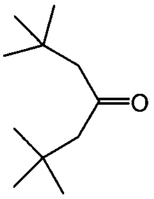
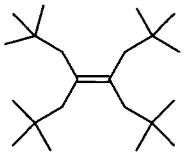
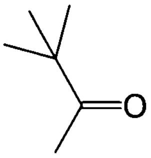
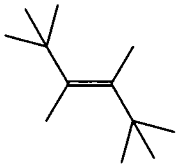
Figure 2.4 The mechanism elaborated by Dam *et al.* for low valent titanium catalysed carbonyl coupling reaction.

The proposed sequence of events is depicted mechanistically in the above figure. In the initial step (a), titanium donated an electron to the carbonyl group generating a radical anion, which has been detected by ESR spectroscopy. The ketyl radical then dimerised forming bound pinacol (b). Deoxygenation of the pinacol occurred readily, step (c) and (d), leading to an alkene, due to the high affinity of titanium for oxygen. It was postulated that all of these reaction occurred on the surface of a titanium particle.

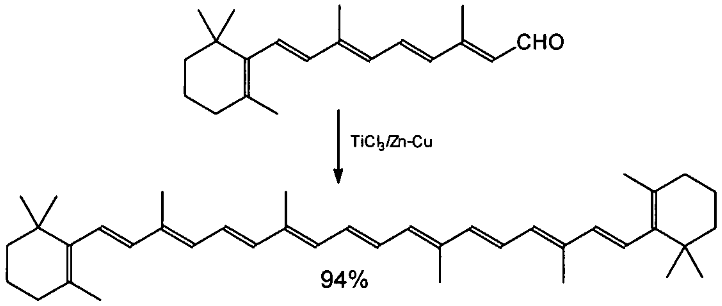
2.2.3 **Scope and limitations**

Preparation of strained olefins was one of the earliest uses of the McMurry carbonyl coupling reaction.[9] Several aliphatic olefins (*Table 2.1*) have been produced by this method. Lenoir reported sterically crowded and uncrowded aromatic ketones could be coupled yielding the corresponding olefins.[8] For instance, *tert*-butyl phenyl ketone yielded 42% the corresponding stilbene. Diaromatic ketones, for example, benzophenone, fluoroenone and 1,1′-dinaphthyl ketone could also be coupled to give olefins in excellent yield.

Table 2.1. Strained aliphatic olefins prepared via McMurry reaction.

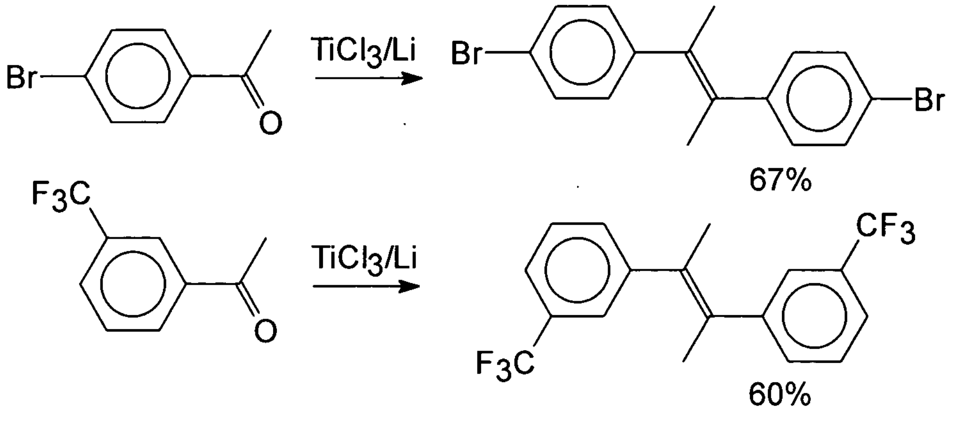
Starting Material	Product	Reagent	Yield(%)
		$TiCl_3$/K/THF $TiCl_3$/$LiAlH_4$/THF $TiCl_3$/Zn-Cu/DME	37 12 94
		$TiCl_3$/$LiAlH_4$/THF	40
		$TiCl_4$/Zn/THF $TiCl_4$/$LiAlH_4$/THF	68 70

Alkenes are inert to low-valent titanium and a large number of successful coupling reactions have been carried out in the presence of carbon-carbon double bonds.[7] β-Carotene, for example, can be prepared in high yield from retinal (*Scheme 2.3*).



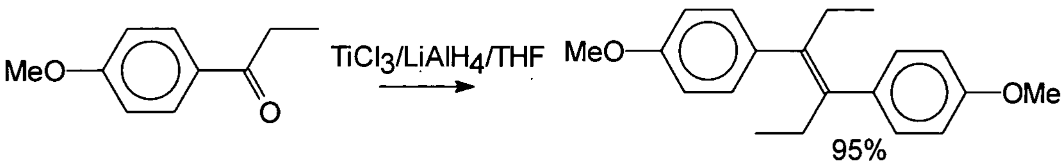
Scheme 2.3 The synthesis of β-Carotene via McMurry reaction.

Organohalides with the exception of 1,2-dihalides could also be coupled using low-valent titanium reagents (*Scheme 2.4*).[9]



Scheme 2.4 The McMurry coupling of carbonyl compounds carrying halogen functionality.

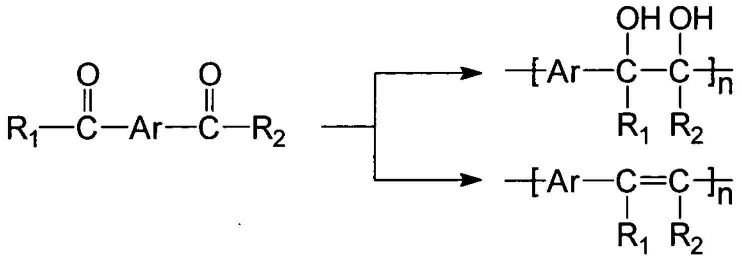
Methoxy substituted aromatic ketones are also susceptible to carbonyl coupling as indicated below, and the methoxy donors do not inhibit the reaction.[8]



Scheme 2.5 The McMurry coupling reaction of a methoxy substituted aromatic ketone.

Carbonyl coupling reactions have also been used to synthesis molecules with unusual structures and natural products,[9] indeed the reaction has become a standard method in synthetic organic chemistry.

The McMurry reaction has potential as the coupling reaction in condensation polymerisation to give high molecular weight polymers. As mentioned in Chapter 1, this method has already been extended to the synthesis of poly(arylene vinylene)s. Since Mukaiyama and co-workers[3] reported that only aromatic aldehydes and ketones could be coupled in high yield, only monomers which possessed aromatic moieties have been studied so far.[4,5] In principle, both polyenes and polypinacols could be obtained via this route. *Scheme 2.6* outlines the possible outcomes of reductive coupling of aromatic diketones.



Scheme 2.6 The possible outcomes of McMurry coupling of aromatic diketones.

2.3 The synthesis of aromatic diketone monomers

Aromatic diketone monomers were prepared using the Friedel-Crafts reaction which is of great value in organic syntheses and has been the subject of extensive documentation.[16] The synthesis involves reaction between an acid halide and an aromatic substrate in the presence of a catalyst. The reaction mechanism is summarised in *Figure 2.5,* for a metal halide catalyst (MX_n), an acid halide component RCOY and benzene as the substrate.

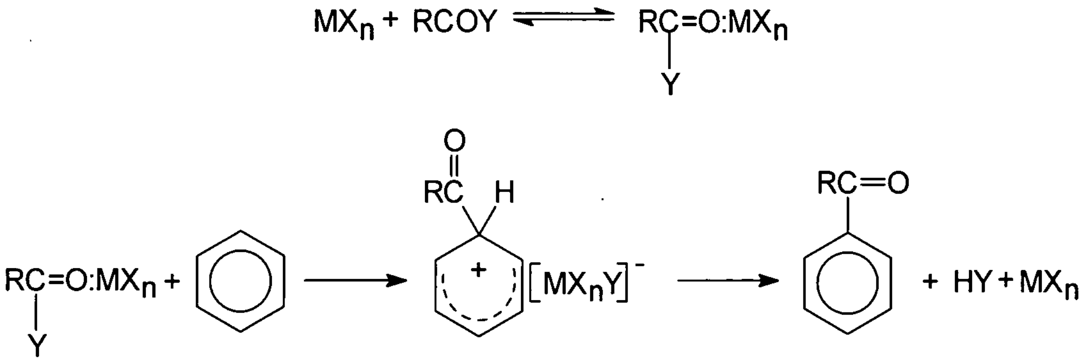


Figure 2.5 The mechanism of the Friedel-Crafts acylation of benzene as substrate.

The most popular choice of catalyst has been aluminium chloride because it is cheap and possess high catalytic activity. Other metal halides used include $AlBr_3$, $FeCl_3$, $SbCl_3$, $SbCl_5$, $SnCl_4$, $SbBr_3$, $TiCl_4$ and $ZrCl_4$. Rates of benzoylation have been found to follow the sequence below:

$$SbCl_5 > FeCl_3 > AlCl_3 > SnCl_4 > SbCl_3$$

In practice the optimum number of moles of $AlCl_3$ to acyl component has been found to be 1.1:1 for acid chlorides.[16] A deficiency of catalyst tends to lower the overall yield because of incomplete utilisation of the acid halide component. In most cases excess catalyst gives appreciable amounts of tar, making ketone purification extremely difficult.

The reaction can be performed with neat reactants or in the presence of a suitable polar solvent. Frequently nitrobenzene or carbon disulfide are used;

however, solvents of intermediate polarity and low susceptibility to electrophilic attack, such as dichloromethane, can also be used.

Usually the deactivating effect of an araroyl group on a benzene ring limits the reaction to monosubstitution. A second group may, however, be introduced if this deactivation is offset by substitution with powerfully electron releasing hydroxyl or alkoxyl groups or if high temperatures and prolonged reaction times are used.

2.4 Results and Discussion

2.4.1 Aromatic diketone monomers

2.4.1.1 *4,4′-Dibenzoylbiphenyl*

The synthesis procedure outlined by Andrews[18] was followed; namely, Friedel-Crafts benzoylation of biphenyl. Reported reaction periods for this benzoylation varied in the range four to twenty hours. However, for this work, the reaction was terminated after heating the reaction mixture at about 80°C for four hours, since at this time gas evolution appeared to have stopped. The dark red viscous liquid reaction mixture was poured into acidified ice-water and immediately gave a white precipitate. This was washed with aqueous base and water, dried and recrystallised from toluene at least five times to yield white crystals of 4,4′-dibenzoylbiphenyl. (*Figure 2.6*)

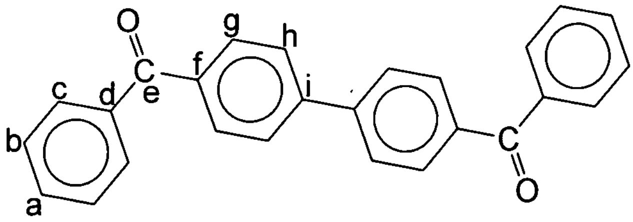


Figure 2.6 4,4′-Dibenzoylbiphenyl.

In this work a more than four-fold increase in yield was observed in comparison to that reported by Millichamp.[17] The melting point of the product was found to be in agreement with the values reported earlier[17,18], and satisfactory elemental analysis was obtained. The FTIR spectrum is presented in *Appendix 1.1.1*. A strong signal at 1646cm^{-1} is attributed to the **C=O** stretching, characteristic of conjugated ketone with benzenoid units. Aryl hydrogen stretching was observed at 3050cm^{-1}. There was also a peak at 1603cm^{-1} which is characteristic of an aryl carbon skeleton breathing vibration mode.

The ^{13}C and ^{1}H nmr assignments are summarised in *Table 2.1* and *Table 2.2* respectively, they follow straightforwardly from literature data and are consistent with the assigned structure (*Figure 2.6*).[21] ^{1}H and ^{13}C Nmr spectra are presented in *Appendix 1.2.1* and *Appendix 1.3.1* respectively.

Table 2.1 Summary of ^{13}C nmr assignment of 4,4′-dibenzoylbiphenyl.

chemical shift (ppm)	carbon assignment
127.1	b,c,g,h
128.2	b,c,g,h
129.9	b,c,g,h
130.7	b,c,g,h
132.4	a
136.9	d,f
137.4	d,f
143.7	i
196.1	e

Table 2.2 Summary of ^{1}H nmr assignment of 4,4′-dibenzoylbiphenyl.

chemical shift (ppm)	multiplicity (apparent)	H integration	H assignment
7.52	dd	4	b
7.62	t	2	a
7.77	d	4	h
7.85	d	4	c
7.94	d	4	g

While the spectra are deceptively simple they are really complex ABB'CC' and AA'BB' systems and under expansion the small peaks of these systems could be detected. Full analysis was deemed to be unnecessary and so no coupling constants are quoted.

2.4.1.2 *1,3-Dibenzoylbenzene*

The reaction procedure described by Millichamp[17] was followed, namely, Friedel-Crafts benzoylation of benzene with isophthaloyldichloride. The recovered crude product was a pale yellow solid which was recrystallised repeatedly from cyclohexane to give colourless crystals of pure 1,3-dibenzoylbenzene (*Figure 2.7*). The reaction yield obtained represented a more than three-fold increase compared to the figure reported earlier.[17]

In the FTIR spectrum (*Appendix 1.1.2*), the peak at 1657cm^{-1} is assigned to the conjugated ketone stretching absorption, it occurs at slightly higher frequency than that of 4,4'-dibenzoylbiphenyl indicating a stronger bond in this case consistent with a less conjugated system. The aryl carbon skeleton breathing mode can be seen at 1597cm^{-1}.

In the ^{1}H nmr spectrum (*Appendix 1.1.2*) the six proton peaks expected in the aromatic region were reduced to five resolved peaks, the multiplet peak centred at 7.62 ppm arises from overlap of the two pseudo triplets due to H_a and H_i. The ^{13}C nmr spectrum (*Appendix 1.3.2*) shows the number of peaks expected. Summaries of ^{1}H and ^{13}C nmr assignments are presented in *Table 2.3* and *Table 2.4* respectively.

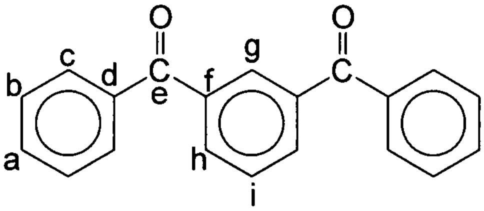


Figure 2.7 1,3-Dibenzoylbenzene.

Table 2.3 Summary of ^{1}H nmr assignment of 1,3-dibenzoylbenzene.

chemical shift (ppm)	multiplicity (apparent)	H integration	H assignment
7.50	dd	4	b
7.62	m	3	a,i
7.83	d	4	c
8.03	d	2	h
8.19	s	1	g

Table 2.4 Summary of ^{13}C nmr assignment of 1,3-dibenzoylbenzene.

chemical shift (ppm)	C assignment
195.8	e
137.8	d,f
136.9	d,f
133.5	g,h,i
132.9	g,h,i
131.2	g,h,i
130.1	b,c
128.5	a
128.5	b,c

2.4.1.3 *1,3-Dimesitoylbenzene*

The synthesis was analogous to that of 1,3-dibenzoylbenzene except that mesitylene replaced benzene.[18] The product was characterised by melting point, elemental analysis, FTIR and Mass Spectrometry (*Appendix 1.4.3*). Andrews[18] reported that the yield of the synthesis of this diketone was only about 13%, however, in this work yields as high as 89% were obtained. It was observed that the melting point of the product was slightly higher than the value reported earlier.[18]

In the FTIR spectrum (*Appendix 1.1.3*), a strong peak can be seen at 1680cm^{-1} which can be assigned to the conjugated ketone stretching absorption. The frequency of the carbonyl absorption increases in the sequence 4,4'-dibenzoylbiphenyl, 1,3-dibenzoylbenzene and 1,3-dimesitoylbenzene confirming the decreasing conjugation, in the present case indicating that the *ortho* methyl groups inhibit the carbonyl and mesityl units obtaining the planarity required for conjugation. Another strong peak is observed at 1608cm^{-1}, again this peak can be attributed to the aryl carbon skeleton breathing vibration mode. There are also two broad multiple peaks centred at 2917cm^{-1} and 3100cm^{-1} which are attributed to the methyl hydrogen (Csp^3-H) and aryl hydrogen (Csp^2-H) stretching modes respectively.

In the ^{1}H nmr spectrum (*Appendix 1.2.3*), four signals in aromatic region and two signals in up field region can be seen as expected for the diketone illustrated in *Figure 2.8*. The ^{13}C nmr spectrum (*Appendix 1.3.3*) also shows the expected number of peaks and is consistent with the assigned structure (*Figure 2.8*). *Table 2.5* and *Table 2.6* present the summaries of the ^{1}H and ^{13}C nmr assignments, respectively.

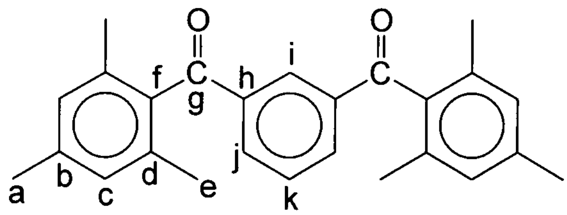


Figure 2.8 1,3-Dimesitoylbenzene.

Table 2.5 Summary of ^{1}H nmr assignment of 1,3-dimesitoylbenzene.

chemical shift (ppm)	multiplicity (apparent)	H integration	H assignment
2.06	s	12	e
2.33	s	6	a
6.89	s	4	c
7.52	t	1	k
7.96	d	2	j
8.23	s	1	i

Table 2.6 Summary of ^{13}C nmr assignment of 1,3-dimesitoylbenzene.

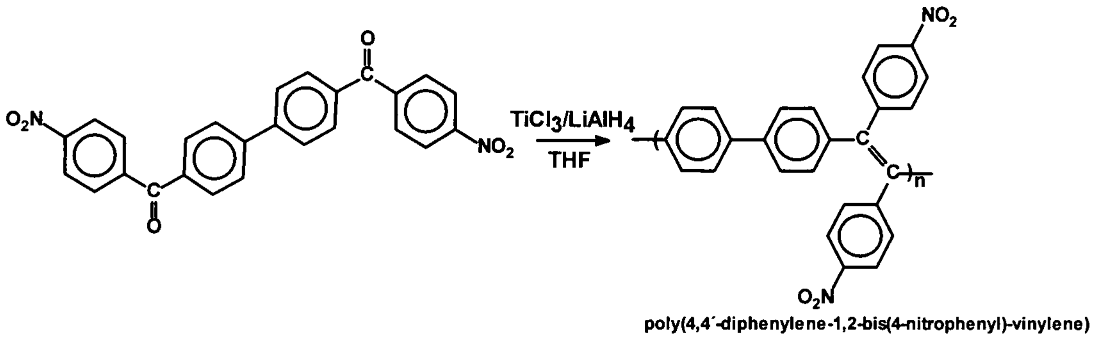
chemical shift (ppm)	C assignment
19.3	e
21.0	a
128.4	c
129.3	i,j,k
129.7	i,j,k
133.9	b,i,j,k
134.0	b,i,j,k
136.0	d
137.9	f,h
138.8	f,h
199.8	g

2.4.1.4 *4,4′-Di(4-nitrobenzoyl)biphenyl*

The polymer represented in *Scheme 2.7* was the ultimate aim of this piece of work. Introduction of nitro phenyl unit into arylene vinylene polymers based on the idea that varying the pendant groups may alter the energy gap as well as solubility of the polymer.[19] Nitro groups would, of course, need to be protected during the

McMurry coupling and in the end these monomers were dropped from the polymerisation studies. These results are presented for the sake of completion and in case future workers might find them useful since nitro groups can be convenient precursors of amines and related functionalities.

Initial attempts to synthesise the required monomer using Friedel-Crafts nitrobenzoylation of biphenyl were run using $AlCl_3$ as the catalyst. The product, recovered in 69% yield after chromatography, was not the expected product. Spectroscopic analyses (FTIR, *Appendix 1.1.4*, ^1H nmr, *Appendix 1.2.4*, ^{13}C nmr, *Appendix 1.3.4*, and MS *Appendix, 1.1.4*) showed that the compound produced was 4-nitrobenzoylbiphenyl (*Figure 2.9*). This is possibly due to deactivation towards disubstitution in 4-nitrobenzoylbiphenyl.[20]



Scheme 2.7 The McMurry approach to the targeted poly(arylene vinylene).

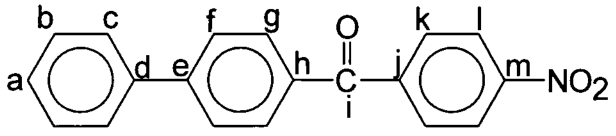


Figure 2.9 4-Nitrobenzoylbiphenyl.

In the IR spectrum, the peak at 1649cm^{-1} is assigned to the conjugated ketone carbonyl stretching absorption and the peaks at 1519cm^{-1} and 1353cm^{-1} are attributed to the symmetric and asymmetric stretching modes of the nitro group respectively. There is also a peak at 1600cm^{-1} which can be attributed to the aromatic ring vibration mode. The ^{13}C and ^{1}H nmr assignments are summarised in *Table 2.7* and *Table 2.8* respectively, they follow straightforwardly from literature data and are consistent with the assigned structure (*Figure 2.9*).[21]

Table 2.7 Summary of ^{13}C nmr assignment of 4-nitrobenzoylbiphenyl.

chemical shifts (ppm)	carbon assignment
194.3	i
149.7	m
146.2	h,j
143.0	h,j
139.5	d,e
134.8	d,e
130.7	k,l
130.6	k,l
129.0	b,c,f,g
128.5	a
127.2	b,c,f,g
127.2	b,c,f,g
123.5	b,c,f,g

Table 2.8 Summary of ^{1}H-nmr assignment of 4-nitrobenzoylbiphenyl.

chemical shift (ppm)	multiplicity (apparent)	H integration	H assignment
8.36	d	2	l
7.97	d	2	k
7.89	d	2	g
7.74	d	2	f
7.65	d	2	c
7.48	dd	2	b
7.42	t	1	a

An attempt to react 4-nitrobenzoylbiphenyl with fresh 4-nitrobenzoylchloride and $AlCl_3$ was carried out but only the 4-nitrobenzoylbiphenyl was recovered.

Ferric chloride, which is expected to form a weaker complex with the primary product, was examined as an alternative catalyst, in this experiment 1,2-dichloroethane was used as the solvent.[20] A creamy crystalline product was recovered after recrystallisation from toluene of the crude orange product. Spectroscopic analyses of this compound, including FTIR (*Appendix 1.1.5*), ^{1}H nmr (*Appendix 1.2.5*), ^{13}C nmr (*Appendix 1.3.5*), and MS (*Appendix 1.4.5*) showed that the recovered product is the desired compound, 4,4′-di(4-nitrobenzoyl)biphenyl. The ^{1}H and ^{13}C nmr assignments are summarised in *Table 2.9* and *Table 2.10* respectively, they follow straightforwardly from literature data and are consistent with the structure shown in *Figure 2.10*.[21]

Table 2.9 Summary of ^{1}H nmr assignment of 4,4'-di(4-nitrobenzoyl)biphenyl.

chemical shift (ppm)	multiplicity (apparent)	H integration	H assignment
8.38	d	2	b
7.99	d	2	c
7.95	d	2	g
7.82	d	2	h

Table 2.10 Summary of ^{13}C nmr assignment of 4,4'-di(4-nitrobenzoyl)biphenyl.

chemical shift (ppm)	C assignment
194.1	e
149.8	a
144.3	d,f
142.6	d,f
135.8	i
130.7	b,c
130.6	b,c
127.5	g
123.5	h

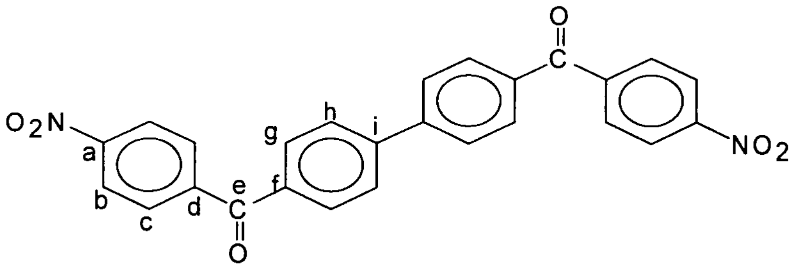


Figure 2.10 4,4′-Di(4-nitrobenzoyl)biphenyl.

2.4.1.5 *4,4′-Bis(pentafluorobenzoyl)biphenyl*

4,4′-Bis(pentafluorobenzoyl)biphenyl was obtained by Friedel-Crafts pentafluorobenzoylation of biphenyl, it was a new compound and its structure (*Figure 2.11*) was confirmed by elemental and spectroscopic analyses.

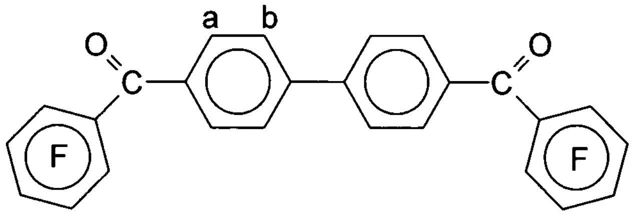


Figure 2.11 4,4′-Bis(pentafluorobenzoyl)biphenyl.

In the FTIR spectrum (*Appendix 1.1.6*), the peak corresponding to conjugated ketone carbonyl stretching can be seen at 1655cm^{-1}, the slight increase in the stretching frequency, compared to the non-fluorinated analogue, being consistent with a slight increase in bond strengths consequent on fluorination. The peak at 1604cm^{-1} can be assigned to the aryl carbon skeleton vibration mode. The ^{1}H nmr spectrum (*Appendix 1.2.6*) showed two proton peaks in aromatic region as expected, centred at 7.97 ppm and 7.79 ppm respectively. The ^{1}H nmr assignment is summarised in *Table 2.11* and is consistent with the assigned structure (*Figure 2.11*). The mass spectrum (*Appendix 1.4.6*) showed the expected molecular ion.

Table 2.11 Summary of ^{1}H nmr assignment of 4,4′-bis(pentafluorobenzoyl)biphenyl.

chemical shift (ppm)	multiplicity (apparent)	H integration	H assignment
7.97	d	2	a
7.79	d	2	b

2.4.1.6 *Attempted synthesis of 3-pentafluorobenzoylbenzophenone*

In order to vary the pendant groups on the polymer chain, an attempt to synthesise 3-pentafluorobenzoylbenzophenone, the diketone represented in *Figure 2.12,* was also carried out using pentafluorobenzoylchloride and benzophenone as starting materials. Only starting material could be recovered in all of several attempts.

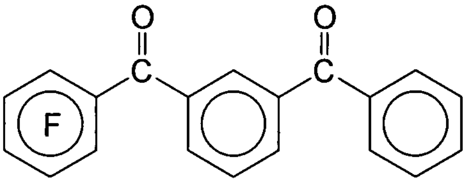


Figure 2.12 3-Pentafluorobenzoylbenzophenone.

2.4.1.7 *Attempted synthesis of 1,3-bis(pentafluorobenzoyl)benzene*

In an attempt to prepare 1,3-bis(pentafluorobenzoyl)benzene, pentafluorobenzoylchloride and benzene were used. Reactions were carried out using both $AlCl_3$ and $FeCl_3$ as the catalysts. However, in both cases the only recovered compound was pentafluorobenzoylbenzene (*Figure 2.13*), identified by ^{1}H nmr and mass spectroscopy.

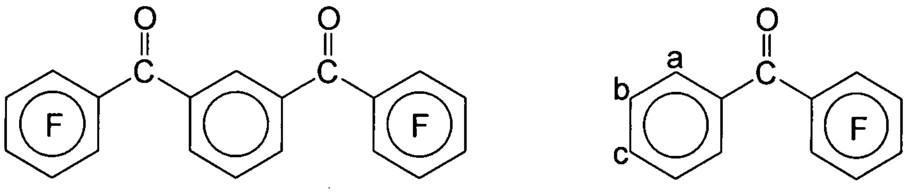


Figure 2.13 1,3-Bis(pentafluorobenzoyl)benzene (left) and pentafluorobenzoylbenzene (right).

The ^{1}H nmr assignments are summarised in *Table 2.12* and are consistent with the structure shown in *Figure 2.13*. The full ^{1}H nmr spectrum is presented in *Appendix 1.2.5*.

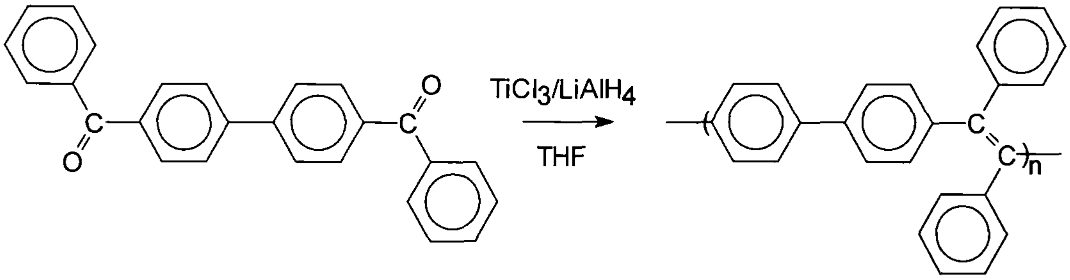
Table 2.12 Summary of ^{1}H nmr assignment of pentafluorobenzoylbenzene.

chemical shift (ppm)	multiplicity (apparent)	H integration	H assignment
7.86	d	2	a
7.68	t	1	b
7.53	dd	2	c

2.4.2 **Poly(4,4′-diphenylene diphenylvinylene)**

2.4.2.1 ***Preliminary experiments***

The coupling reagent was prepared by adding $LiAlH_4$ to a solution of $TiCl_3$ (1:2 molar ratio) in dry THF and stirring; the diketone monomer was added and the mixture refluxed. On completion of the reaction the excess coupling reagent was quenched by addition of dilute hydrochloric acid and the polymer recovered by extraction into chloroform (see experimental section for details). In the first polymerisation, the reaction was run for 16 hours and a yellow granular solid of poly(4,4′-diphenylene diphenylvinylene) (*Scheme 2.8*) was recovered in 49% yield.



Scheme 2.8 The synthesis of poly(4,4'-diphenylene diphenylvinylene) via McMurry reaction.

The FTIR spectrum (*Appendix, 1.1.7*) shows peaks at 1599cm^{-1} and 1660cm^{-1}. These peaks are assigned to an aromatic ring mode and carbon-oxygen double bond respectively. The intensity of the **C=O** peak decreased compared to the corresponding peak in the spectrum of the monomer, and was shifted slightly to higher frequency. The decrease in intensity means that some carbonyl units were consumed during this attempted polymerisation, and the shift in frequency is consistent with the decrease in conjugation for a chain end carbonyl on polymerisation. The broad peak centred at 3450cm^{-1} is assigned to hydroxyl groups. This could be a pinacol formed during incomplete coupling or residual methanol from the reprecipitation. It could also be a benzhydrol groups resulting from chain termination by $LiAlH_4$ reduction of a carbonyl group. Prolonged drying of the polymer under vacuum resulted in no decrease in intensity of this peak.

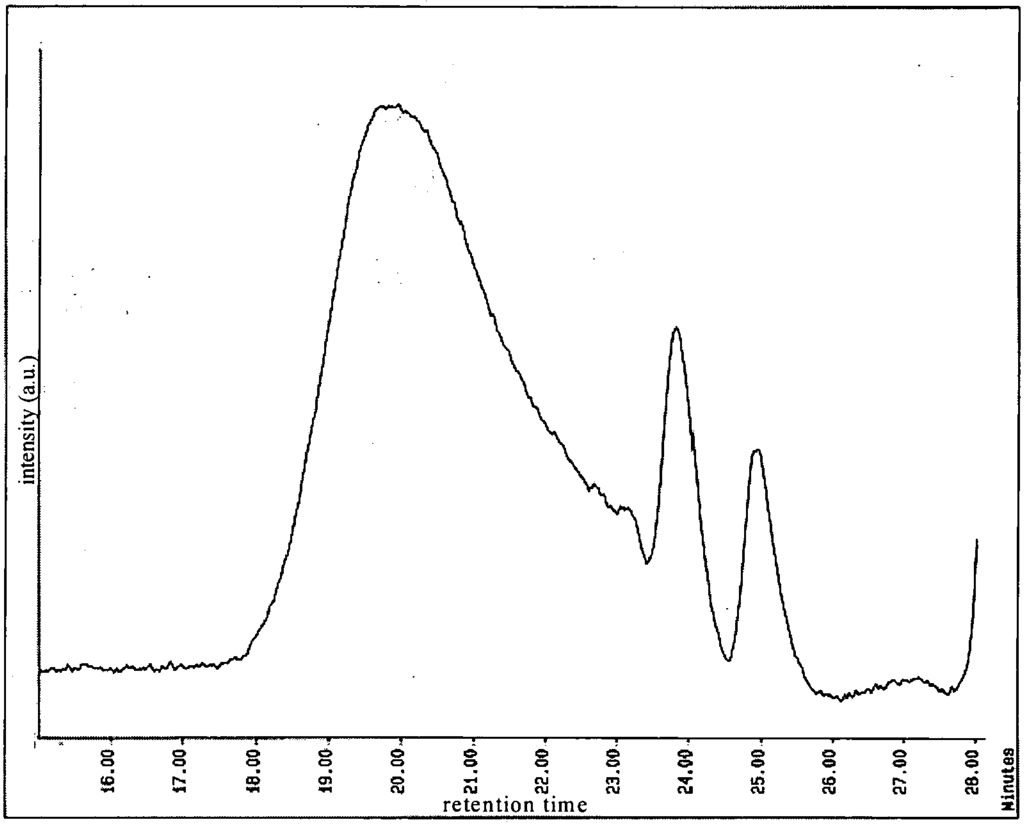


Figure 2.14 GPC trace of poly(4,4′-diphenylene diphenylvinylene).

Molecular weight determination was made on this polymer using gel permeation chromatography (GPC) in which molecules are separated on the basis of their hydrodynamic volume. The chromatogram obtained showed a leading peak which was broad followed by sharper peaks probably corresponding to telomeric units (*Figure 2.14*). Monodisperse polystyrene standards were used for calibration and the values quoted in this work are polystyrene equivalents. GPC sorts polymer coils in dilute solution on the basis of the hydrodynamic volume, this polymer will have *trans* and *cis* vinylene units, the *trans* leading to rodlike segments and *cis* leading to to fairly tight coiling possibilities. The relation between the hydrodynamic volume for polystyrenes and poly(4,4'-diphenylene diphenylvinylene)s of the same molecular weight is almost impossible to predict but we do not expect the values of $\overline{M}_n$ and $\overline{M}_w$ determined using polystyrene calibration to be incorrect by a large factor since both polymers have pendant phenyl groups and some back bone flexibility. It is worth pointing out here that in later work we established that these polymers have an approximately 50:50 *cis:trans* vinylene content (see Chapter 3).

The number average molecular weight ($\overline{M}_n$) and weight average molecular weight ($\overline{M}_w$) obtained were 1600 and 6800 respectively with a polydispersity value of 4.3. These figures implied that some of polymer molecules reached the degree of polymerisation of at least 4, that is the average number of repeat units per polymer chain. It means, according to the Carothers' equation for a condensation polymerisation, that, on average, the reaction conversion achieved in this synthesis was only 75%. Since $\overline{M}_n$ is very sensitive to the amount of low molecular weight molecules and $\overline{M}_w$ is more affected by high molecular weight molecules present in the sample, the molecular weight was recalculated on the basis of the area under the leading broad peak which was extrapolated to the base line, without taking into account the sharper peaks corresponding to the telomeric units. Follow this extrapolation procedure the $\overline{M}_n$, $\overline{M}_w$ and polydispersity obtained were 23000, 72500 and 3.2 respectively. This indicates a number average degree of polymerisation of more than 60 was reached for the bulk of the product. The nature of the low molecular weight telomers was not known with certainty at this stage in the investigation.

It was also found that poly(4,4′-diphenylene diphenylvinylene) was soluble in organic solvents including chloroform, THF, toluene and dichloromethane. This characteristic offers potential for the polymer to be fabricated into thin films by solution processing, thus the first prerequisite for application in light emitting devices had already been fulfilled.

The polymer was also found to show a strong yellowish green fluorescence when illuminated with u.v. radiation. This aspect of the polymer will be further discussed in Chapter 5.

2.4.2.2 *Influence of reaction time*

The second set of polymerisation experiments were run to study the influence of the reaction time on the nature of the product. The GPC analyses showed a leading broad peak followed by sharper peaks for all the samples. It should be noted that all the molecular weight data were obtained by including the sharper peaks in the analysis. The following table presents the results obtained from this set of polymerisations.

Table 2.13 Mass recovery and molecular weight data for polymerisation of 4,4'-dibenzoylbiphenyl for various reaction time.

run	1	2	3	4
reaction time(hrs)	4	20	44	168(7 days)
recovered material(%)	41	45	26	68
$\overline{M}_n$	1500	2200	2600	2400
$\overline{M}_w$	4700	6300	28000	11000
PDI	3.0	2.8	10.0	4.7
DP	5	7	8	7

The trends observed are as expected for a polycondensation polymerisation, in the sense that the molecular weight increased with reaction time up to the third sample (44 hrs). However, an absolutely unambiguous conclusion, that the molecular weight increases with reaction time can not be made since the molecular weight decreased when the reaction time was extended to seven days and the fact that less than 100% mass balance was obtained limits the value of these data.

The values of DP, which are derived from the $\overline{M}_n$ values, are less than ten for all samples. However, as mentioned earlier, $\overline{M}_n$ is influenced by the presence low molecular weight molecules, and due to the fact that telomers were present in all samples, the DP values presented in *Table 2.13* are somewhat pessimistic. Therefore it is clear that there is a need to remove the telomers from the as made polymer in order to produce a high molecular weight polymer (see later).

Results of FTIR spectroscopy (*Appendix 1.1.8-1.1.11*) were consistent with the general trends indicated by the GPC analysis as the intensity of the carbonyl peak in the product decreased with reaction time up to the third sample. In the third sample (44 hrs) the carbonyl peak had almost completely disappeared. However it appeared again in the last sample (7 days) indicating incomplete monomer coupling possibly as a consequence of the "capriciousness" of the reagent or the occurrence of a side reaction regenerating carbonyl. Thus, it was possible to presume at this stage that the two day reaction time is probably the most suitable length for attaining high molecular weight polymers. The appearance of the broad peak centred at 3450cm^{-1} in all of the samples shows that hydroxyl groups were present although the origin of these groups was uncertain.

2.4.2.3 *Recoupling of poly(4,4'-diphenylene diphenylvinylene)*

In the third polymerisation experiment polymer produced in the 4 hours reaction time run was recoupled using fresh $TiCl_3/LiAlH_4$ and refluxed for two days. *Table 2.14* shows the result obtained.

Table 2.14 Results for recoupling experiment.

	4 hrs polymer	recoupled
recovered material(%)	41	60
$\overline{M}_n$	1500	3000
$\overline{M}_w$	4700	11500
PDI	3.0	3.6

The molecular weight doubled after the recoupling reaction. The carbonyl peak in the FTIR spectrum (*Appendix 1.1.12*) of the recoupled sample decreased tremendously as expected for coupling. Because coupling took place it is possible to say that at least half of the chain ends were carbonyl groups. The presence of hydroxyl groups at some chain ends can not be ruled out.

2.4.2.4 ***Influence of $TiCl_3/LiAlH_4$ molar ratio***

Exactly stoichiometrically equivalent proportions of reactants play a very important role in achieving the high reaction conversion essential for a condensation polymerisation and this is assured in the pure difunctional monomer, no trace of monofunctional, chain growth terminating impurity could be detected by our analytical techniques (FTIR, ^{1}H nmr, ^{13}C nmr, MS and C, H and N analysis). It has been reported that the molar ratio between $TiCl_3$ and $LiAlH_4$ is a crucial factor in obtaining the maximum yield of this carbonyl coupling reaction which in its turn, is crucial to obtaining a high degree of polymerisation. It has been shown that the most efficient ratio is 2:1.[14] If the molar ratio between $TiCl_3$ and $LiAlH_4$ is not precisely controlled, the extent of the reaction drops. To check these aspects of the polymerisation procedure, the set of experiments summarised in *Table 2.15* was carried out.

Table 2.15 Results for various $LiAlH_4/TiCl_3$ molar ratio experiment.

run*	$TiCl_3/LiAlH_4$ molar ratio	molecular weight	
		$\overline{M}_n$	$\overline{M}_w$
1	1.80	1700	2900
2	1.82	2200	6300
3	2.00	5400	37100

* reactions were run for 20 hours

Run 3 in the above table, in which the molar ratio between $TiCl_3$ and $LiAlH_4$ is 2:1, yielded the highest molecular weight polymer underlining the requirement for exactly 2:1 molar ratio between $TiCl_3$ and $LiAlH_4$, Haylett has shown that increasing the molar ratio above 2:1 results in a decrease in molecular weight.[28] Using the correct reagent ratios may be the key factor in the more than three-fold increase in molecular weight values reached in run 3 in comparison to that of run 1. The value of $\overline{M}_n$ for reprecipitated product of run 3 is 5400. This gives at least 16 repeating units in a polymer chain with the reaction conversion of 94%. It was found that free standing and transparent yellow film could be formed from the polymer obtained from run 3 by spin-casting under reduced pressure from chloroform.

It should be noted that all the molecular weight data discussed above were obtained by including the sharper low mass peaks in the analysis. Extrapolations of the leading broad peak for the run 3 in *Table 2.15* was made ignoring the telomer peaks and molecular weight was calculated from the area under this peak, the $\overline{M}_n$ obtained was 50,700. This means the number average degree of polymerisation for the bulk of material produced in run 3 was more than 150, corresponding to a reaction conversion greater than 99% for this part of the product; however, while this indicates the potential of the reaction, the low molecular weight telomers are always present under our experiment conditions.

2.4.2.5 *Influence of monomer concentration*

To obtain high molecular weight polymers high monomer concentration is advantageous and usually required in polycondensation.[22] Therefore, with this in mind, the set of experiments summarised in *Table 2.16* was carried out.

Table 2.16 Results for polymerisation of 4,4'-dibenzoylbiphenyl at various monomer concentrations.

Run[1]	monomer conc(% w/v)	crude product[2]			reprecipitated product			recovered material(%)[3]
		$\overline{M}_n$	$\overline{M}_w$	PDI	$\overline{M}_n$	$\overline{M}_w$	PDI	
1	4.43	1500	2700	1.8	1700	2900	1.7	50.0
2	7.10	4800	29100	6.1	5000	29800	5.9	69.0
3	10.00	4700	37800	8.0	5400	37100	6.9	77.3

[1] reactions were run for 20 hours [2] total chloroform soluble organic product
[3] before reprecipitation

The general trend of the result is as expected in that the molecular weight achieved increases with increasing monomer concentration. Results summarised in the *Table 2.16* suggests that a monomer concentration of 10% is the most suitable for this particular polymerisation, in terms of achieving high molecular weight polymers. Polymerisations with monomer concentration of more than 10% have also been tried, however, the polymerisation did not proceed as desired since the reaction mixture solidified soon after the addition of $LiAlH_4$. It should be noted that increasing the concentration of the monomer also inevitably increases the concentration of $LiAlH_4$ and, since $LiAlH_4$ is not very soluble in THF, the reagent slurry is incapable of keeping the forming polymer and coupling reagent in solution. Thus, there has to be a compromise in determining optimum polymerisation conditions.

The FTIR spectra for samples listed in *Table 2.16* are consistent with the GPC analyses, the carbonyl peak in samples from run 2 and 3 had almost completely disappeared (*Appendix 1.1.13-1.1.15*). This means the carbonyl was almost completely consumed during the polymerisations. However the broad peak centred at 3450cm^{-1} appeared in the spectra of all samples. As mentioned before, absorption in this region could be attributed to either the pinacol formed during incomplete coupling or benzhydrol groups at the chain ends. It is unlikely to be the methanol residues since the peaks did not decrease in intensity even after prolonged pumping under vacuum; however, there may be some contribution from moist KBr.

2.4.2.6 *Fractionation of poly(4,4′-diphenylene diphenylvinylene)*

Materials for use in electro-optic devices should ideally be well defined structurally and of high purity. In the case of poly(4,4′-diphenylene diphenylvinylene), the relatively high molecular weight and telomeric molecules are present in all polymers obtained and the nature of the telomeric molecules as well as the frequency and distribution of *cis* and *trans* vinylenes along the polymer backbone are not known. Attempts have been made to rectify these deficiencies by undertaking a careful equilibrium fractionation of the as made polymer at 20°C using chloroform and heptane as solvent and non-solvent respectively (see experimental section for details). As a result, a series of 18 fractions was collected varying from $\overline{M}_n$ ~88,000 down to $\overline{M}_w$ ~1,000 (*Table 2.17*) with molecular weight distributions of the order of about two as compared with a value of ten for the as made polymer.

The first fraction shows a degree of polymerisation of more than 260 which corresponding to the reaction conversion, for this fraction of the polymer, of more than 99.6%. This implies that the McMurry reaction has a great potential as a condensation polymerisation method for synthesis poly(arylene vinylene)s, as long as a procedure to extract the high molecular weight fractions from the as made polymer is available.

Table 2.17 Results for fractionation of poly(4,4′-diphenylene diphenylvinylene).

Samples	Mass(%)[1]	$\overline{M}_n$[2]	$\overline{M}_w$[2]	PDI	DP[3]
pristine	100.00	3100	30000	9.7	9
fraction 1	9.00	88060	166890	2.0	266
fraction 2	0.80	49880	225400	4.5	151
fraction 3	16.33	42920	78100	1.8	130
fraction 4	16.00	19280	28100	1.5	58
fraction 5	14.47	16500	22400	1.4	50
fraction 6	7.47	13625	16600	1.2	41
fraction 7	5.00	9850	11600	1.2	29
fraction 8	4.53	7040	8800	1.3	21
fraction 9	2.47	5740	7100	1.2	17
fraction 10	2.00	4160	5900	1.4	12
fraction 11	0.80	3840	5200	1.4	11
fraction 12	0.60	3620	5000	1.4	10
fraction 13	1.00	3100	4100	1.3	9
fraction 14	0.47	2470	3260	1.3	7
fraction 15	0.20	1970	2515	1.3	6
fraction 16	1.20	1765	2330	1.3	5
fraction 17	2.40	1150	1560	1.4	3
fraction 18	2.47	793	798	1.0	2

[1] total mass of the pristine polymer 15.00g
[2] "polystyrene equivalent" values
[3] degree of polymerisation

Polymer fractions of various molecular weights were examined for their film forming characteristics, for samples with molecular weight distribution of the order of about two, polystyrene equivalent number average molecular weights in excess of 19,000 are required in order to obtained free standing films. Samples with number average molecular weights below 19,000 do not form free standing film, however, homogeneous transparent films can be formed when solution of these samples were spun cast onto substrates, such as a glass or a quartz.

As mentioned earlier, telomers were always present in all samples and as a result of the fractionation experiment, one of the low molecular weight components was isolated (fraction 18) from the residual solution as a pure microcrystalline solid and although GPC analysis suggested this was a dimer it was proved by ^{1}H nmr (*Appendix 1.2.8*), ^{13}C nmr (*Figure 2.16*), FTIR (*Appendix 1.1.16*) and MALDI-TOF (*Figure 2.17*) spectroscopies to be the cyclic trimer shown in *Figure 2.15*. This compound constitutes about 2.5% of the pristine polymer. This demonstrates unambiguously that the coupling process can form *cis* vinylenes. None of the other low molecular weight peaks were isolated in a pure form.

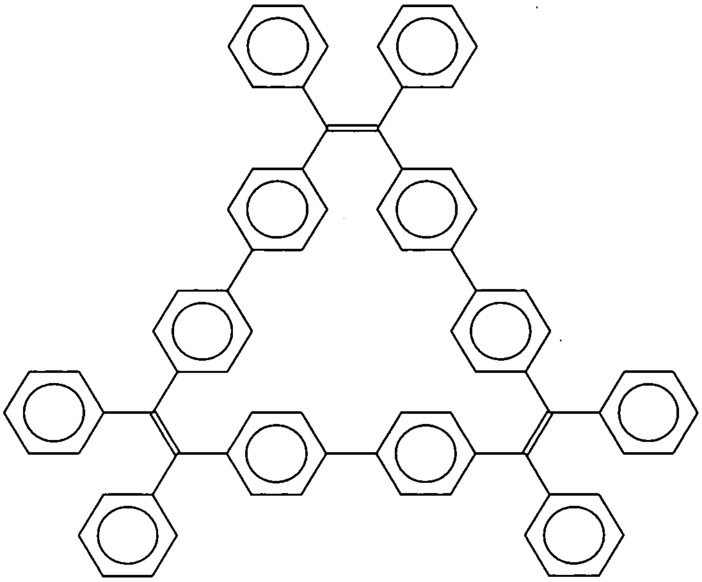


Figure 2.15 Cyclic trimer isolated from the pristine poly(4,4′diphenylene diphenylvinylene.

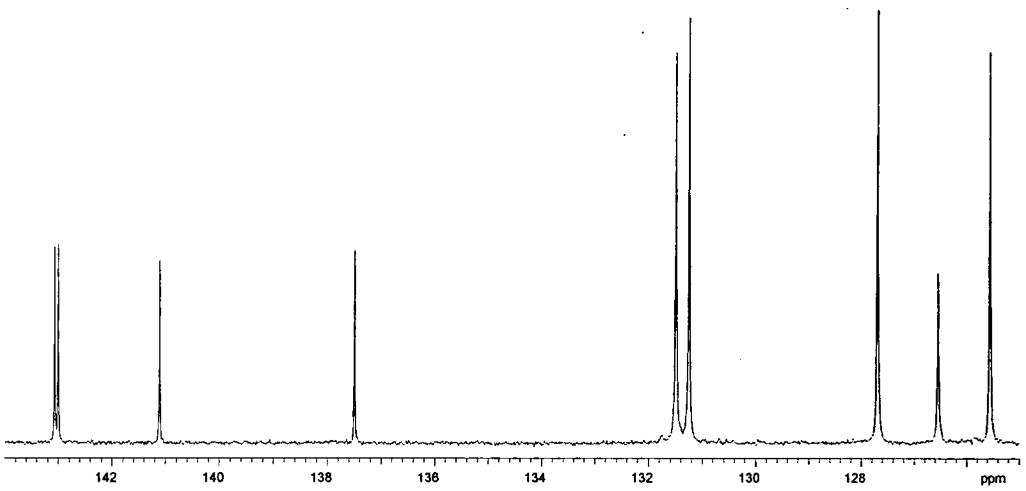


Figure 2.16 ^{13}C nmr spectrum of the cyclic trimer.

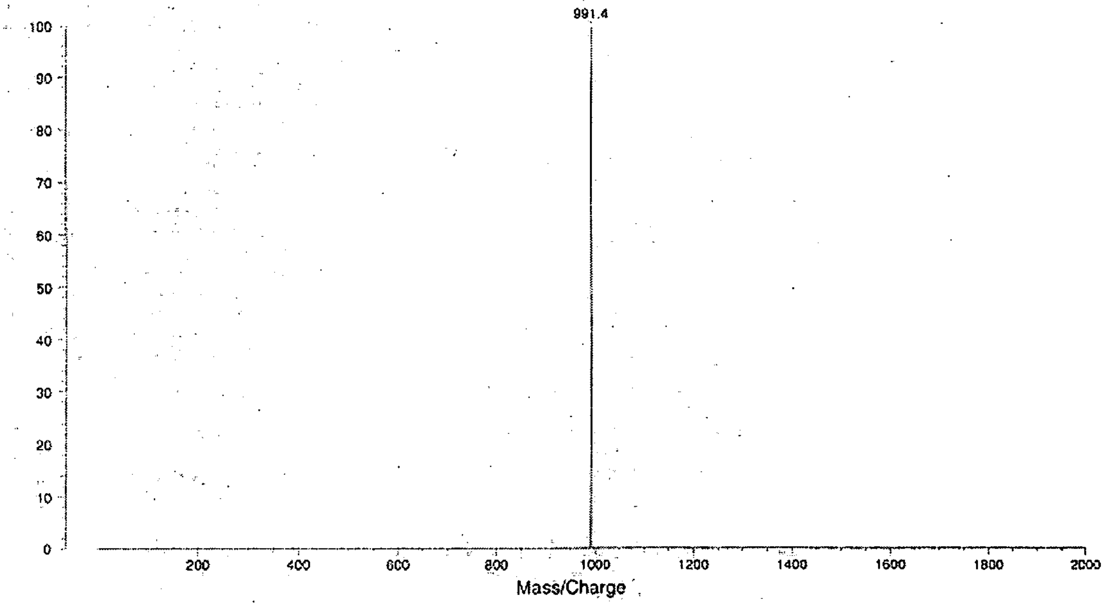


Figure 2.17 MALDI-TOF MS spectrum of the cyclic trimer.

Samples of the first three fractions do not show any carbonyl peak at all in the FTIR spectra (*Appendix 1.1.17-1.1.19*). This suggests that, for these fractions of polymer, the polymerisation reaction proceeded to completion or at least to the extent where the presence of the carbonyl groups is reduced to only a trace, thus it can not be detected by FTIR. However, for the rest of the fractions the carbonyl peak increases as the molecular weight decreases. Therefore, it is again possible to conclude that some chain ends are carbonyls, which is consistent with result from the recoupling experiment described earlier. .

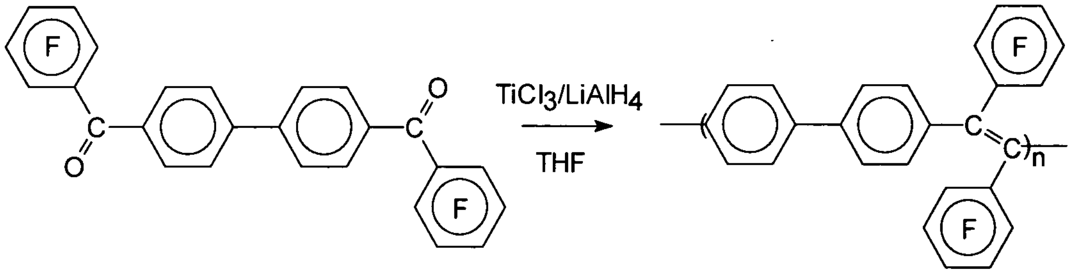
2.4.2.7 *Thermal properties of poly(4,4′-diphenylene diphenylvinylene)*

Thermogravimetric analysis (TGA) of the sample of run 3 in *Table 2.15* shows the onset decomposition temperature at 370°C, and even at 490°C the polymer only loses less than 5% of its weight, indicating a very good stability against heat. The polymer was found to have a glass transition temperature of 231°C, as measured by DSC.

The isolated cyclic trimer shows even better thermal stability. At 490°C, the compound loses only 2% of its weight, however, it has not been possible to detect either melting or glass transition temperature below 490°C. Attempts to obtain crystals for an X-ray structure determination were unsuccessful since the crystals were twinned and unsuitable for X-ray analysis.

2.4.3 **Poly(4,4′-diphenylene-1,2-bis(pentafluorophenyl)vinylene)**

Poly(4,4′-diphenylene-1,2-bis(pentafluorophenyl)vinylene) (*Scheme 2.9*) was prepared from the corresponding diketone, namely 4,4′-bis(pentafluorobenzoyl)biphenyl, by the method described previously. The objective of this experiment was to produce poly(arylene vinylene)s with a larger band gap. As mentioned in the preceding chapter, poly(arylene vinylene)s with blue electroluminescence are of special interest, due the fact that their inorganic counterparts with blue emission are not readily available, and tuning towards blue emission involves synthesising polymers with larger bad gaps. Horhold *et al.* have shown that by incorporating electron acceptor substituents onto the polymer back bone, the oxidation potential of the polymer can be increased, consistent with an increase in the band gap.[23,24]



Scheme 2.9 The McMurry route to poly(4,4′-diphenylene-1,2-bis(pentafluorophenyl)vinylene).

An orange solid of poly(4,4′-diphenylene-1,2-bis(pentafluorophenyl)vinylene) was produced in 70% material recovery. The FTIR spectrum (*Appendix 1.1.23*) shows major peaks at 1499cm^{-1} and 1522cm^{-1}, the assignment is uncertain but they are probably due to carbon-fluorine vibrations. The carbonyl peak had almost disappeared compared to the corresponding peak in the spectrum of the monomer. This means that the carbonyl is almost completely consumed during the attempted polymerisation. The broad peak centred at 3422.0cm^{-1} can be assigned to the hydroxyl group. This could be either the pinacol formed during incomplete coupling or benzhydrol groups resulting from chain termination by $LiAlH_4$ reduction of carbonyl groups (it may also be due to "damp KBr").

Molecular weight determination was made on this polymer using gel permeation chromatography. The chromatogram obtained shows a broad peak with partially resolved peaks on the trailing edge, possibly corresponding to telomeric units (*Figure 2.18*).

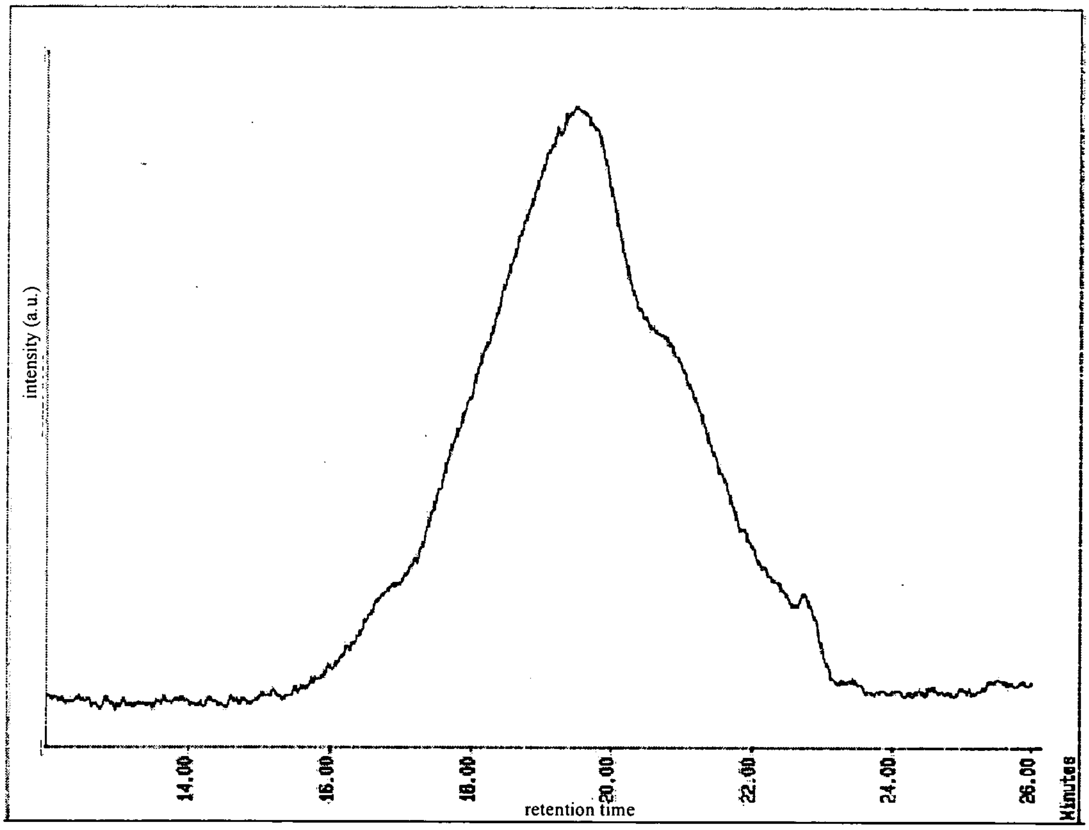


Figure 2.18 GPC trace of poly(4,4′-diphenylene-1,2-bis(pentafluorophenyl)vinylene).

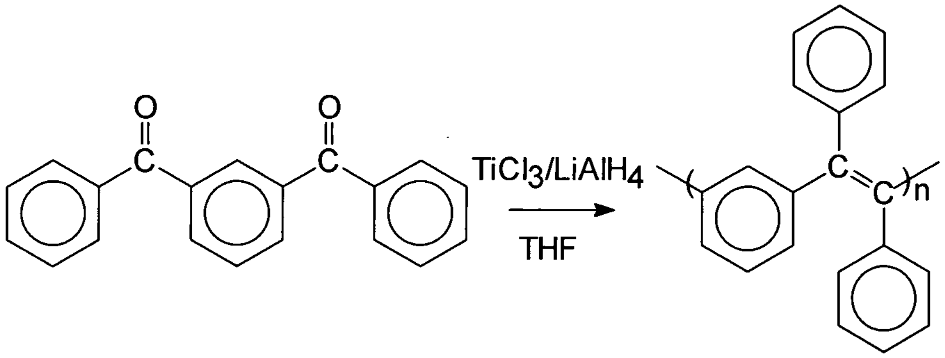
The number average molecular weight ($\overline{M}_n$) and weight average molecular weight ($\overline{M}_w$) obtained were 13,800 and 45,800 respectively, with a polydispersity of 3.3. This figures implied that some of polymer molecules reached a degree of polymerisation of at least 25, that is the average number of repeat units per polymer chain. It means, according to the Carothers' equation for condensation polymerisation, the average reaction conversion achieved in this synthesis is 96%.

It has been found that this polymer is photoluminescent. It shows an orange fluorescence when illuminated with u.v. radiation. This characteristic of the polymer will be discussed further in Chapter 5. It was also found that poly(4,4′-diphenylene-1,2-bis(pentafluorophenyl)vinylene) is soluble in common organic solvents including, dichloromethane, chloroform, toluene and THF. This allows spin casting from solution which is a processing technique commonly used in light emitting device applications.

Thermogravimetric analysis (TGA) shows that this polymer is remarkably thermally stable. It loses 2% of its weight at 400°C and even at 490°C the polymer shows only 5% weight lost. The polymer was shown to have a glass transition temperature of 222°C, as measured by DSC.

2.4.4 **Poly(1,3-phenylene diphenylvinylene)**

Some reports in the literature suggest that a *meta* linkage in the in-chain phenyl ring in polymers such as in poly(*m*-phenylene) decreases the planarity of the conjugated backbone.[25,26] This leads to a decrease in electron delocalisation along the backbone, and consequently to an increase in band gap. Therefore, with this in mind, the general polymerisation procedure described in section 2.6 was followed to synthesis poly(1,3-phenylene diphenylvinylene) from 1,3-dibenzoylbenzene (*Scheme 2.10*).



Scheme 2.10 The synthesis of poly(1,3-phenylene diphenylvinylene) via McMurry reaction.

The polymer was recovered as a pale yellow solid which gave a faint yellow luminescence when illuminated with u. v. radiation. The FTIR spectrum

(*Appendix 1.1.24*) shows three strong peaks at 1442, 1491 and 1596cm^{-1}. The first two peaks have been attributed to aromatic carbon-hydrogen bending modes and the later peak can be attributed to aromatic carbon skeleton breathing mode. The peak corresponding to the aromatic hydrogen stretching mode can be seen at 3051cm^{-1}.

Results from ^{1}H and ^{13}C nmr (*Appendix 1.2.9 and 1.3.9*) are entirely consistent with the structure expected and assigned to the polymer shown in *Scheme 2.10*, however, the frequency and distribution of *cis* and *trans* vinylenes along the backbone can not be established.

Elemental analysis of the polymer showed that the carbon content was slightly lower than that calculated; found (%): C 90.53, H 5.73, $C_{20}H_{14}$ requires (%): C 94.45, H 5.55. It should be noted that the calculation is based on the elements present in the repeat unit of the polymer, without taking into account the elements in the chain end groups. Therefore the slightly lower carbon content observed is possibly due to the benzoyl or benzhydrol groups which might be present at some of the chain ends or in-chain pinacol defects.

The GPC trace of the polymer is presented in *Figure 2.19*. Low molecular weight molecules are clearly present as partially resolved peaks on the trailing edge. The number average and weight average molecular weights obtained for this polymer are 7490 and 45,800 respectively, with a molecular weight distribution of 6.1. This indicates that, on average, the number of repeat units in the polymer produced was 29, corresponding to a reaction conversion of about 97%. The polymer was also found to be soluble in organic solvents such as chloroform, toluene and THF, thus allows the solution processing.

Thermogravimetric analysis shows that the polymer decomposes very slowly when heated under nitrogen. It loses 2% of its weight at 215°C but only by 3% at 490°C. It was found that the glass transition temperature of the polymer was 188°C, as measured by DSC.

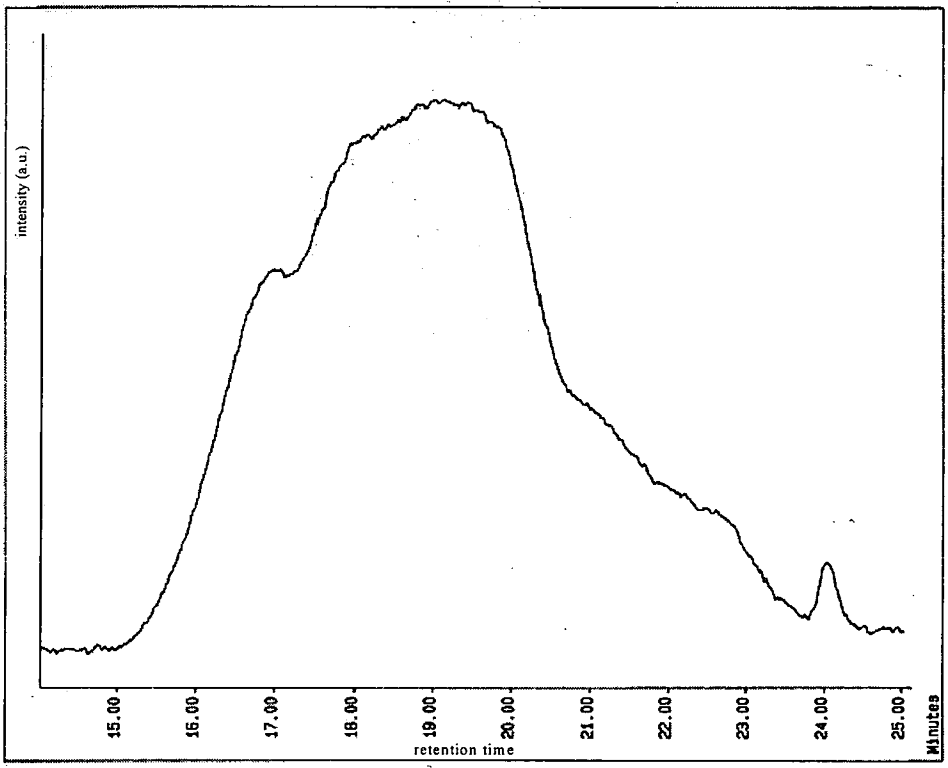


Figure 2.19 GPC trace of poly(1,3-phenylene diphenylvinylene)

In order to remove the low molecular weight molecules in the sample and also to improve the molecular weight distribution, an equilibrium fraction similar to that described earlier was carried out. As a result, a series of fractions of various molecular weights was collected, varying from a $\overline{M}_n$ of 27300 down to a $\overline{M}_n$ of 1400 (*Table 2.17*) with molecular weight distributions of the order of about 2.5. The degree of polymerisation obtained for the first fraction, which constitutes about 33% of the pristine polymer, was 107. This corresponding to a reaction conversion of

99% in this sample, again underlining the potential of the McMurry reaction as an approach to poly(arylene vinylene)s.

Table 2.17 Results from the fractionation of poly(1,3-phenylene diphenylvinylene).

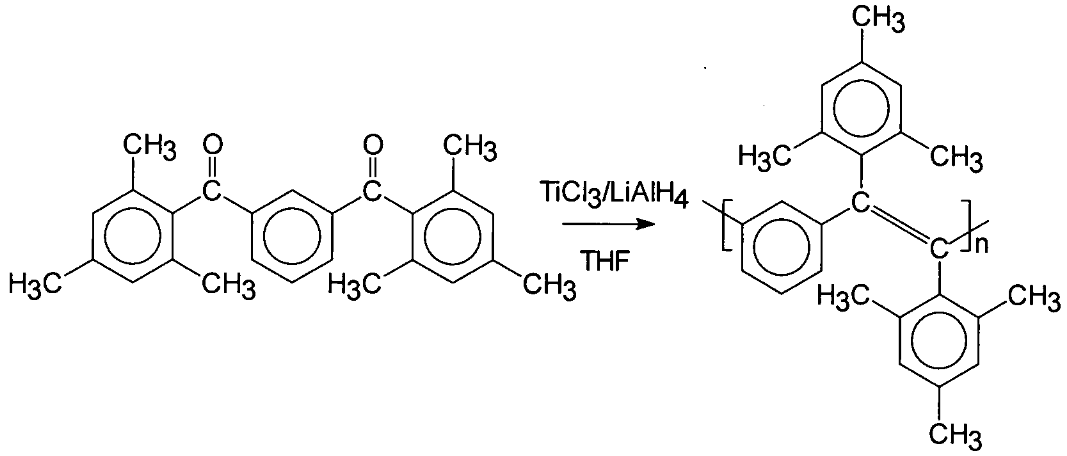
Sample	Mass (%)[1]	$\overline{M}_n$	$\overline{M}_w$	PDI	DP[2]
pristine	100.00	7490	45800	6.1	29
fraction 1	33.14	27300	70800	2.6	107
fraction 2	3.78	19000	53700	2.8	75
fraction 3	12.28	17400	49900	2.8	69
fraction 4	6.82	14600	35000	2.4	57
fraction 5	6.24	12700	29250	2.3	50
fraction 6	5.65	8000	15400	1.9	32
fraction 7	8.97	5200	6810	1.3	20
fraction 8	4.48	2500	3370	1.3	10
fraction 9	2.14	2060	2580	1.3	8
fraction 10	1.17	1740	2250	1.3	7
fraction 11	1.36	1400	1810	1.3	6

[1] total mass of the pritine polymer is 5.13g
[2] degree of polymerisation

Polymers of the various molecular weights recovered were examined for film forming characteristics and it was found that none of the fractions could form free standing films. However, homogeneous transparent film can be cast onto glass or quartz substrates by using solution processing techniques.

2.4.5 Poly(1,3-phenylene dimesitylvinylene)

Poly(1,3-phenylene dimesitylvinylene) was synthesised from the corresponding diketone, namely 1,3-dimesitoylbenzene (*Scheme 2.11*). The idea of producing polymers with larger band gaps by incorporating phenyl ring with *meta* linkage in the conjugated backbone is extended in this experiment. As mentioned earlier, the *meta* linkage of the in-chain phenylene in the polymer backbone should reduce conjugation and increase the band gap of the polymer. The *ortho* methyl substituted phenyl groups attached to the vinylene segments of the polymer chain was expected to inhibit conjugation via steric hindrance to planarity of the pendant aromatic groups with the conjugated backbone. In these ways it was hoped that electron delocalisation along the conjugated polymer chain would be decreased leading to a further increase in the band gap.



Scheme 2.11 The synthesis of poly(1,3-phenylene dimesitylvinylene) via McMurry reaction.

A pale yellow polymer was recovered and found to emit faint yellow fluorescence when illuminated with u. v. radiation. However, the number average and weight average molecular weights obtained were only 1040 and 1280 respectively, with molecular weight distribution of 1.2. This means that the degree of polymerisation achieved in this attempt is only of the order of 3, corresponding to a reaction conversion of only 67%. This is possibly due to the bulky pendant groups which in addition to inhibiting conjugation might quite reasonably be expected to inhibit the condensation reaction required. In the FTIR spectrum (*Appendix 1.1.25*), there is a strong peak at 1610cm^{-1} which can be ascribed to the aromatic carbon skeleton vibration mode, and both peaks at 1449 and 1481cm^{-1} are attributed to the aromatic hydrogen vibration modes. The peak of methyl hydrogen stretching absorption can be seen at 2918cm^{-1}.

It was found that the poly(1,3-phenylene dimesitylvinylene) decomposes at about 240°C and loses its weight rapidly when heated beyond 270°C; so, all in all, this was not a particularly attractive material but never-the-less it was hoped that study of the spectra might throw some light on structure/property correlations.

2.4.6 Coupling reaction of 4-nitrobenzoylbiphenyl

A coupling reaction of 4-nitrobenzoylbiphenyl was carried out using a similar method to that described earlier. A brown powder with 94% recovery of material was produced. FTIR spectroscopy analysis (*Appendix 1.1.26*) showed that a reaction took place since the carbonyl peak almost completely disappeared. However the peaks at around 1519cm^{-1} and 1353cm^{-1} which are attributed the nitro group also disappeared and there are multiple peaks between 3200cm^{-1} and 3400cm^{-1} which can be assigned to the primary amine group. This result suggests that nitro group reduction competes with McMurry coupling which is not unexpected. The complex mixture was not analysed in detail, but this result suggests that it may be possible to produce amine substituted materials via this route and the result is included here as a matter of record.

2.5 Conclusions

In summary, it has been shown that the poly(arylene vinylene)s presented in *Figure 2.20* have been synthesised successfully via the McMurry reaction, except m-PPV-DM which resulted in the production of oligomers only. The optimum conditions for the McMurry polycondensation of diketone monomers have been identified. It has also been shown that a fractionation procedure allows high molecular weight and relatively narrow molecular weight distribution fractions to be obtained from a broad molecular weight distribution in the as made polymers. Thus, a route to clean and high molecular weight polymer has been established.

All polymers have been shown to have good solubility in common organic solvents, such as THF, toluene, and chloroform, as well as good thermal stability; especially poly(4,4′diphenylene diphenylvinylene) and poly(4,4′diphenylene-1,2-bis(pentafluophenyl)vinylene). The route gives no control over the *cis/trans* content and/or distribution but the isolation of a cyclic trimer in the case of PDPV shows that at least some *cis* units are formed, subsequent work (see Chapter 3) establishes that in PDPV an approximately 50:50 *cis:trans* vinylene content is produced by this synthetic procedure.

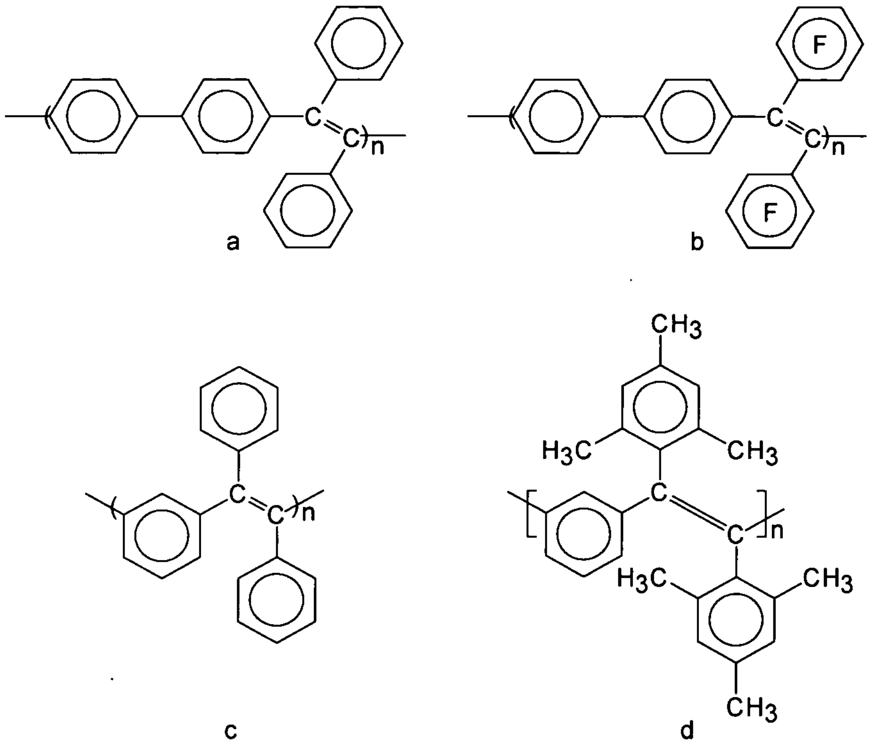


Figure 2.20 Polymers prepared via McMurry coupling of diketones; a) poly(4,4′-diphenylene diphenylvinylene) (**PDPV**), b) poly(4,4′-diphenylene-1,2-bis(pentafluorophenyl)vinylene) (**PDPV-DF**), c) poly(1,3phenylene diphenylvinylene) (**m-PPV-DP**), d) poly(1,3-phenylene dimesitylvinylene) (**m-PPV-DM**).

2.6 Experimental

Biphenyl, benzoylchloride, pentafluorobenzoylchloride, isophthaloyldichloride, mesitylene, 4-nitrobenzoylchloride, aluminium chloride, ferric chloride, lithium aluminium hydride, titanium(III) chloride, benzene, heptane and 1,2-dichloroethane were purchased from Aldrich Company Ltd. Dichloromethane, hexane, ethyl acetate, and THF were purchased from BDH Chemical Company Ltd. All reagents and solvents were used without further purification except THF, which was dried by distillation from sodium metal/sodium benzophenone ketyl radical, and isophthaloyldichloride, which was distilled prior to use.

^{1}H and ^{13}C Nmr spectra were recorded using a Varian 400MHz spectrometer and were referenced to internal Me_4Si. IR Spectra were recorded using a Perkin-Elmer 1600 series FTIR spectrometer. GPC analyses were performed using a Waters differential diffractometer as detector, three Polymer Laboratories gel columns (exclusion limits 100, 10^3, 10^5Å) and chloroform as eluent. Columns were calibrated using polystyrene standards (Polymer Labs). DSC measurements were performed using a Perkin-Elmer DSC7, at scanning rate of 10°C/min, the temperature scale was calibrated using the melting points of indium at 100°C and zinc at 400°C. Thermogravimetric analysis was carried out under nitrogen using a TG 760 series instrument (Rheometric Scientific Ltd.) at scanning rate of 10°C/min.

2.6.1 Synthesis of 4,4′-dibenzoylbiphenyl

Biphenyl (25.00g, 0.16mol) was added to benzoylchloride (113ml, 0.97mol) as reagent and solvent in a five necked flange flask fitted with overhead stirrer, water cooled condenser and thermometer. The mixture was stirred and aluminium chloride (140.50g, 1.05mol) was slowly added as a fine powder via a solids funnel over a period of 30 minutes, keeping the temperature below 10°C with external cooling (ice/water). The mixture was stirred at room temperature for 30 minutes before heating at 80°C for 4 hours. After cooling to room temperature the mixture was poured into ice-water (3l) with rapid stirring to give a white precipitate. The precipitate was collected by filtration, washed with 5% KOH and water until the washings were no longer acidic (litmus paper). The white powder was then dried in the vacuum oven (8 hours, 45°C) and recrystallised from toluene (five times) to yield 4,4′-dibenzoylbiphenyl (48.77g, 83 mole % yield w.r.t. biphenyl), m. pt. 215-218°C (lit.[18] 214.5-215.5°C). The product was characterised by: MS; M+1 ion = 362 determined by EI mass spectrometry, ^1H nmr (δ, $CDCl_3$, 400MHz): 7.52 (pseudo dd, 4, aromatic), 7.62 (pseudo t, 2, aromatic), 7.77 (pseudo d, 4, aromatic), 7.85 (pseudo d, 4, aromatic), 7.94 (pseudo d, 4, aromatic), ^{13}C nmr (δ, $CDCl_3$, 100MHz): 127.1 (aromatic CH), 128.2 (aromatic CH), 129.9 (aromatic CH), 130.7 (aromatic CH), 132.4 (aromatic CH), 136.9 (aromatic C), 137.4 (aromatic C), 143.7 (aromatic C), 196.1 (C=O), FTIR (KBr disc, ν_{max}/cm^{-1}): 1073, 1151, 1178, 1285, 1331.2, 1394, 1444, 1549, 1603, 1650.

2.6.2 **Synthesis of 1,3-dibenzoylbenzene**

Freshly distilled isophthaloyldichloride (8.11g, 40mmol) was dissolved in dry benzene (78ml) with vigorous stirring. Finely ground anhydrous aluminium chloride (12.25g, 92mmol) was added in small portions to the stirred solution over a period of 30 minutes. The reaction mixture was then refluxed for five hours, cooled and poured into acidified ice-water (1000ml, containing 43ml conc. HCl). The organic product was extracted into benzene (3 x 50ml) and all extracts were combined. After evaporating the solvent, a pale yellow solid was recovered. This was recrystallised repeatedly from cyclohexane to give pure 1,3-dibenzoylbenzene (8.59g 75 mole % yield w.r.t. isophthaloyldichloride), m. pt. 105.4-106.0°C (lit.[18] 103-104°C). The product was characterised by: Elemental analysis; found: C 83.60, H 4.81; $C_{20}H_{14}0_2$ requires C 83.89, H 4.93, MS M+1 ion = 286 determined by EI mass spectrometry, ^{1}H nmr (δ, $CDCl_3$, 400MHz): 7.50 (pseudo dd, 4, aromatic), 7.62 (m, 3, aromatic), 7.83 (pseudo d, 4, aromatic), 8.03 (pseudo d, 2, aromatic), 8.19 (pseudo s, 1, aromatic), ^{13}C nmr (δ, $CDCl_3$, 100MHz): 128.5 (aromatic **C**H), 128.5 (aromatic **C**H), 130.1 (aromatic **C**H), 131.2 (aromatic **C**H), 132.9 (aromatic **C**H), 133.5 (aromatic **C**H), 137.0 (aromatic **C**), 137.8 (aromatic **C**), 195.8 (**C**=O), FTIR (KBr disc, ν_{max}/cm^{-1}): 1004, 1116, 1166, 1269, 1286, 1319, 1445, 1576, 1597, 1657, 3061.

2.6.3 Synthesis of 1,3-dimesitoylbenzene

To a stirred solution of isophthaloyldichloride (6.00g, 30mmol) in mesitylene (50ml), powdered anhydrous aluminium chloride (15.00g, 112mmol) was added in small portions over a period of 30 minutes. The resulting mixture was heated at 90°C for five hours, cooled and poured into acidified ice-water (500ml, containing 22ml conc. HCl). The product was then extracted into toluene (3 x 50ml) and the combined extracts were evaporated to dryness to give a crude 1,3-dimesitoylbenzene. Recrystallisations of this solid from ethanol gave pure 1,3-dimesitoylbenzene (9.71g, 89 mole % yield w.r.t. isophthaloyldichloride) as colourless crystals, m. pt. 154.2-

156.0°C (lit.[18] 150.5-152.0°C). The product was characterised by: Elemental analysis; found: C 83.21, H 7.08, $C_{26}H_{26}O_2$ requires C 84.28; H 7.08, MS M+1 ion = 370 determined by EI mass spectrometry, ^{1}H nmr (δ, $CDCl_3$, 400MHz): 2.06 (s, 12, CH_3), 2.33 (s, 6, CH_3), 6.89 (pseudo s, 4, aromatic), 7.52 (pseudo t, 1, aromatic), 7.96 (pseudo d, 2, aromatic), 8.23 (pseudo s, 1, aromatic), ^{13}C nmr (δ, $CDCl_3$, 100MHz): 19.3 (CH_3), 21.0 (CH_3), 128.4 (aromatic CH), 129.3 (aromatic CH), 129.7 (aromatic CH), 133.9 (aromatic CH), 134.0 (aromatic CH), 136.0 (aromatic CH), 137.9 (aromatic CH), 138.7 (aromatic CH), 199.8 (C=O), FTIR (KBr disc, ν_{max}/cm^{-1}): 612, 720, 850, 992, 1095, 1157, 1254 1442, 1592, 1608, 1680, 2917.

2.6.4 Synthesis of 4-nitrobenzoylbiphenyl

4-Nitrobenzoylchloride (9.63 g, 52 mmol) was dissolved in dichloromethane (300 ml) in a four necked flask (500 ml) fitted with a thermometer, a condenser and a nitrogen inlet. Biphenyl (2.00 g, 13 mmol) was then added while flushing with nitrogen. Aluminium chloride (10.38 g, 78 mmol) was slowly added as a fine powder, keeping the mixture rapidly stirred and the temperature below 10°C. After refluxing for five hours the reaction was quenched by pouring the mixture into acidified ice-water (1000ml, containing 43ml conc. HCl) while stirring rapidly. The product was extracted into dichloromethane (3 x 50 ml). All the extracts were combined, washed with sodium hydroxide (1 l, 5% w/v) and water until the washings were neutral and dried over $MgSO_4$. Solvent was evaporated and the residue was dried under vacuum giving a crude brown product of 4-nitrobenzoylbiphenyl. This crude product was further purified by column chromatography (neutral alumina, 50:50 v/v hexane/ethyl acetate) giving 4-nitrobenzoylbiphenyl (2.71 g, 69 mole % w.r.t. biphenyl) as a slightly yellow solid, m. pt. 166.5-168.5°C (lit.[27], 165°C). The product was characterised by: MS M+1 = 304 determined by CI spectrometry, ^{1}H nmr (δ, $CDCl_3$, 400MHz): 7.42 (pseudo t, 1, aromatic), 7.49 (pseudo dd, 2, aromatic), 7.65 (pseudo d, 2, aromatic), 7.73 (pseudo d, 2, aromatic), 7.88 (pseudo d, 2, aromatic), 7.95 (pseudo d, 2, aromatic), 8.34 (pseudo d, 2, aromatic), ^{13}C nmr (δ, $CDCl_3$, 100MHz): 123.6 (aromatic CH), 127.3 (aromatic CH), 127.3 (aromatic CH), 128.5 (aromatic CH), 129.1 (aromatic CH), 130.6 (aromatic CH), 130.8 (aromatic CH), 134.3 (aromatic C), 139.5 (aromatic C), 143.0 (aromatic C), 146.2 (aromatic C), 149.7 ($C\text{-}NO_2$), 194.3 (C=O), FTIR (KBr disc, ν_{max}/cm^{-1}): 1282, 1317, 1351, 1519, 1600, 1649.

2.6.5 Synthesis 4,4′-di(4-nitrobenzoyl)biphenyl

1,2-Dichloroethane (100ml) was placed in a four necked round bottomed flask (250ml) fitted with a thermometer, a condenser and a nitrogen inlet. 4-Nitrobenzoylchloride (5.30g, 29mmol) and biphenyl (2.00g, 13mmol) were added while flushing with nitrogen and stirring rapidly, followed by a slow addition of ferric chloride (5.00g, 31mmol). The temperature was maintained below 10°C while adding the ferric chloride. The mixture was then refluxed for four hours, cooled and poured into acidified ice-water (1000ml, containing 43ml conc. HCl). Organic product was extracted into 1,2-dichloroethane (3 x 40ml). The combined organic extracts were washed with sodium hydroxide (200ml, 2M) and water until the washings were neutral and dried over $MgSO_4$. A pale red solid was obtained after evaporating the solvent. This solid was further purified by recrystallisation from toluene (3 times) giving a creamy crystals of 4,4′-di(4-nitrobenzoyl)biphenyl (0.99 g, 18 mole % w.r.t. biphenyl), m. pt. 208.0-210.0°C (lit.[20]211-212°C). The product was characterised by: MS M+1 = 452 determined by EI spectrometry. ^{1}H nmr (δ, $CDCl_3$, 400MHz): 7.81 (pseudo d, 4, aromatic), 7.94 (pseudo d, 4, aromatic), 7.99 (pseudo d, 4, aromatic), 8.38 (pseudo d, 4, aromatic), ^{13}C nmr (δ, $CDCl_3$, 100MHz): 123.5 (aromatic **C**H), 127.5 (aromatic **C**H), 130.6 (aromatic **C**H), 130.7 (aromatic **C**H), 135.8 (aromatic **C**), 142.7 (aromatic **C**), 144.3 (aromatic **C**), 149.8 (**C**-NO_2), 194.1 (**C**=O), FTIR (KBr disc, ν_{max}/cm^{-1}): 1272, 1317, 1352, 1519, 1600, 1649.

2.6.6 Synthesis 4,4′-bis(pentafluorobenzoyl)biphenyl

Pentafluorobenzoylchloride (25g, 108mmol) was added to dichloromethane (200ml) in a four necked flask (250ml) fitted with a thermometer, a condenser and a nitrogen inlet. Biphenyl (7.27g, 47mmol) was then added to the solution while flushing with nitrogen. Aluminium chloride (43.38g, 325mmol) was slowly added as a fine powder, keeping the mixture rapidly stirred and the temperature below 10°C. The mixture was then refluxed for five hours, cooled and poured into acidified ice-water (1000ml, containing 43ml conc. HCl). The organic product was extracted into dichloromethane (3 x 50ml). All organic extracts were combined, washed with potassium hydroxide (1l, 5% w/v) and water until the washings were neutral, dried over $MgSO_4$ and filtered. After evaporating the solvent, a dark crude solid product was obtained. This was recrystallised repeatedly from toluene to give pure *4,4′-bis(pentafluorobenzoyl)biphenyl* (7.67g, 30 mole % w.r.t. biphenyl) as orange crystals , m. pt. 218.6-220.0°C, found: C 57.44, H 1.31, M+1 = 542 determined by EI spectrometry, $C_{26}H_8F_{10}O_2$ requires C 57.56; H 1.49 %, Molecular mass 542.33, ^{1}H nmr (δ, $CDCl_3$, 400MHz): 7.78 (pseudo d, 4, aromatic), 7.97 (pseudo d, 4, aromatic), FTIR (KBr disc, ν_{max}/cm^{-1}): 999, 1113, 1183, 1230, 1247, 1319, 1332, 1398, 1413, 1504, 1523, 1604, 1655, 1682.

2.6.7 **Attempted synthesis of 3-pentafluorobenzoylbenzophenone**

Dichloromethane (100ml) was placed in a four necked flask fitted with a thermometer, a condenser and a nitrogen inlet. Pentafluorobenzoylchloride (6.30g, 27mmol) and benzophenone (5.00g, 27mmol) were then added while flushing with nitrogen. Aluminium chloride (11.00g, 82mmol) was slowly added as a fine powder while keeping the mixture rapidly stirred and the temperature below 10°C. After refluxing for five hours the reaction was quenched by pouring the mixture into acidified ice-water (1000ml, containing 43ml conc. HCl). The organic product was extracted into dichloromethane (3 x 50ml). All the extracts were combined, washed with sodium hydroxide (300ml, 5% w/v) and water until the washings were neutral and dried over $MgSO_4$. A dark brown powder was obtained after evaporating the solvent and drying the residue under vacuum. This powder was characterised without further purification by ^{1}H nmr (δ, $CDCl_3$, 400MHz): 7.49 (pseudo dd, 4, aromatic), 7.58 (pseudo t, 2, aromatic), 7.80 (pseudo d, 4, aromatic) and was shown to be the starting material benzophenone.

2.6.8 Attempted synthesis of 1,3-bis(pentafluorobenzoyl)benzene

Pentafluorobenzoylchloride (15.50g, 67mmol) was dissolved in 1,2-dichloroethane (150ml) in a four necked flask fitted with a thermometer, a condenser and a nitrogen inlet. Benzene (2.50g, 32mmol) was then added followed by the addition of aluminium chloride (27.00g, 202mmol) in a fine powder form, keeping the mixture rapidly stirred and the mixture temperature below 10°C. After refluxing for five hours the reaction was quenched by pouring the mixture into acidified ice-water (1000ml, containing 43ml conc. HCl). Organic product was extracted into dichloromethane (3 x 50ml). All the organic extracts were combined, washed with sodium hydroxide (250ml, 5% w/v) and water until the washings were neutral and dried over $MgSO_4$. Solvent was evaporated and the solid residue was dried under vacuum giving a dark brown powder. This powder was characterised without further purification by ^1H nmr (δ, $CDCl_3$, 400MHz): 7.53 (pseudo dd, 2, aromatic), 7.68 (pseudo t, 1, aromatic), 7.85 (pseudo d, 2, aromatic), MS M+1 = 272 determined by EI spectrometry, which agreed with the reported data for pentafluorobenzoylbenzene.[21]

2.6.9 Synthesis of poly(arylene vinylene)s via McMurry reaction

The syntheses of poly(4,4′-diphenylene diphenylvinylene), poly(4,4′-diphenylene-1,2-bis(pentafluorophenyl)vinylene), poly(1,3-phenylene diphenylvinylene) and poly(1,2-phenylene dimesitylvinylene) from the corresponding diketones were carried out according to the general procedure described below.

Dry THF was added to $TiCl_3$ (4mol equiv.) in a three necked flask (250ml). Solid $LiAlH_4$ (2mol equiv.) was transferred to the mixture at 0°C under positive pressure of nitrogen. This mixture was then stirred at room temperature for 30 minutes and refluxed for 60 minutes. Diketone (1mol equiv.) was added at room temperature. The mixture was then refluxed for the desired period of time. After slow addition of HCl (60-80ml, 2M) at about 0°C, the product was extracted into chloroform (3 x 50ml). The combined organic extracts were washed with brine, dried over $MgSO_4$ and filtered. After evaporating the solvent, the residue was dried under vacuum. The product was then reprecipitated from chloroform into methanol (three times), giving the desired polymers as clean powders or granules. The polymers were characterised by GPC, FTIR, ^1H nmr, ^{13}C nmr TGA and DSC as described in the Results and Discussion section (see earlier).

2.6.10 **Polymer fractionation**

The polymer was dissolved in chloroform at about 5%-wt concentration in a round bottomed flask (1000ml), which was placed in a water bath and the solution was stirred with a mechanical stirrer at about 20°C. Heptane was added dropwise until the polymer solution started to become turbid and then it was heated slowly until the solution went clear again. Once more heptane was added slowly until the solution became really cloudy. The solution was then heated slowly up to about 45°C. This was left over night to allow it to cool to the original temperature and to allow the equilibrium of high and low molecular weight polymer solution to be established. The fraction with higher molecular weight, which settled at the bottom of the flask was recovered and solvent was evaporated from the solution and the residue was dried under vacuum to give the first fraction. The whole process was repeated using the residue to collect the second fraction, and so on.

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Chapter 3

The Yamamoto polycondensation route to poly(arylene vinylene)s

3.1 Introduction

Metal promoted coupling reactions of organic halides are attractive and useful procedures for the formation of carbon-carbon σ bonds.[1] Low valent transition metals and organometallic compounds hold an important position as coupling reagents for such processes and representative examples include the nickel(0) promoted coupling reactions of Grignard reagents.[2] In 1972 Masse *et al.*[3] and Kumada *et al.*[4] independently reported that nickel-phosphine complexes catalyse the coupling reaction of Grignard reagents with aryl halides. This procedure for carbon-carbon σ bond formation was then investigated intensively by Kumada *et al.* and is often referred to as the Kumada reaction.[5-8] Since it proceeds selectively and in high yield under mild conditions, the Kumada reaction was extended to the synthesis of poly(*p*-phenylene) via the nickel complex catalysed condensation reaction of 1,4-dihalobenzenes in the presence of a stoichiometric amount of magnesium. This type of polymer synthesis was first demonstrated by Yamamoto *et al.*[9], and is often referred to as the Yamamoto polycondensation.

This chapter presents a review of the Kumada coupling reaction including a discussion of the reaction conditions involved, the reaction mechanism and the scope and limitations of the reaction. The chapter is concerned primarily with the author's work on the exploitation of the Yamamoto polycondensation in the synthesis of two poly(arylene vinylene)s; namely, poly(4,4'-diphenylene diphenylvinylene) and poly(4,4'-diphenylene dimethylvinylene). The synthesis of the former via the McMurry reaction has been described in detail in Chapter 2. Even though polymers with a degree of polymerisation of higher than 250 could be achieved via careful fractionation of the product of the McMurry reaction of 4,4'-dibenzoyl biphenyl, the frequency and distribution of *cis* and *trans* vinylenes in the polymer remained unknown. In contrast, the process described here using Yamamoto polycondensation offers the possibility of controlling the frequency, but not the distribution, of *cis* and *trans* vinylenes in the polymer by controlling the configuration of the 1,2-di(4-bromophenyl)-1,2-diphenylethene monomer used in the polymerisation. The same idea was extended to the synthesis of poly(4,4'-diphenylene dimethylvinylene), where the inclusion of methyls rather than phenyls as the vinylene substituents was expected to alter the properties, particularly the electrooptical properties, of the resultant polymer.

3.2 The Kumada reaction

3.2.1 Reaction conditions involved in the Kumada reaction

The cross coupling reaction of alkyl and aryl halides with Grignard reagents catalysed by nickel-phosphine complexes has been shown to be a quite versatile approach to carbon-carbon bond formation in organic synthesis.[10] This catalytic reaction is attractive in synthesis because of: the simple experimental procedure, mild reaction conditions, high yields and purity of the coupling products, and applicability with primary and secondary alkyl, aryl and alkenyl Grignard reagents.[11]

It was reported that the catalytic activity of the nickel complexes depends strongly upon the nature of the ligands.[11] Generally, bidentate phosphine ligands exhibit much higher catalytic activity than their unidentate counterparts. The catalytic activity is dependent on the length of the methylene chain joining the two phosphines in the bidentate ligands $Ph_2P(CH_2)_nPPh_2$ in the order $n = 3$ (dppp) > $n =$

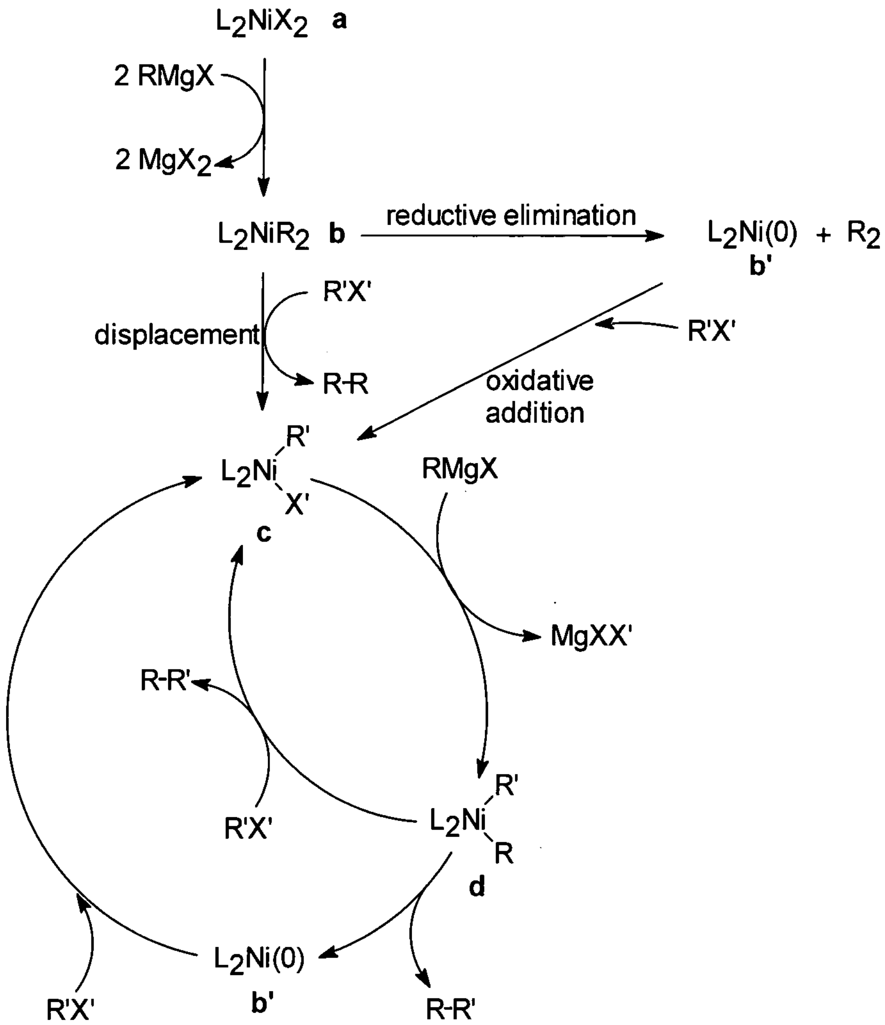
2 (dppe) > n = 4 (dppb).[11] The following general tendencies have also been observed, whereas [$NiCl_2$(dppp)] is most effective for primary and secondary alkyl and aryl Grignard reagents, [$NiCl_2(Me_2P(CH_2)_2PMe_2)$], which contains an electron donating bidentate ligand, is the most suitable catalyst for allylic and vinylic Grignard reagents. Bidentate phosphine ligands were also demonstrated to have a large stabilising effect on the catalytically active species. Triphenylphosphine is the only unidentate ligand which is practically active in the coupling reaction and it was found that for the coupling of sterically hindered aryl Grignard reagents, [$NiCl_2(PPh_3)_2$] is better than the catalysts with bidentate ligands.[11] Neutral phosphine and ligand-free nickel salts, represented by [$Ni(acac)_2$], were also found to be effective catalysts for the coupling reactions of aryl Grignard reagents.[12]

The halides may be chlorides, bromides, or iodides, although chlorides usually give the most satisfactorily results since they exhibit a reasonable reactivity and give little side reaction.[11] In some cases even aryl fluorides react in reasonable yield. However the reactivity of halobenzenes appears to be dependent upon the nature of the catalyst. Thus, while with [$NiCl_2$(dppp)] the reactivity order PhI > PhCl > PhBr > PhF was observed, with [$NiCl_2$(dppe)] the reactivity decreases in the order PhBr > PhCl > PhF.[11]

Grignard reagents are usually prepared either in diethyl ether or in THF, however, the coupling reactions tend to proceed considerably faster in diethyl ether than in THF.[11]

3.2.2 Mechanism

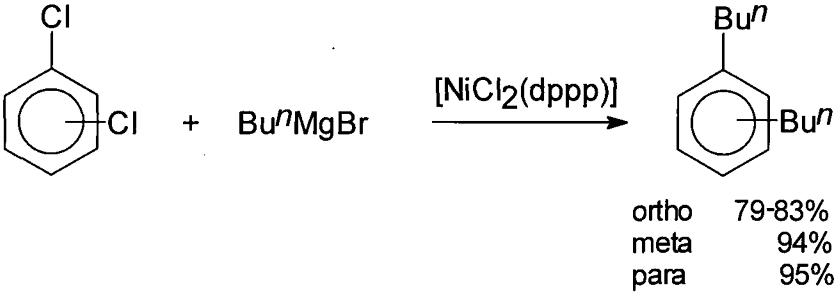
The catalytic cycle depicted in *Scheme 3.1*, which was originally proposed for the Grignard coupling with organic halides, is generally accepted now.[10,11] In *Scheme 3.1*, the square planar nickel(II) dihalide **a** is first arylated by the Grignard reagent to give a nickel complex **b** carrying two organic groups. The driving force being the reaction of the more electropositive Grignard with the less electropositive nickel halide and formation of nickel aryl and magnesium halide bonds. The complex **b** can now lose the two aryl groups via a *cis* reductive elimination, to give a very reactive nickel(0) species **b′** which immediately picks up an aryl halide by oxidative addition to give **c**. Alternatively the intermediate **b** might undergo displacement of R_2 by $R'X'$ to give **c** directly without intervention of the reactive nickel(0) intermediate **b′**. The halogen-nickel bond in **c** is readily arylated by the Grignard reagent to form the corresponding diorganonickel *cis* square planar complex **d** from which the cross-coupling product is released to give the reactive nickel(0) intermediate **b′** or by attack of the organic halide as before. By either route the complex **c** is regenerated to complete the catalytic cycle. The exact mechanism is not unambiguously defined.



Scheme 3.1 The proposed catalytic cycle for the nickel complex catalysed coupling reaction of Grignard reagents and aryl halides.

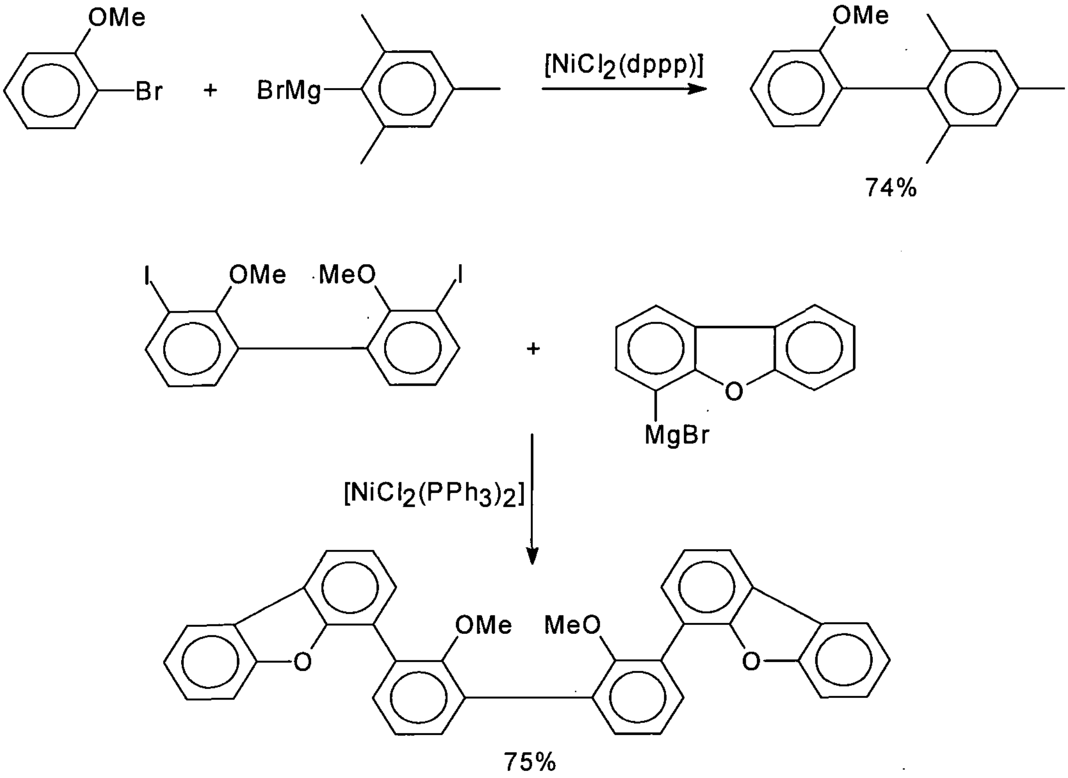
3.2.3 Scope and limitations

Representative applications of the Kumada reaction are shown below. Aromatic polyhalides are easily polyalkylated without any positional scrambling, see *Scheme 3.2.*[11,13,14]



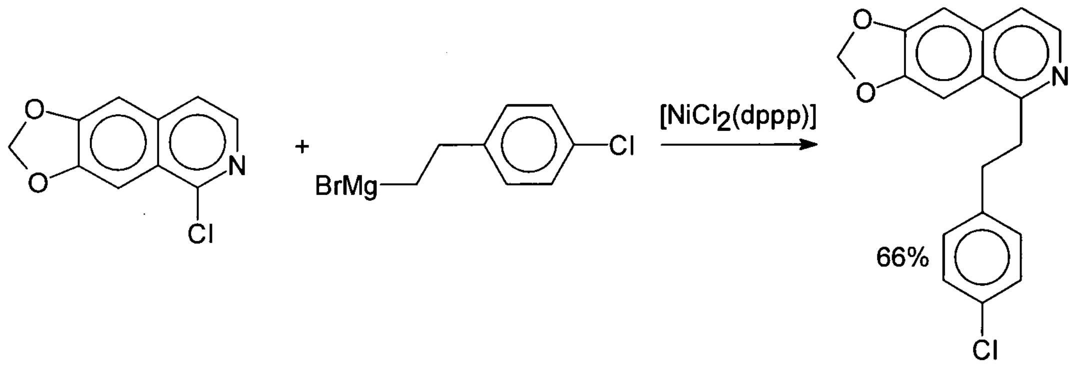
Scheme 3.2 The synthesis of dialkyl substituted benzenes via the Kumada reaction.

The following scheme presents examples of the Kumada reaction with methoxy substituted aryl halides which were reported to be unaffected by Grignard reagents.[11,15] The scheme also shows the versatility of the Kumada reaction in the coupling of sterically hindered aryl halides.



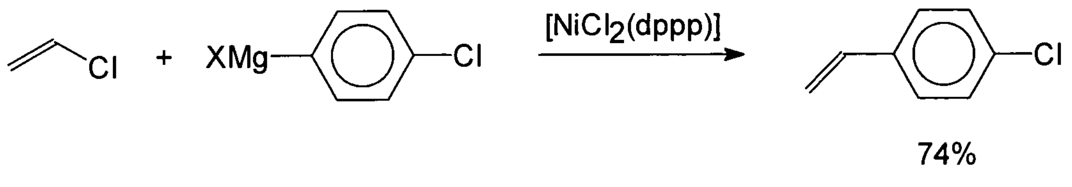
Scheme 3.3 The application of the Kumada reaction in the coupling of methoxy substituted aryl halides.

The ether functional group was shown to survive during the course of the coupling reaction, as an example an isoquinoline compound presented in *Scheme 3.4* could be coupled with Grignard reagent to form the corresponding product in a reasonably good yield.[16]



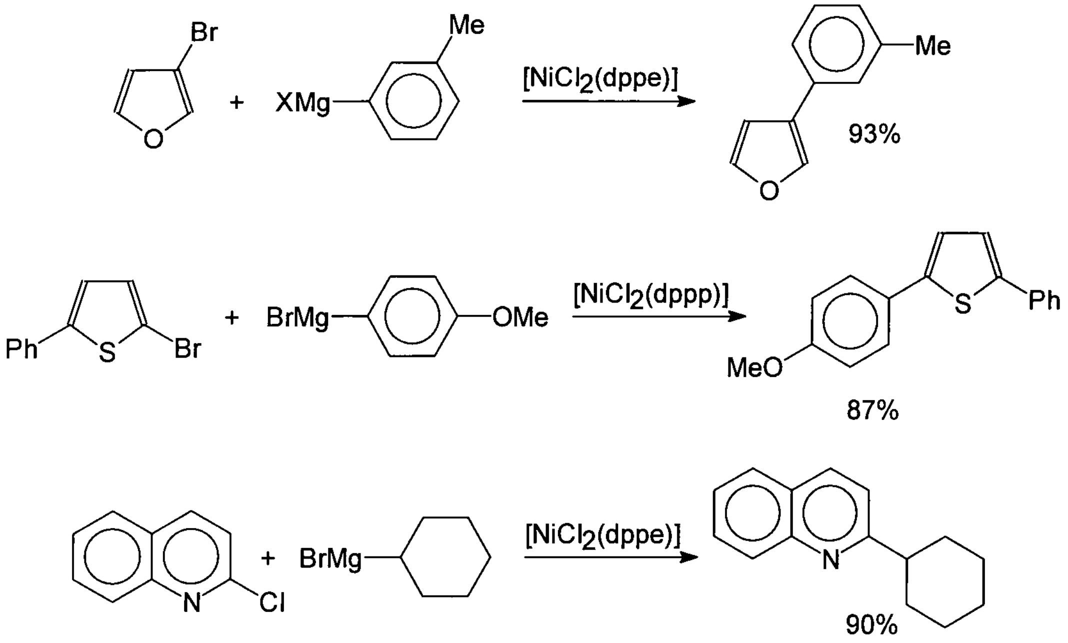
Scheme 3.4 The application of the Kumada reaction in the coupling of a heteroaryl halide bearing an ether functionality.

It was found that alkenyl halides are among the most reactive halides, particularly vinyl chloride.[11] The isomerically pure 4-chlorostyrene shown in *Scheme 3.5*, was produced from vinyl chloride and the corresponding Grignard reagent on an industrial scale.[10]



Scheme 3.5 The synthesis of 4-chlorostyrene via the Kumada reaction.

Also heterocyclic halides, such as furan[17], thiophene[18] and quinoline[16] halides undergo this coupling reaction readily, see *Scheme 3.6*.



Scheme 3.6 Examples of the Kumada reaction involving heterocyclic halides.

It has been shown that the Kumada coupling reaction is widely applicable with a variety of Grignard reagents and various organic halides, with only a few limitations. The most serious limitation is that the substituents on the organic halides are restricted to those which do not react with Grignard reagents.[11]

As mentioned earlier, the application of the Kumada reaction was extended to the synthesis of poly(*p*-phenylene) and analogous polymers.[9,19,20] However, to the best of the author's knowledge, this route has not yet been used in the synthesis of poly(arylene vinylene)s. The polymerisation procedure outlined by Yamamoto *et al.*[9] and Feast *et al.*[19] was to be followed by the author in an effort to make structurally well defined poly(arylene vinylene)s and this work will be discussed in the next sections.

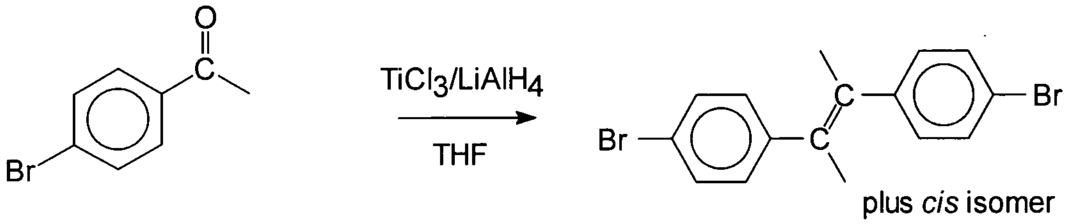
3.3 Results and Discussion

3.3.1 Aryl dibromide monomers

Throughout the course of this piece of work two dibromide monomers were used, namely 2,3-di(4-bromophenyl)-2-butene and 1,2-di(4-bromophenyl)-1,2-diphenylethene. The McMurry reaction, which is a well known method for the synthesis of alkenes from ketones or aldehydes[21], was used to prepare the monomers from the corresponding ketones. The McMurry reagent was prepared, in this case, by reduction of $TiCl_3$ with $LiAlH_4$ in THF, see experimental section for details. A review of the McMurry reaction is presented in Chapter 2.

3.3.1.1 *2,3-Di(4-bromophenyl)-2-butenes*

The synthesis of 2,3-di(4-bromophenyl)-2-butenes (*Scheme 3.7*) was carried out by McMurry coupling of 4-bromoacetophenone.



Scheme 3.7 The synthesis of 2,3-di(4-bromophenyl)-2-butenes via the McMurry reaction.

The product was recovered as colourless crystals which were shown by ^1H nmr spectroscopy to be a mixture of *cis* and *trans* isomers, one of which forms the major product. In the ^1H nmr spectrum, two singlet peaks can be seen at 2.12 and 1.84 ppm with the former peak corresponding to the major product. Both peaks are attributed to methyl hydrogens, CH_3, in *cis* and *trans* isomers, however, it is not certain which one is which.

Inamoto *et al.* have discussed the stereochemical assignment of 2,3-di(4-bromophenyl)-2-butenes.[22] In an attempt to solve this assignment problem, the nmr chemical shifts of the methyl hydrogens for a series of substituted αα′-dimethylstilbenes were measured. The shielding effect experienced by the methyl groups, which arises from the π electron current in the phenyl groups, varies with the position of the phenyl groups in the isomer. Calculations were made in an attempt to correlate the stereochemistry of the various substituted αα′-dimethylstilbenes with the chemical shifts of the methyl hydrogens. On the basis of these calculations, it was suggested that methyl hydrogens in *trans* isomers absorb at higher field than those in *cis* isomers. It was also found that the isomers assigned *trans* stereochemistry on this basis had higher melting points than the corresponding isomers assigned *cis* stereochemistry, which was not unexpected. In the case of 2,3-di(4-bromophenyl)-2-butene, the melting points of *cis* and *trans* isomers were recorded at 82 and 146°C respectively. At least one group, namely Light *et al.*[23], supported the assignment made by Inamoto *et al.*[22]

However, in 1978 McMurry and co-workers reported the synthesis of 2,3-diphenyl-2-butene from acetophenone in which a product with a 9:1 mixture of isomers was recovered.[24] In the ^1H nmr spectra, it was shown that the methyl hydrogen in major and minor products displayed resonances at 2.14 and 1.87 ppm respectively. According to the earlier assignments,[22,23] this was a mixture of 90% *cis* and 10% *trans* isomers, however, McMurry and co-workers believed that these assignments were almost certainly wrong since analogous compounds such as stilbene and stilbestrol (3,4-di(4-hydroxyphenyl)-3-hexene) were known to prefer a *trans* geometry. This argument was supported by Richardson in 1981.[25]

The author has been able to provide an unambiguous resolution of this argument by obtaining the crystal structure of one of the isomers. *Figure 3.1* presents the crystal structure of the major product. This isomer shows a methyl hydrogen resonance at 2.12 ppm in the ^{1}H nmr spectrum, see *Figure 3.2.* Two structures are shown in *Figure 3.1* because there are two independent molecules in the crystal which are not related by any symmetry. The full data for this structure are recorded in *Appendix 2.7.1.*

The ^{13}C nmr spectrum, *Figure 3.3,* shows the expected number of peaks and is consistent with the assigned structure.

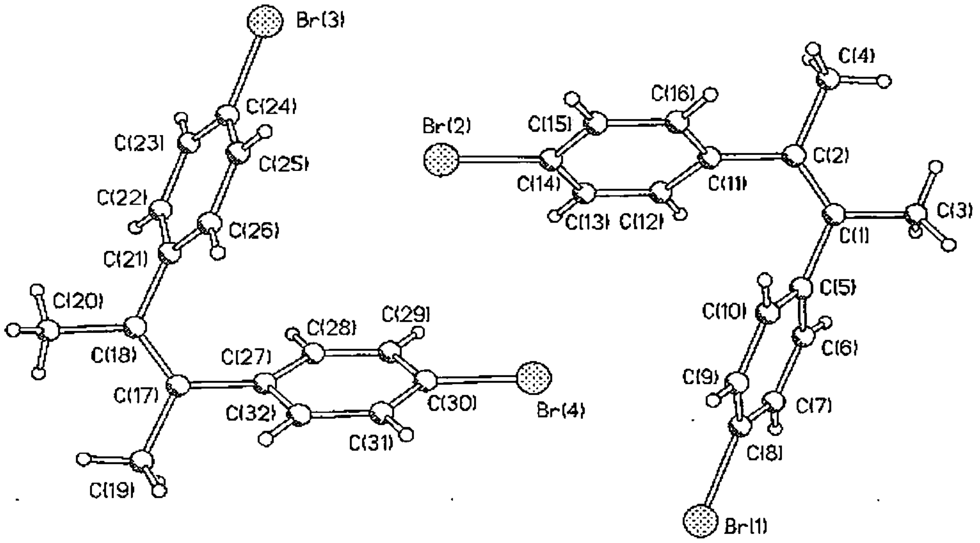


Figure 3.1 The crystal structure of *cis*-2,3-di(4-bromophenyl)-2-butene.

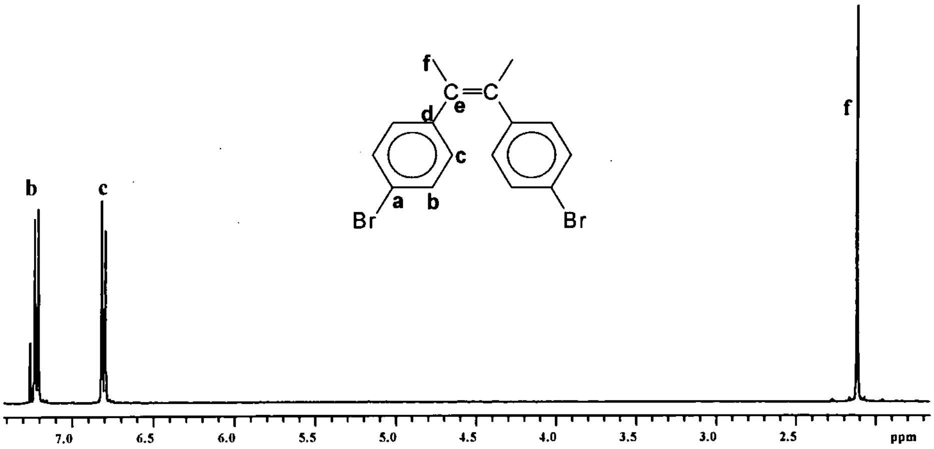


Figure 3.2 ^{1}H Nmr spectrum of *cis*-2,3-di(4-bromophenyl)-2-butene.

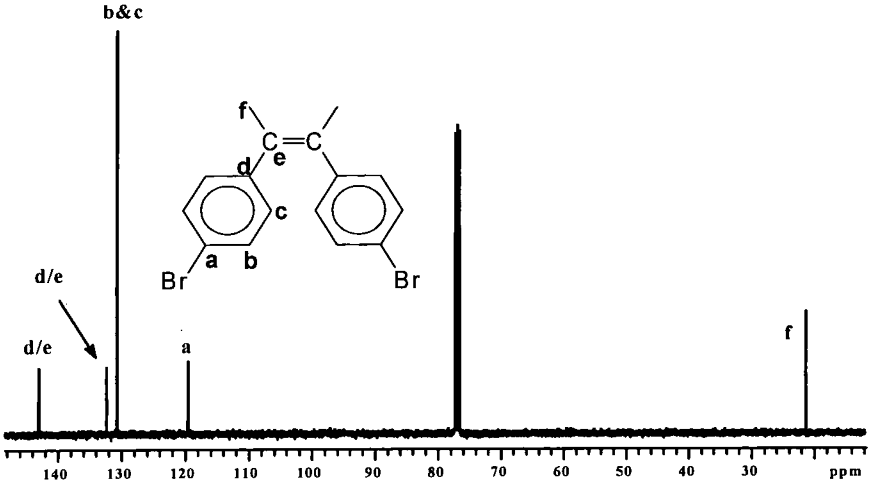


Figure 3.3 ^{13}C Nmr spectrum of *cis*-2,3-di(4-bromophenyl)-2-butene.

Thus it is confirmed that the formation of the *cis* isomer is favoured in the synthesis of 2,3-di(4-bromophenyl)-2-butenes via the McMurry reaction. The *cis* isomer was found to constitute about 88% of the recovered product.

In the FTIR spectrum (*Appendix 2.1.1*) obtained from the *cis*-2,3-di(4-bromophenyl)-2-butene, the peak corresponding to the aryl carbon skeleton breathing mode can be seen at 1584cm^{-1} and the peak at 1482cm^{-1} can be attributed to an aryl carbon-hydrogen bending mode. The peak centred at 2915cm^{-1} is attributed to the methyl hydrogen stretching mode and the peak corresponding to the aryl hydrogen stretching mode is partially overlapped by this methyl hydrogen peak.

Since the isomer with the methyl hydrogen resonance at 2.12 ppm in ^1H nmr turned out to be the *cis* isomer, it is also confirmed that the methyl hydrogens in the *trans* isomer of 2,3-di(4-bromophenyl)-2-butene absorb at higher field in the ^1H nmr than those in the *cis* isomer, see *Figure 3.4.* The ^{13}C nmr spectrum presented in *Figure 3.5* shows the expected number of peaks and is consistent with the assigned structure.

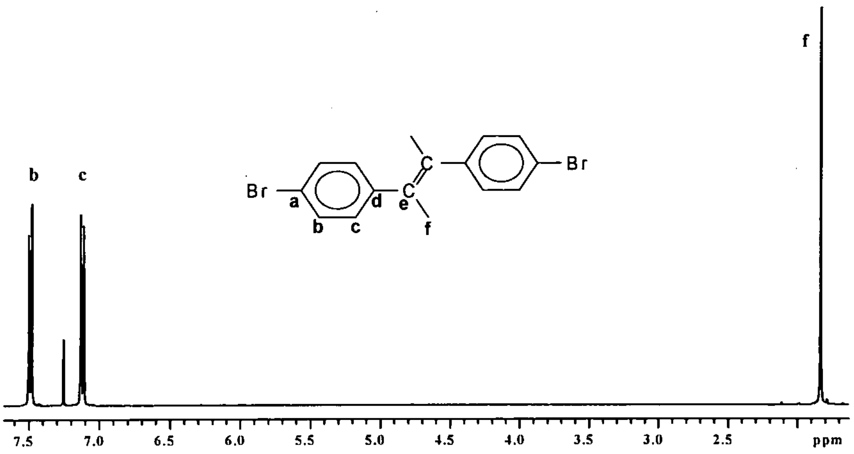


Figure 3.4 ^1H Nmr spectrum of *trans*-2,3-di(4-bromophenyl)-2-butene.

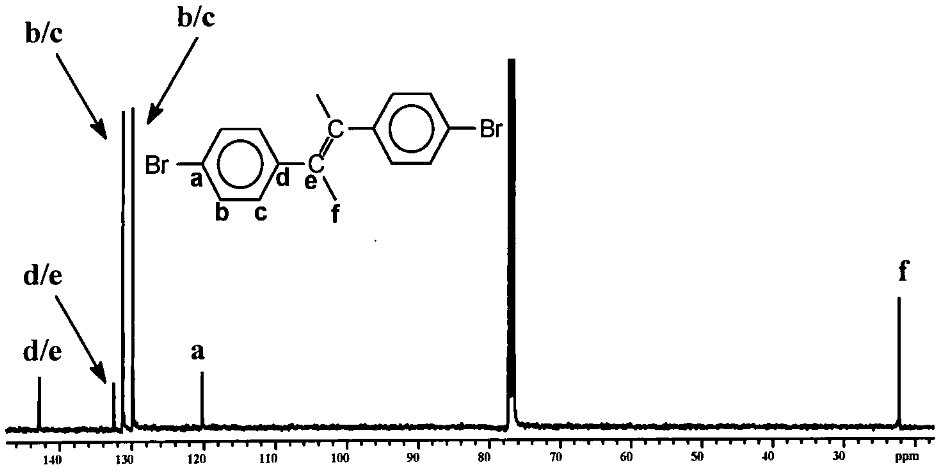
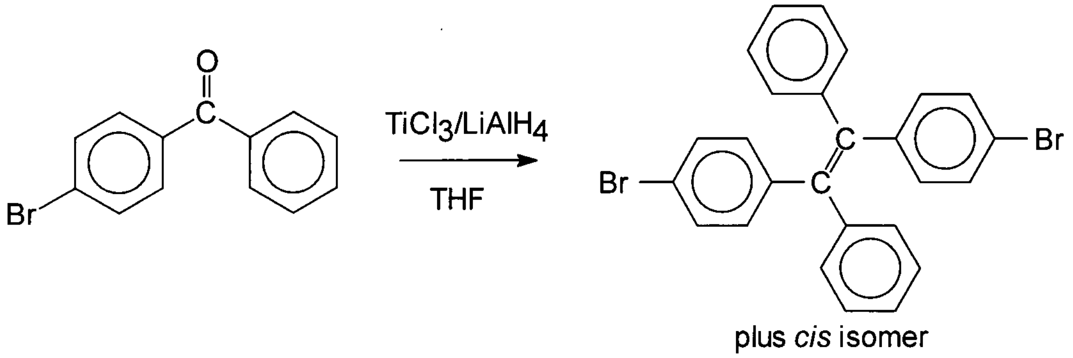


Figure 3.5 ^{13}C Nmr spectrum of *trans*-2,3-di(4-bromophenyl)-2-butene.

In the FTIR spectrum (*Appendix 2.1.2*) of *trans*-2,3-di(4-bromophenyl)-2-butene, the peak at 1583cm^{-1} can be assigned to the aryl carbon skeleton breathing mode. The peak attributed to an aryl hydrogen bending mode is present at 1486cm^{-1}, indicating a small shift towards higher frequency in comparison to the corresponding peak found in the *cis* isomer. The methyl hydrogen stretching mode can be seen at 2914cm^{-1}. This peak partially overlaps the peak corresponding to the aryl hydrogen stretching mode. The MS spectrum (EI) of the *trans*-2,3-di(4-bromophenyl)-2-butene shows the expected molecular ion and is presented in *Appendix 2.4.1*.

3.3.1.2 *1,2-Di(4-bromophenyl)-1,2-diphenylethenes*

A similar procedure to that described in the synthesis of 2,3-di(4-bromophenyl)-2-butene was followed for the preparation of 1,2-di(4-bromophenyl)-1,2-diphenylethene except 4-bromoacetophenone was replaced by 4-bromobenzophenone, see experimental section for details.



Scheme 3.8 The synthesis of 1,2-di(4-bromophenyl)-1,2-diphenylethenes via the McMurry reaction.

A similar product to that found in the synthesis of 2,3-di(4-bromophenyl)-2-butene was produced in the sense that the product was a mixture of *cis* and *trans* isomers, in this mixture the 'major' isomer constitutes about 56% of the overall yield. Both isomers were obtained in their pure forms by repeated recrystallisation from a 2:3 mixture of toluene and ethanol, the major isomer proving to be the least soluble. Each isomer collected showed a purity in excess of 98% as measured by ^{1}H nmr spectroscopy. The assignments of the *cis* and *trans* isomers were made on the basis of the crystal structure obtained for a sample of the 'major' isomer, see *Figure 3.6* (full data are recorded in *Appendix 2.7.2*)

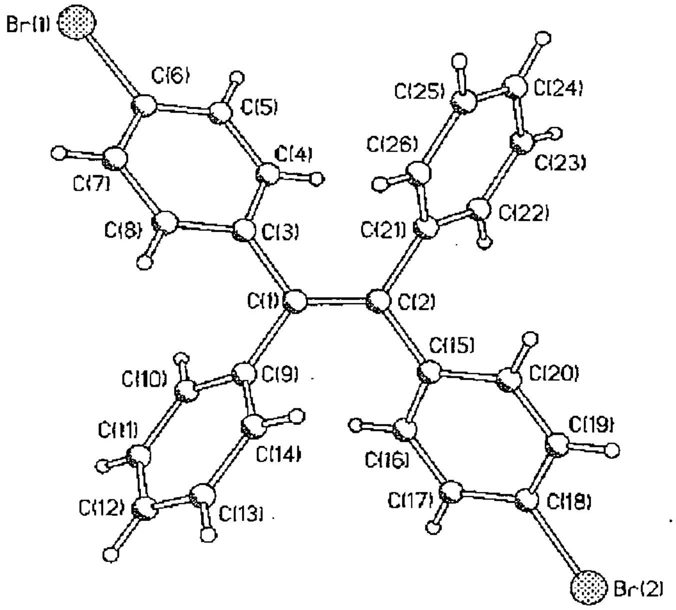


Figure 3.6 The crystal structure of the 'major' product, namely *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene.

In contrast to the case of 2,3-di(4-bromophenyl)-2-butene in which the *cis* isomer forms the major product, the formation of the *trans* isomer was slightly favoured in the synthesis of 1,2-di(4-bromophenyl)-1,2-diphenylethene via the McMurry reaction. *Figure 3.7* presents the ^{1}H nmr spectra of both *cis*- and *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene.

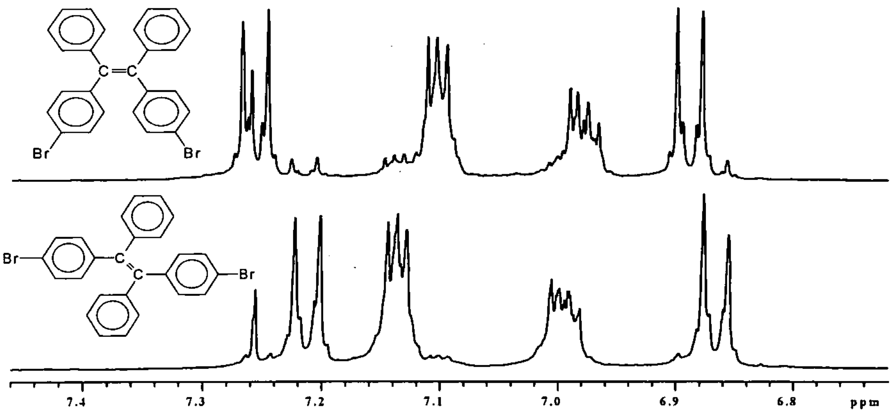


Figure 3.7 ^{1}H Nmr spectra of *cis*- (top) and *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene (bottom).

The ^{13}C nmr spectra (*Figure 3.8*) of the both *cis*- and *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene show the expected number of signals and are consistent with the assigned structures. The expected molecular ion for the *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene was shown in the MS spectrum, see *Appendix 2.4.2*.

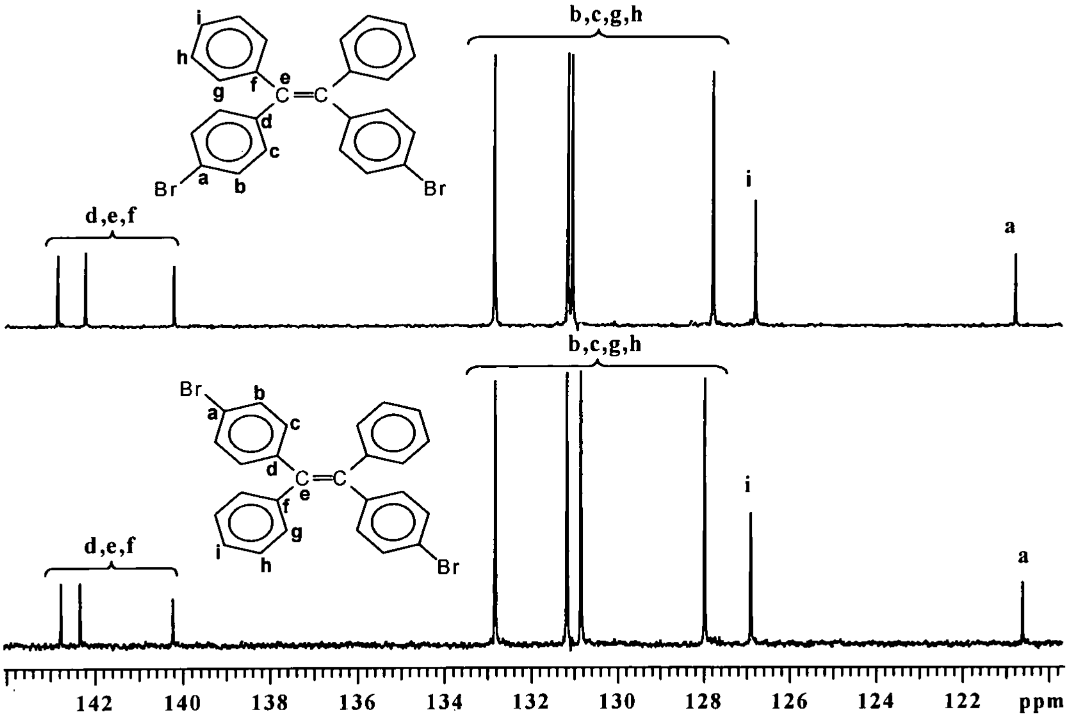


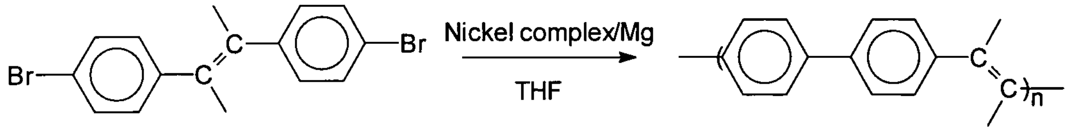
Figure 3.8 ^{13}C Nmr spectra of the *cis*- (top) and *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene (bottom).

In the FTIR spectrum (*Appendix 2.1.3*) of the mixture of isomers, the peak corresponding to the aryl carbon skeleton breathing mode can be seen at 1598cm^{-1} and the strong three peaks at 1487, 1442 and 1392cm^{-1} are attributed to the aryl hydrogen bending modes. The multiple peak centred at 3022cm^{-1} is assigned to the aryl hydrogen stretching mode.

3.3.2 **Polymers**

3.3.2.1 ***Poly(4,4'-diphenylene dimethylvinylene)s***

The synthetic procedure outlined by Yamamoto *et al.*[9] and Feast *et al.*[19] was followed to prepare poly(4,4'-diphenylene dimethylvinylene)s from the corresponding dibromides, see experimental section for details. Throughout these studies of the synthesis of these polymers, two nickel complexes were examined as the catalysts, namely bis(triphenylphosphine)nickel dichloride and 1,3-bis(diphenylphosphino)propane nickel dichloride.



Scheme 3.9 The synthesis of poly(*trans*-4,4'-diphenylene dimethylvinylene) via the Yamamoto polycondensation.

The polymer was recovered as a faint yellow powder and was found to give a weak fluorescence in the yellow region of the spectrum when exposed to u.v. radiation. The results obtained and the reaction condition used in this synthesis are summarised in *Table 3.1*.

Table 3.1 Molecular weight data and the reaction conditions used in the synthesis of poly(4,4'-diphenylene dimethylvinylene)s via the Yamamoto polycondensation.

run	reaction time (days)	% *cis* isomer	catalyst[1,2]	$\overline{M}_n$	$\overline{M}_w$	DP[3]
1	2	100	B	1080	1800	5
2	2	90	B	1300	2110	6
3	2	80	B	1330	2480	7
4	4	80	B	1230	2110	6
5	2	100	D	2660	4000	13
6	2	90	D	2850	4600	14
7	2	80	D	2915	5000	14

[1] B = bis(triphenylphosphine)nickel dichloride
[2] D = 1,3-bis(diphenylphosphino)propane nickel dichloride
[3] DP = degree of polymerisation

In general the molecular weights obtained for all samples were quite low. The highest degree of polymerisation obtained, which was 14, is just in excess of the best value reported by Feast *et al.* in the synthesis of dialkyl substituted poly(*p*-phenylene).[19] Although Feast *et al.* reported that nickel complex B was found to give the best result in terms of molecular weight in their work, the application of nickel complex D in this synthesis resulted in a two-fold increase in molecular weight as compared to that obtained when the nickel complex B was used.

As shown in *Table 3.1*, the same trend is observed regardless of the catalyst used in the polymerisation, in the sense that the molecular weight obtained increases when the *cis* isomer content of the monomer mixture used decreases. In the range studied, the molecular weight obtained reached a maximum value when a monomer mixture with about 80% *cis* isomer was used, however, due to the limited availability of the *trans* monomer, the optimum *cis*:*trans* isomer ratio required to produce high molecular weight polymer was not established. Doubling the length of the reaction time from two to four days did not result in improved molecular weight.

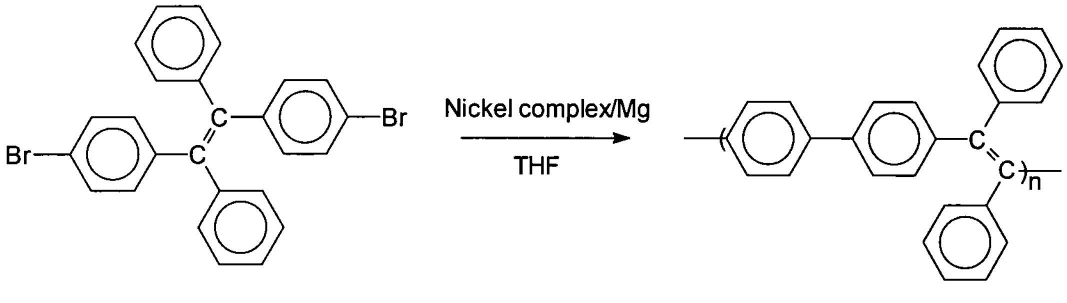
In the ^{1}H nmr spectra (*Appendix 2.2.5-2.2.7*), peaks attributed to the methyl hydrogens and aryl hydrogens were broadened as compared to the corresponding peaks in the monomer, which is not unexpected. The spectra also show that no significant impurity was present in the samples. The ^{13}C nmr spectra (*Appendix 2.3.5-2.3.6* show the expected number of signals and are consistent with the assigned structure.

In the FTIR spectra (*Appendix 2.1.4-2.1.6*), the peak at 1604cm^{-1} can be attributed to the aryl carbon skeleton breathing mode and the peak corresponding to an aryl hydrogen bending mode can be seen at 1492cm^{-1}. Another peak which is assigned to aryl hydrogen stretching is seen at 3021cm^{-1}. The multiple peak centred at 2909cm^{-1} is attributed to the methyl carbon-hydrogen stretching mode.

Thermogravimetric analysis (TGA) shows that thermal stability of the polymer is not as good as that found for other members of poly(arylene vinylene)s. The polymer starts to decompose at about 140°C and gradually loses weight showing 3.5% loss at 300°C. Other thermal characteristics of the polymer such as glass transition and melting temperatures were not detected in the range of 25 to 140°C; measurement above 140°C could not be done since the polymer starts to decompose at this temperature.

3.3.2.2 *Poly(4,4'-diphenylene diphenylvinylene)s*

The synthesis of poly(4,4'-diphenylene diphenylvinylene) from the corresponding dibromide monomer as shown in *Scheme 3.10* was carried out according to the procedure outlined by Yamamoto *et al.*[9] and Feast *et al.*[19] In the course of this study three nickel complexes were used as the catalysts, namely bis(triphenylphosphine)nickel dichloride, 1,3-bis(diphenylphosphino)propane nickel dichloride and nickel acetylacetonate.



Scheme 3.10 The synthesis of poly(*trans*-4,4'-diphenyelne diphenylvinylene) via the Yamamoto polycondensation.

In the first set of experiments, polymerisations were carried out using the dibromide monomer with about 1:1 mixture of *cis* and *trans* isomers with three different nickel catalysts and two days reaction duration. The results obtained and the catalysts used are tabulated below.

Table 3.2 Molecular weight data and catalysts used in the synthesis of poly(4,4'-diphenylene diphenylvinylene)s via the Yamamoto polycondensation.

run	catalyst[1,2,3]	$\overline{M}_n$	$\overline{M}_w$	DP[4]
1	B	3600	4900	11
2	C	900	1650	3
3	D	2900	3700	9

[1] B = bis(triphenylphosphine)nickel dichloride, [2] C = nickel acetylacetonate,
[3] D = 1,3-bis(diphenylphosphino)propane nickel dichloride,
[4] DP = degree of polymerisation

The polymer was recovered as a yellow precipitate and was found to give a strong greenish yellow fluorescence when irradiated with u.v. light. The results obtained are in agreement with the report of Feast *et al.* in the sense that the application of the nickel complex B produced the best polymer in terms of molecular weight achieved.[19] However, the degree of polymerisation obtained shows a slightly lower value than that found by Feast *et al.* in the synthesis of dialkyl substituted poly(*p*-phenylene).

Based on the results obtained in the first set of experiments, polymerisations of the dibromide monomer mixture with various of *cis*:*trans* isomer ratios were carried out using nickel complex B as the catalyst. The results obtained and the reaction conditions used are summarised in *Table 3.3*.

Table 3.3 Molecular weight data and the reaction conditions used in the synthesis of poly(4,4'-diphenylene diphenylvinylene)s via the Yamamoto polycondensation.

run	reaction time (days)	% *cis* isomer	$\overline{M}_n$	$\overline{M}_w$	DP[1]
1	2	59	1200	2200	4
2	2	48	3600	4900	11
3	2	37	3300	4400	10
4	4	48	4300	5600	13

[1] DP = degree of polymerisation

As shown in *Table 3.3*, a similar trend to that observed in the synthesis of poly(4,4'-diphenylene dimethylvinylene) can be seen, in that the molecular weight obtained increases as the proportion of *cis* isomer in the monomer mixture used decreases. The number average molecular weight reached a maximum value when the monomer mixture with about 1:1 mixture of *cis* and *trans* isomers was used. Thus it is possible to conclude that, in this case, the application of the monomer with about 1:1 ratio of *cis* and *trans* isomers is required in order to produce high molecular weight polymer. The degree of polymerisation obtained from the sample of run 4 in *Table 3.3* was 13, in which the reaction time was extended from two to four days. This figure is as the same as the best degree of polymerisation reported by Feast *et al.* in the synthesis of dialkyl substituted poly(*p*-phenylene).[19]

In the FTIR spectra (*Appendix 2.1.7-2.1.9*), the peak at 1596cm^{-1} is attributed to the aryl carbon skeleton breathing mode and the peak corresponding to an aryl carbon-hydrogen bending mode can be seen at 1493cm^{-1}. The aryl hydrogen stretching mode is seen at 3024cm^{-1}. The ^{1}H and ^{13}C nmr spectra were straightforward and consistent with the assigned structure (see *Appendix 2.2.7-2.2.8* and *2.3.7-2.3.8*). In these cases it was possible, to assign polymer signals to *cis* and *trans* vinylene repeat units and using this data to assign the *cis/trans* distribution in the analogous polymer made by McMurry coupling (see Chapter 2). The data is not good enough to make an accurate assignment but it is clear that in McMurry coupling there is a roughly 50:50 *cis:trans* distribution with a slight predominant of *trans* vinylenes in the poly(4,4'-diphenylene diphenylvinylene) product.

Thermogravimetric analysis (TGA) shows that the polymer (run 4 *Table 3.3*) starts to decompose at 320°C and, as measured by DSC, the polymer was found to have a glass transition temperature of 230°C, which is the same value as that found for the poly(4,4'-diphenylene diphenylvinylene) prepared via the McMurry reaction and adds further support to the assignment of roughly 50:50 *cis:trans* isomer distribution in that polymer.

3.4 Conclusions

Although restrictions imposed by time and monomer costs have limited the range of experiments carried out in this study it has been shown that the application of Yamamoto polycondensation provides a potentially useful route for the synthesis of poly(4,4'-diphenylene dimethylvinylene)s and poly(4,4'-diphenylene diphenylvinylene)s and related systems. Although the degree of polymerisation achieved in this work is generally just in excess of 10, this represents a chain with 20 phenylene and 10 vinylene units and this was felt to be long enough to establish whether or not these materials had potentially interesting luminescence characteristics (see Chapter 5). Rather more importantly, it has been shown that poly(arylene vinylene)s with controllable composition of *cis* and *trans* vinylenes in the polymer chain can be successfully synthesised via this route.

It was found that, particularly in the synthesis of poly(4,4'-diphenylene diphenylvinylene), a monomer mixture with about 1:1 ratio of *cis* and *trans* isomers gives the highest molecular weight polymers. The polymers produced in this work were found to have good solubility in common organic solvents such as chloroform, toluene and THF as well as good thermal stability, particularly poly(4,4'-diphenylene diphenylvinylene).

3.5 **Experimental**

4-Bromobenzophenone, 4-bromoacetophenone, lithium aluminium hydride, magnesium turnings, bis(triphenylphsophine)nickel dichloride, 1,2-bis(diphenylphosphino)propane nickel dichloride and nickel acetylacetonate were purchased from Aldrich Company Ltd. THF was purchased from BDH Chemical Company Ltd. All reagents were used without further purification except 4-bromoacetophenone which was recrystallised from ethanol (2 times). THF was dried by distillation from sodium metal/sodium benzophenone ketyl radical prior to use.

^1H Nmr and ^{13}C nmr were recorded using a Varian 400MHz spectrometer and were referenced to Me_4Si. IR Spectra were recorded using a Perkin-Elmer 1600 series FTIR spectrometer. GPC analyses were performed using a Waters differential diffractometer as detector, three Polymer Laboratories gel columns (exclusion limits 100, 10^3, 10^5Å) and chloroform as eluent. Columns were calibrated using polystyrene standards (Polymer Labs). DSC measurements were performed using a Perkin-Elmer DSC7, at scanning rate of 10°C/min, the temperature scale was calibrated using the melting points of indium at 100°C and zinc at 400°C. Thermogravimetric analysis was carried out under nitrogen using a TG 760 series instrument (Rheometric Scientific Ltd.) at scanning rate of 10°C/min.

3.5.1 **Synthesis of 2,3-di(4-bromophenyl)-2-butenes**

$TiCl_3$ (11.70g, 76mmol) and dry THF (150ml) were transferred under a dry oxygen free nitrogen atmosphere into a two-necked round bottomed flask (250ml) fitted with a condenser, dry nitrogen inlet and a magnetic stirrer. The dry oxygen free nitrogen atmosphere was maintained through the experiment until destruction of excess reagents. After immersing the flask into an ice bath, $LiAlH_4$ (1.43g, 38mmol) was slowly added over a period of approximately half an hour while stirring rapidly. The mixture was refluxed for one hour. The resultant black slurry was allowed to cool to room temperature and 4-bromoacetophenone (7.55g, 38mmol) was added. After a further 20 hours at reflux, the mixture was cooled in an ice bath and dilute HCl (100ml, 2M) was added slowly to quench the reaction and destroy excess coupling reagents. The product was then extracted into chloroform (3 x 100ml), solvent was evaporated from the combined extracts to give a yellow oil which was then eluted through neutral alumina using hexane to give as a colourless oil a mixture of *cis*-and *trans*-2,3-di(4-bromophenyl)-2-butene (3.35g, 51 mole % yield w.r.t. 4-bromoacetophenone). Recrystallisation from hexane repeatedly gave the pure *cis*-2,3-di(4-bromophenyl)-2-butene, m.p. 80.2-81.8°C (lit.[22] 82°C); found: C 52.39, H 3.59, $C_{16}H_{14}Br_2$ requires C 52.49, H 3.85 %, ^{1}H nmr (δ, $CDCl_3$, 400MHz): 7.22 (pseudo d, 4, aromatic C**H**), 6.81 (pseudo d, 4, aromatic C**H**) and 2.12 (s, 6, C**H**$_3$), ^{13}C nmr (δ, $CDCl_3$, 100MHz): 21.4 (**C**H$_3$), 119.7 (**C**Br), 130.8 (aromatic **C**H), 130.9 (aromatic **C**H), 132.5 (alkylidene **C**) and 143.1 (aromatic **C**), FTIR (KBr disc, ν_{max}/cm^{-1}): 2987, 2915, 1584, 1482, 1392, 1074, 1007, 827, 725, 559, 525, 476. The same procedure was applied to isolate the pure *trans*-2,3-di(4-bromophenyl)-2-butene, m.p. 140.3-142.1°C (lit.[22] 146°C). The product was characterised by: Mass Spectroscopy; M+1 ion = 365 determined by EI mass spectrometry, ^{1}H nmr (δ, $CDCl_3$): 7.49 (pseudo d, 4, aromatic C**H**), 7.14 (pseudo d, 4, aromatic C**H**) and 1.84 (s, 6, C**H**$_3$), ^{13}C nmr (δ, $CDCl_3$, 100MHz): 22.3 (**C**H$_3$), 120.2 (**C**Br), 130.0 (aromatic **C**H), 131.4 (aromatic **C**H), 132.6 (alkylidene **C**) and 142.9 (aromatic **C**), FTIR (KBR disc, ν_{max}/cm^{-1}): 2940, 2914, 1583, 1486, 1443, 1391, 1069, 1005, 828, 784, 719, 608, 527.

3.5.2 Synthesis of 1,2-di(4-bromophenyl)-1,2-diphenylethenes

Lithium aluminium hydride (1.45g, 38mmol) was slowly added to a slurry of titanium(III)chloride (11.80g, 76mmol) in dry THF (150ml) under a dry nitrogen atmosphere at about 0°C while stirring rapidly. The mixture was then refluxed for one hour. At room temperature, 4-bromobenzophenone (10.00g, 38mmol) was added and this mixture was refluxed for 20 hours. The reaction was quenched by adding dilute hydrochloric acid (2M, 100ml) into the mixture at room temperature while stirring. The product was extracted into chloroform (3 x 50ml), washed with brine and dried over magnesium sulphate. The solvent was evaporated from the combined extracts and the residual yellow oil was reprecipitated into methanol. The precipitate was collected and dried to give a *cis/trans* mixture of 1,2-di(4-bromophenyl)-1,2-diphenylethene (7.30g, 78% mole yield w.r.t. 4-bromobenzophenone). Crystallisation from a mixture of ethanol and toluene (3:2, v/v) repeatedly, yielded the pure *cis-1,2-di(4-bromophenyl)-1,2-diphenylethene*, m.p. 214.3-214.6°C. The product was characterised by: ^{1}H nmr (δ, $CDCl_3$, 400MHz), see *Appendix 2.2.3*, ^{13}C nmr (δ, $CDCl_3$, 100MHz): 120.8 (**C**Br), 126.8 (aromatic **C**H), 127.8 (aromatic **C**H), 131.1 (aromatic **C**H), 131.2 (aromatic **C**H), 132.9 (aromatic **C**H), 140.2 (alkylidene **C**), 142.3 (aromatic **C**) and 142.9 (aromatic **C**). The same procedure was applied to isolate the pure *trans-1,2-di(4-bromophenyl)-1,2-diphenylethene*, m.p. 214.5-214.9°C; found: C 63.82, H 3.49, M+1 ion = 490 determined by EI mass spectrometry, $C_{26}H_{18}Br_2$ requires C 63.70; H 3.70 %, Molecular mass, 490.24, ^{1}H nmr (δ, $CDCl_3$, 400MHz), see *Appendix 2.2.4,* ^{13}C nmr (δ, $CDCl_3$, 100MHz): 120.6 (**C**Br), 126.9 (aromatic **C**H), 128.0 (aromatic **C**H), 130.9 (aromatic **C**H), 131.2 (aromatic **C**H), 132.8 (aromatic **C**H), 140.2 (alkylidene **C**), 142.3 (aromatic **C**) and 142.8 (aromatic **C**), FTIR (KBr disc, ν_{max}/cm^{-1}):, 3022, 1597, 1487, 1442, 1392, 1071, 1010, 759, 697.

3.5.3 Synthesis of poly(4,4'-diphenylene dimethylvinylene)s

Dry THF (40ml) was added to a mixture 2,3-di(4-bromophenyl)-2-butene (1.60g, 4mmol) and magnesium turnings (0.10g, 4mmol) under a dry nitrogen atmosphere in a two necked round bottomed flask (100ml) fitted with a condenser and a magnetic stirrer. Once the Grignard reaction started (cloudiness and heat) the mixture was maintained at reflux for about one hour. At room temperature bis(triphenylphosphine)nickel dichloride (86mg, 3 mole % w.r.t. dibromide) was added to the reaction mixture while flushing with dry nitrogen. After about 2 days at reflux, the reaction mixture was concentrated to about 25ml and poured into methanol (ca 200ml). The precipitate was collected, washed with dilute hydrochloric acid and dried. This product was extracted into chloroform using a Soxhlet apparatus for about 20 hours. The resultant extract was concentrated to about 10ml and reprecipitated into acetone. The precipitate was collected and dried under vacuum giving the desired poly(4,4'-diphenylene dimethylvinylene)s as clean faint yellow powders. The polymer was characterised by GPC, FTIR, ^{1}H nmr, ^{13}C nmr, TGA and DSC (see Results and Discussion section).

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

Magnesium turnings (0.09g, 3.7mmol) and 1,2-di(4-bromophenyl)-1,2-diphenylethene (1.80g, 3.7mmol) were placed in a two necked round bottomed flask (100ml) to which dry THF (50ml) was added under a dry nitrogen atmosphere. After initiation of the Grignard reaction the mixture was maintained at reflux for about one hour. Bis(triphenylphosphine)nickel dichloride (72mg, 3 mole % w.r.t. dibromide) was added to the reaction mixture at room temperature while flushing with dry nitrogen. After refluxing the mixture for about two days, it was concentrated to about 25ml and poured into methanol. The resultant precipitate was collected, washed with dilute hydrochloric acid and dried. This product was extracted with chloroform using a Soxhlet apparatus for about 20 hours. The extract was concentrated to about 10ml and reprecipitated into acetone. The product was collected and dried under vacuum giving the clean poly(4,4'-diphenylene diphenylvinylene) as a yellow precipitate. The polymer was characterised by GPC, ^{1}H nmr ^{13}C nmr, FTIR, TGA and DSC (see Results and Discussion section).

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Chapter 4

The Suzuki coupling approach to poly(arylene vinylene)s

4.1 Introduction

In 1981, Suzuki and his co-workers reported that benzene boronic acid could be coupled with aryl halides to form the corresponding biaryls.[1] This cross-coupling reaction, now usually known as the Suzuki reaction, which is catalysed by tetrakis(triphenylphosphine)palladium(0), in benzene or toluene and requires two equivalents of aqueous sodium carbonate solution, has turned out to be a very useful method for the synthesis of poly(arylene)s[2-6] and poly(arylene vinylene)s.[7,8] The polymers are structurally pure and, in favourable cases, show a degree of polymerisation of 100 or more.[5] The synthesis proceeds under mild conditions and tolerates functional groups.[9]

This chapter presents a review of the Suzuki cross-coupling reaction between aryl boronic acids and aryl halides, including a discussion of the reaction conditions, the reaction mechanism and the scope and limitations of the reaction. The latter sections of this chapter are concerned with the author's work on the application of the Suzuki cross-coupling reaction in the synthesis of a series of poly(arylene vinylene)s with a view to producing structurally defined polymers as well as to expand the number and structural varieties of polymers accessible.

4.2 The Suzuki cross-coupling reaction

4.2.1 Palladium catalysed cross-coupling reaction of aryl boronic acids with aryl halides

The cross coupling reaction of organoboron compounds, which involves transmetallation from boron to a palladium(II)[9] centre as the key step, was found to proceed smoothly when activated with suitable bases and has proved to be a quite versatile technique for a wide range of selective carbon-carbon bond forming reactions.[10] Many organometallic reagents undergo similar cross-coupling reactions, but much attention has been focused recently on the use of organoboronic acids in both academic and industrial laboratories.[11] This is due to a combination of reasons. In the first place, the reagents and catalysts are compatible with the presence of electrophilic functional groups, such as aldehydes, ketones and esters.[12] Many arylboronic acid compounds are thermally stable and inert to oxygen.[11] The synthetic routes to arylboronic acids are well established and several aryboronic acids are commercially available.[12] The inorganic by-products of the reaction are non-toxic and water soluble. Lastly, the reaction conditions tolerate aqueous media, which renders elimination of the boron containing reaction by-products easy.[12]

A very wide range of palladium(0) catalysts or precursors can be used for cross-coupling reactions. However, $Pd(PPh_3)_4$ is the most commonly used.[11] Other palladium(II) catalysts or precursors to catalysts, have been employed with success, such as $Pd(dppb)Cl_2$, $Pd(OAc)_2$, $PdCl_2$, and $Pd(dppf)(OAc)_2$.[13] The use of $PdCl_2(PPh_3)_2$ and $Pd(OAc)_2$ in the presence of Ph_3P or other exchangeable ligands is also efficient since these compounds are stable to air and readily reduced to Pd(0) complexes by added organometallics or phosphines used in cross-coupling reactions.[11]

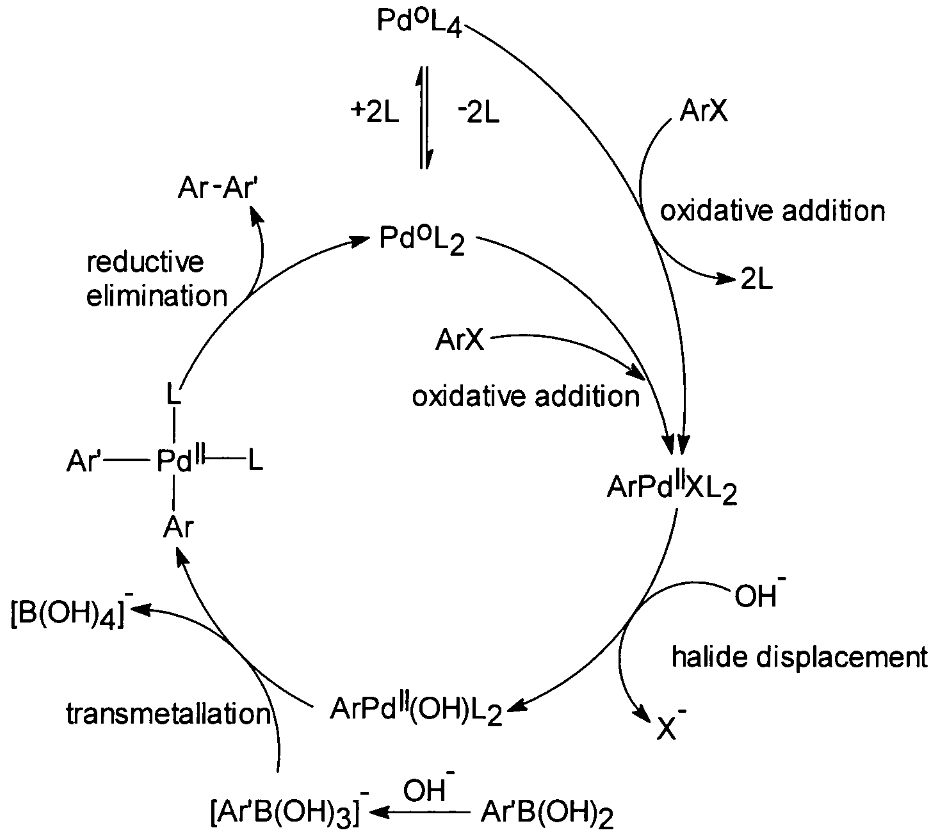
In contrast with other cross-coupling reactions, such as those involving tin, zinc, or nickel reagents which do not need the presence of base, the Suzuki cross-coupling reaction does require base. In the original procedure reported by Suzuki and his co-workers, an aqueous solution of sodium carbonate was used as the source of the base.[1] Since then the application of a variety of bases has been examined including bases such as Et_3N, $NaHCO_3$, NaOH, $Ba(OH)_2$, Cs_2CO_3, Tl_2CO_3, K_2CO_3 and also K_3PO_4.[13,14] However, sodium carbonate is the most frequently used.[13]

The reaction proceeds more rapidly in homogeneous conditions in which water miscible solvents, such as DME[14], THF[15] and DMF[14] are used; however, reasonable yields can be obtained under heterogeneous conditions as well. In the latter case, the commonly used solvents are benzene[14] and toluene.[16]

The most frequently employed halides in the Suzuki cross-coupling reaction are aryl bromides, but the reactivity of halides decreases in the order of Ar-I > Ar-Br > Ar-Cl.[13] Usually aryl chlorides are not reactive enough to participate in the cross-coupling reaction[17], an exception is when electron deficient heteroaryl chlorides are used.[18]

4.2.2 **Mechanism**

A widely accepted catalytic cycle (*Scheme 4.1*) for aryl-aryl coupling was proposed by Suzuki.[9] The cycle is initiated by the oxidative addition of the organic halide to a Pd(0) species, either to the species carrying four triphenyl phosphines with displacement of two phosphines or to the species formed by loss of two phosphines, to form an organopalladium(II) halide ($ArPdXL_2$). This step is followed by displacement of halide by hydroxide which, in turn, is followed by transmetallation in which the Ar′ group from the boron is transferred to the palladium to generate diorganopalladium(II) intermediate. A reductive elimination from this intermediate produces the coupling product, Ar-Ar′, and regenerates the Pd(0) catalyst carrying two ligands.



Scheme 4.1 Catalytic cycle proposed for the Suzuki cross-coupling reaction.

In its general outline the cycle is similar to other cycles proposed for cross couplings induced by other metals. The difference is the inclusion of a step in which a base is introduced into the coordination sphere of Pd. The reason is that the presence of a mineral base seems to be essential to the success of the Suzuki cross-coupling reaction. The cycle proposed in *Scheme 4.1* accounts for the requirement for two equivalents of base, the first is involved in the metathetical displacement of the halide ion from $ArPdXL_2$ to give an organopalladium hydroxide and the second converts the arylboronic acid to the $[Ar'B(OH)_3]^-$ species involved in the transmetallation step.[13]

The mechanism of the oxidative addition and reductive elimination sequences have been intensively studied, and are reasonably well understood. In the oxidative reaction, the increase in the oxidation state of the metal is usually accompanied by an increase in the coordination number, as shown, for a four coordinate metal going to six coordinate, in *Figure 4.1*.[19] The R-X compound in this case is an aryl halide.

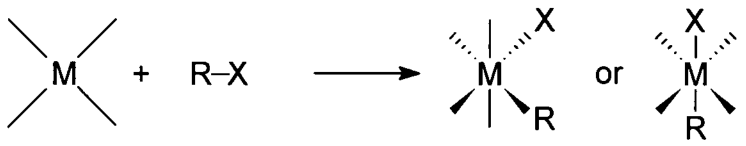


Figure 4.1 Oxidative addition of aryl halide to the ligand stabilised-metal.

A number of factors determine the ability of transition metals to undergo oxidative addition. The transition metal must be in a low valent state, behaving either as a nucleophile or a reductant in which electrons are removed from the electron-rich metal centre. The coordination number of the metal and the type of ligand is also important. In order for oxidative addition to take place, prior generation of a vacant site may occur to give a coordinatively unsaturated species. For example, the complexes $M(PPh_3)_4$ (M = Ni, Pd, Pt) are coordinatively saturated and undergo dissociation of phosphine ligands in solution to form three- and two coordinate compounds which are reactive towards oxidative addition. The phosphine ligands are σ donors which increase the electron density on the metal. This makes the metal a good nucleophile, and, at the same time, increases the tendency for the phosphines to dissociate. There is good evidence, however, that steric effects are much more important than electronic effects in determining the dissociation of phosphine ligands from transition metal complexes. The greater the size of the ligand, the greater is the tendency for dissociation.

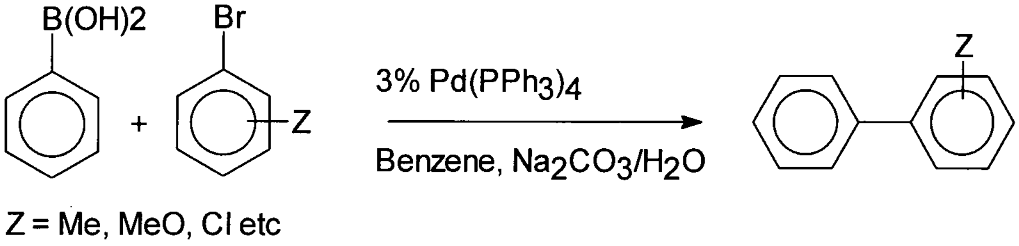
The 1,1-reductive elimination reaction, requires that the formal oxidation state and the coordination number of the metal are reduced by two, bond breaking is accompanied by bond making.[20] One of the problems in such a 1,1-reductive elimination reaction is the mechanism by which the two organic groups in a *trans* position, see *Figure 4.1*, eventually become coupled. In order for 1,1-reductive elimination to take place the organic moieties must occupy adjacent positions in the complex. There are a number of pathways by which the two organic groups in a trans complex could gain positions adjacent to one another prior coupling: 1) prior dissociation of a phosphine to give a three-coordinate intermediate, 2) prior association of a phosphine to give a five-coordinate complex, 3) conversion of the complexes in 1 or 2 to the *cis*-square planar complex by recoordination or dissociation of phosphine.

Much less is known about the transmetallation reaction, the inclusion of a base in the transmetallation step makes the Suzuki coupling different from other coupling reactions and it has been suggested that the transmetallation takes place by an electrophilic substitution with the organopalladium compound acting as the electrophile.[13]

As shown in *Scheme4.1* and mentioned earlier, two equivalent of base are required in this catalytic cycle. One equivalent is utilised in the formation of boronate, a tetracoordinate species, which is consistent with the fact that boronic acids act as acids in the Lewis sense. The anionic nature of the organic group in organoboronic acids is expected to be enhanced by the formation of an organoboronate. The second equivalent of base is consumed in the metathetical displacement of halide to form an organopalladium hydroxide. The organopalladium hydroxide should be more reactive than the organopalladium halide, since Pd-O is more polar than the Pd-Br bond, owing to the greater electronegativity of oxygen relative to bromine (the palladium is the positive end and the oxygen is the negative end of the dipole). As a result the electrophilicity of the organopalladium hydroxide is stronger than that of the organopalladium bromide, and the electrophilic transmetallation is facilitated. Thus, the transmetallation reaction is favoured by the formation of both the aryl boronate and the organopalladium hydroxide.

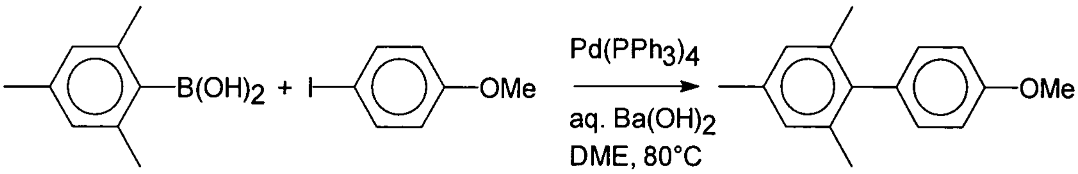
4.2.3 Scope and limitations

The first reported method to prepare biaryls via the Suzuki cross-coupling reaction is shown in *Scheme 4.2.*[1] After this discovery, various modifications of reaction conditions have been made.



Scheme 4.2 Synthesis of substituted biaryls via the Suzuki cross-coupling reaction.

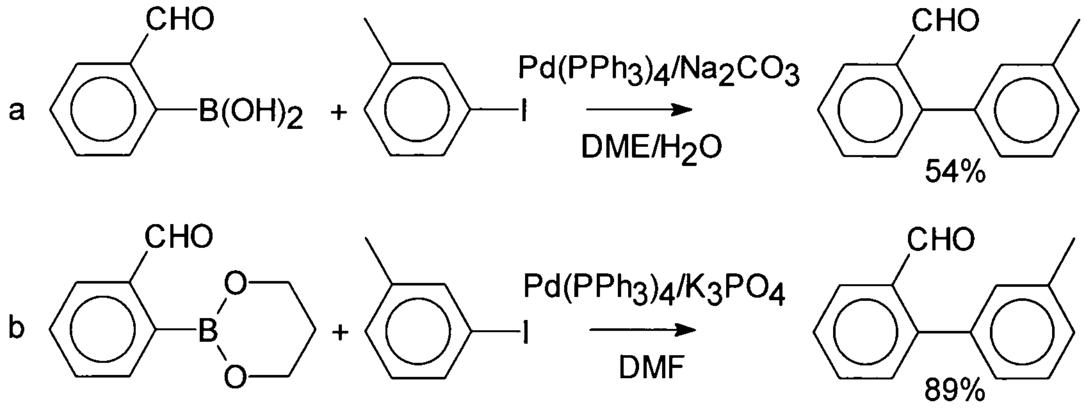
The original procedure, in which $Pd(PPh_3)_4$, aqueous Na_2CO_3 and benzene were used, was found to be effective for most arylboronic acids, however, it was pointed out that sterically hindered arylboronic acids never give satisfactory results.[21] For example, the reaction with mesitylboronic acid (*Scheme 4.3*) proceeds only slowly.[14]



Scheme 4.3 The Suzuki coupling reaction of sterically hindered aryl boronic acid.

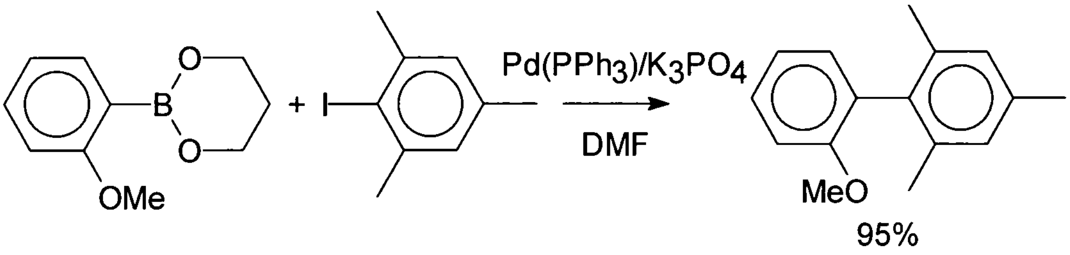
The addition of strong bases, such as, aqueous NaOH or $Ba(OH)_2$, both in benzene and DME exerts a remarkable acceleration effect on the coupling rate. Although weak bases usually give better results for less hindered arylboronic acids, the order of reactivity for mesitylboronic acids is $Ba(OH)_2$ > NaOH > K_3PO_4 > Na_2CO_3 > $NaHCO_3$, which corresponds to the base strengths.[14]

Even if there is no great steric hindrance, the reaction under aqueous conditions often gives undesirable results due to competitive hydrolytic deboronation. For example, the coupling of 2-formylphenylboronic acid with 3-iodotoluene at 80°C using aqueous Na_2CO_3 in DME gives only 54% of biaryl accompanied by 39% of benzaldehyde (*Scheme 4.4*). Aprotic conditions are desirable for such boronic acids which are sensitive to aqueous base.[14] It has been found that the trimethylene glycol ester of 2-formylphenylboronic acid readily couples with 3-iodotoluene at 100°C in the presence of K_3PO_4 in DMF in a yield of 89%, although less than 10% of benzaldehyde was still present as a by-product, see *Scheme 4.4*.



Scheme 4.4 The Suzuki cross-coupling reaction in a) aqueous system and b) in anhydrous system.

The non aqueous base system has been applied to the coupling reaction of *ortho* methoxy substituted phenylboronic acids, where the rate of deboronation may be decreased significantly, as compared to the heterogeneous system using aqueous base, see *Scheme 4.5*.[14]



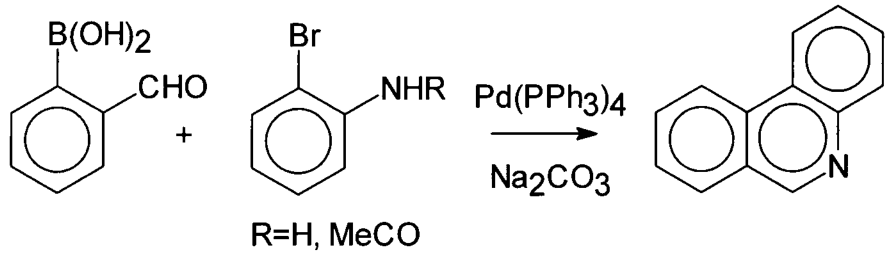
Scheme 4.5 The Suzuki cross-coupling reaction of *ortho* methoxy substituted phenyl boronic acid.

Electron-rich aryl boronic acids are prone to be deboronated under Suzuki coupling conditions, however it was found that such deboronations could be suppressed by using DME as the solvent.[13] Since then a number of electron-rich substituted biaryls and heteroaryls have been prepared. *Table 4.1* lists some of the biaryls prepared by this coupling reaction. A wide variety of aryl boronic acids such as benzene, thiophene, furan, and pyridine boronic acids, have been coupled to various aryl halides, including phenyl, thienyl, pyridyl, and furanyl halides.[13]

Table 4.1 Synthesis of biaryls from electron-rich aryl boronic acids via the Suzuki reaction.

ArX	Ar'B(OH)$_2$	Ar-Ar'
1-MeOPh-Br	Phenyl	1-MeOPh-Ph
4-ClPh-Br	Phenyl	4-ClPh-Ph
4-MeO$_2$CPh-Br	Phenyl	4-MeO$_2$CPh-Ph
2-NO$_2$,3-Br,thiophene	3-thienyl	2-NO$_2$-3,3'-bithienyl
2-CHO,3-Br,thiophene	3-thienyl	2-CHO-3,3'-bithienyl
Br-pyridyl	thienyl	thienylpyridines
2-NO$_2$Ph-Br	2-CHO,3-furanyl	3-(2'-NO$_2$Ph)-2-CHO-furan

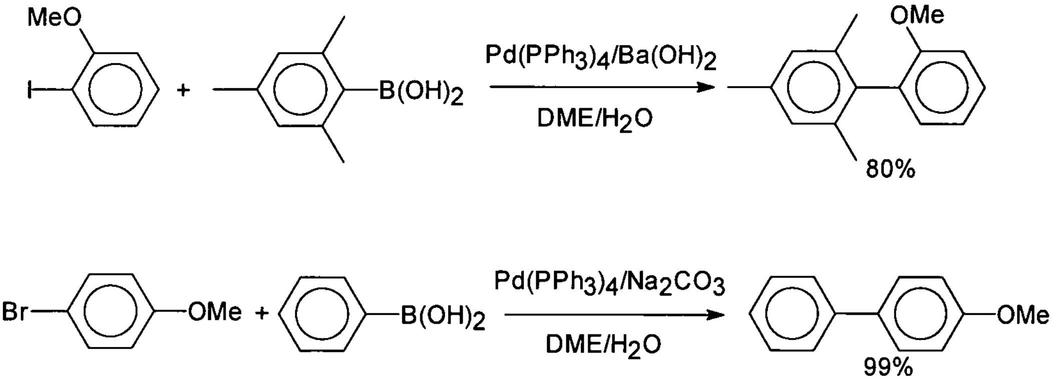
One of the main applications of the Suzuki reaction is the synthesis of condensed ring systems, as an example, the synthesis of tricyclic aromatics, see *Scheme 4.6.*[13] Since the cross coupling of aryl boronic acid and aryl halide tolerates almost all kinds of functionality on either coupling partner, suitably substituted aryl boronic acid and aryl halide partners can be chosen so that the biaryl formed in the coupling process will undergo spontaneous ring closure to tricyclic or polycyclic aromatic compounds.



Scheme 4.6 Application of the Suzuki reaction in the synthesis of tricyclic aromatic compound.

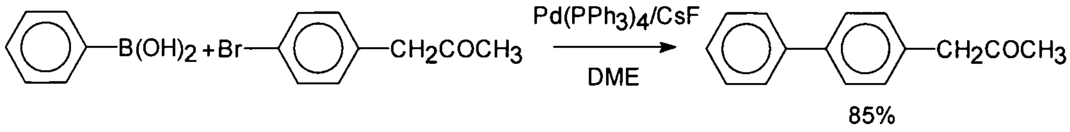
Reaction between an aryl group at the palladium(II) centre and a phosphine ligand has been found as a side reaction which may occur during the coupling reaction.[24,25] This reaction is enhanced by the presence of electron donating substituents on either coupling partners. The synthesis of biaryl substituted with electron donating groups results in contamination of the coupling product with an aryl group attached to a phosphine ligand. The use of tris(2-methoxyphenyl)phosphine instead of triphenylphosphine, is effective in reducing the formation of such by-products while maintaining a high yield of the desired biaryl.[24]

The Suzuki coupling conditions tolerate a wide range of functional groups. *Scheme 4.7* presents two biaryls bearing methoxy functionality prepared by the Suzuki reaction.[1,14]



Scheme 4.7 The synthesis of methoxy substituted biaryls via the Suzuki reaction.

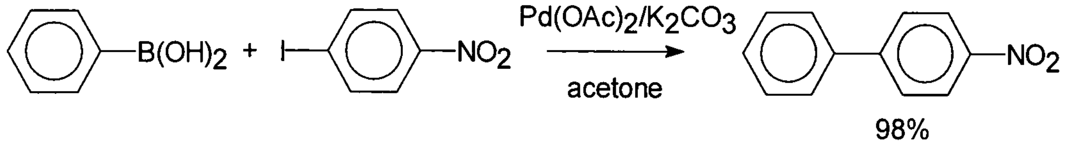
Ketone functional groups are unaffected by the Suzuki coupling conditions, but mild conditions using CsF in DME are required, see *Scheme 4.8*.[22]



Scheme 4.8 The synthesis of ketone substituted biaryl via the Suzuki reaction.

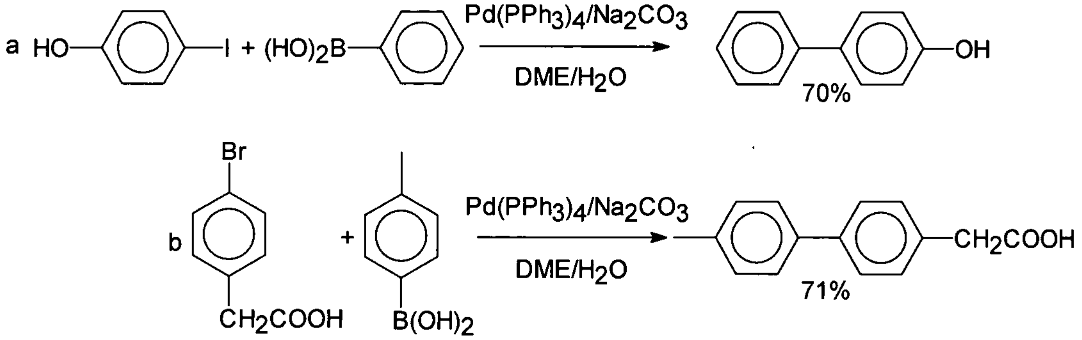
In the case of coupling reaction between phenyl boronic acid and 4-nitrophenyl iodide, the corresponding biaryl was obtained only in 23% yield when

$Pd(PPh_3)_4$ was used. However, as presented in *Scheme 4.9*, the yield could be improved to 98% by using $Pd(OAc)_2$ as the catalyst.[22]



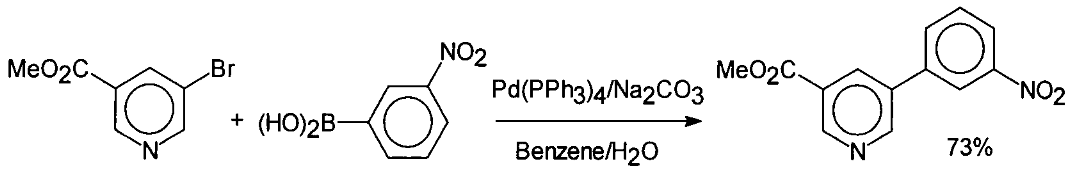
Scheme 4.9 The application of the Suzuki reaction in the synthesis of nitro substituted biaryl.

The Suzuki reaction was also shown to tolerate hydroxy and carboxy functional groups. *Scheme 4.10* provides an example for each of these functional groups.[13,27]



Scheme 4.10 The synthesis of a) hydroxy and b) carboxy substituted biaryls via the Suzuki reaction.

The reaction offers an additional advantage of being insensitive to the presence of *meta* functional groups or heterocyclic rings. As an example, Thompson has reported the arylation of 5-bromonicotinates via the Suzuki reaction, see *Scheme 4.11* below.[28]



Scheme 4.11 The synthesis of heterocyclic biaryl via the Suzuki reaction.

It has been shown that the Suzuki coupling reaction has a great versatility and high reaction conversion as well as toleration of a variety of functional groups, underlining its potential as a synthetic approach to produce not only small compounds but also high molecular weight and structurally defined polymers. In fact, as mentioned in Chapter 1, the Suzuki cross-coupling reaction has been used extensively in the synthesis of a variety of poly(*p*-phenylene) and its derivatives during the last ten years.[2-6] However, only during the course of this work was the application of this route to the synthesis of poly(arylene vinylene)s reported.[7,8]

4.3 Results and Discussion

4.3.1 Monomers

Throughout the course of this work two aryl dibromides and two aryl diboronic acids monomers were used, *see Figure 4.2.* The synthesis and characterisation of 1,2-di(4-bromophenyl)-1,2-diphenylethene and 2,3-di(4-bromophenyl)-2-butene was described in the preceding chapter. As mentioned earlier, in both cases the products were recovered as a mixture of *cis* and *trans* isomers which could be separated by repeated recrystallisation. Thus, these isomers alone or their mixtures could be used in conjunction with either 1,4-benzene diboronic acid or 4,4'-biphenyl diboronic acid to produce structurally defined poly(arylene vinylene)s. Both aryl diboronic acid monomers were purchased from Lancaster Synthesis Ltd. (>98% purity) and were used without further purification.

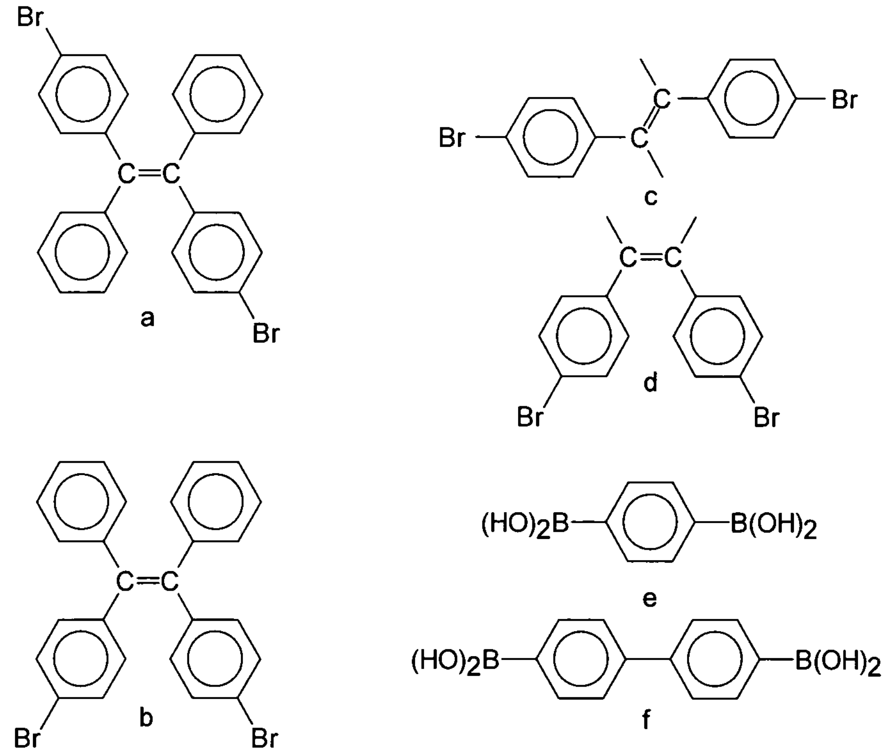
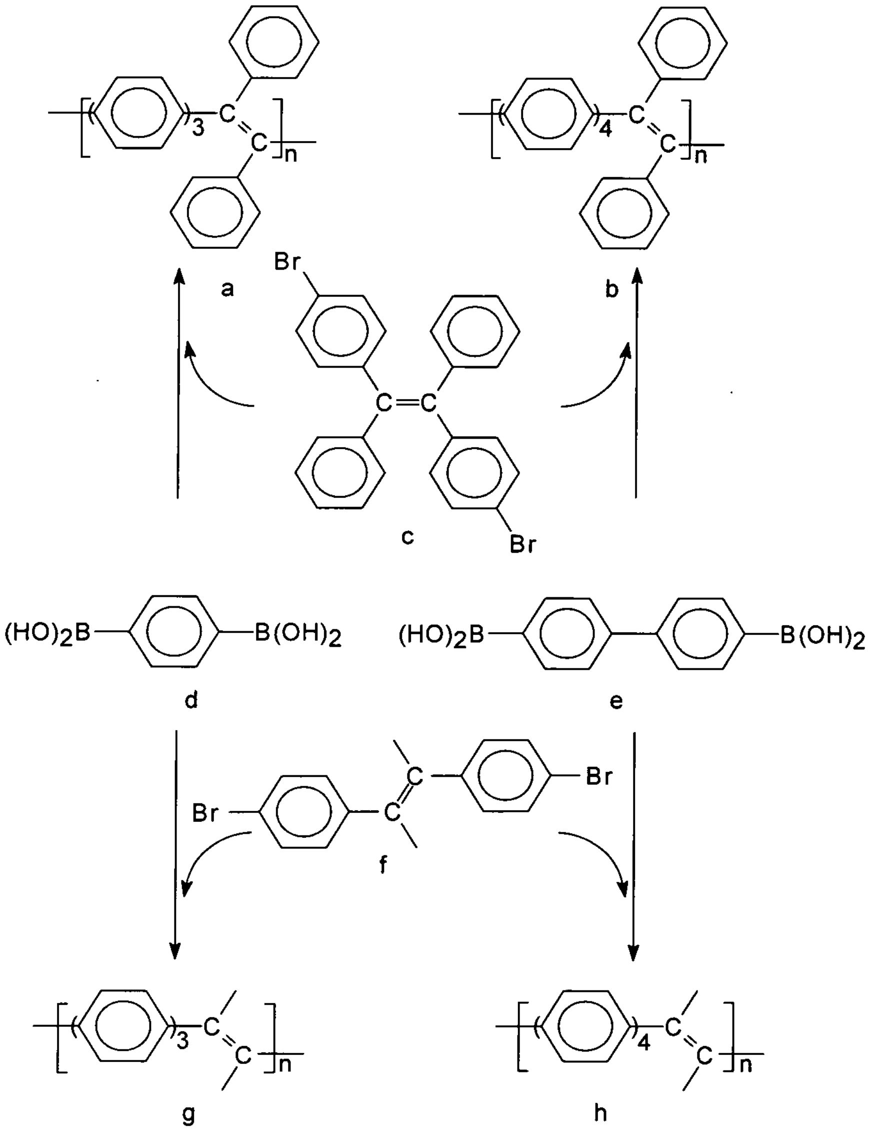


Figure 4.2 a) *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene, b) *cis*-1,2-di(4-bromophenyl)-1,2-diphenylethene, c) *trans*-2,3-di(4-bromophenyl)-2-butene, d) *cis*-2,3-di(4-bromophenyl)-2-butene, e) 1,4-benzene diboronic acid, f) 4,4'-biphenyl diboronic acid.

4.3.2 **Polymers**

The Suzuki cross-coupling reaction between aryl dibromides and aryl diboronic acids was applied in the synthesis of a series of poly(arylene vinylene)s. The work was carried out to explore the possibility of expanding the number and structural varieties of poly(arylene vinylene)s accessible. One objective was to vary the number of in-chain phenylene rings in the repeat units while maintaining the solubility of the polymer. The motivation being the hypothesis that the bigger the number of in-chain phenylene rings, the more similar the structure and properties of the polymer would be to those of poly(*p*-phenylene), which had been shown to emit in the blue region of the spectrum.[29] A second objective of the work was to produce poly(arylene vinylene)s with controllable composition of *cis* and *trans* vinylene units in the polymer chains by controlling the *cis* and *trans* vinylene composition in the dibromide monomers used in the polymerisation. Therefore studies of how the *cis* and *trans* vinylene composition affects the properties of the resultant polymers, particularly the electrooptical properties would be possible.

Scheme 4.12 presents a summary of polymers obtained in this work, however only *trans* isomers are shown for reasons of simplification.



Scheme 4.12 a) Poly(tri-*p*-phenylene diphenylvinylene), b) poly(tetra-*p*-phenylene diphenylvinylene), c) *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene, d) 1,4-benzene diboronic acid, e) 4,4'-biphenyl diboronic acid, f) *trans*-2,3-di(4-bromophenyl)-2-butene, g) poly(tri-*p*-phenylene dimethylvinylene, and h) poly(tetra-*p*-phenylene dimetylvinylene).

4.3.2.1 *Preliminary experiments*

In the first polymerisation experiments, the route to poly(arylene)s outlined by Feast *et al.*[2] was followed using a heterogeneous system with aqueous sodium carbonate as base and benzene as solvent. Poly(tetra-*p*-phenylene diphenylvinylene) was prepared by using 1,2-di(4-bromophenyl)-1,2-diphenylethene with an approximately 1:1 ratio of *cis* and *trans* isomers and 4,4'-biphenyl diboronic acid as monomers and tetrakis(triphenylphosphine)palladium as the catalyst. After refluxing the reaction mixture under inert atmosphere for two days, a yellow precipitate was recovered when the reaction mixture was poured into methanol, see experimental section for details.

The recovered product was found to be photoluminescent, giving a strong greenish yellow emission when irradiated with u.v. radiation. Even though Feast *et al.*[2] reported that degrees of polymerisation as high as 30 could be achieved in the synthesis of dialkyl substituted poly(*p*-phenylene)s, the polystyrene equivalent number average molecular weight, $\overline{M}_n$, and weight average molecular weight, $\overline{M}_w$, obtained for this polymer were only 1300 and 1600 respectively which, disappointingly, corresponds to a degree of polymerisation of less than 3.

It has been reported that the use of an aqueous solution of barium hydroxide in conjunction with dimethoxy ethane as solvent can improve the yield of the Suzuki coupling reaction of sterically hindered compounds.[14] Thus, in a second polymerisation attempt a similar procedure to that described earlier was used, except barium hydroxide and dimethoxy ethane replaced sodium carbonate and benzene. However, in terms of molecular weight, a worse product was recovered in comparison to that obtained in the first trial. The GPC trace obtained

(*Appendix 3.4.2*) shows that most of monomers used were consumed in the formation of low molecular weight oligomers since a few resolved high retention volume peaks were observed. Even the peak corresponding to the highest molecular weight present in the sample gave an $\overline{M}_n$ value of only about 1000. This is possibly due to the low solubility of the oligomers formed in dimethoxy ethane which results in precipitation and prevents them from participating in further coupling reactions.

In the next polymerisation attempt THF, which was expected to be a better solvent for the oligomers, was used instead of dimethoxy ethane. However, the molecular weight obtained for the recovered polymer did not show any improvement. It was clear that the reaction was failing and probably because a good solvent system had not been found.

In the fourth polymerisation attempt, barium hydroxide was replaced by potassium carbonate which was found to have better solubility in the THF and water mixture. As a result, $\overline{M}_n$ and $\overline{M}_w$ obtained for the recovered polymer were 1600 and 2900 respectively with a molecular weight distribution of 1.8. Even though the $\overline{M}_n$ obtained corresponded to a degree of polymerisation of less than 4, this result indicated the potential of the reaction and the importance of the conditions used in this Suzuki coupling route to poly(arylene vinylene)s. Thus, the onset of the GPC peak for this sample occurred at an $\overline{M}_n$ value of about 10600, which corresponds to a degree of polymerisation of about 22 for the polymer molecules in this highest mass part of the distribution. If the polymer fractionation described in Chapter 2 was applied to this product, the production of a polymer sample with a reasonably high molecular weight ought to be possible. In the GPC trace

(*Appendix 3.4.4*), the few resolved peaks at the low molecular weight end of the chromatogram, presumably correspond to oligomers, were much less intense in this sample in comparison to earlier samples, which is additional support for the view that the reaction could be developed for effective polymerisation. *Table 4.2* summarises the results obtained and reaction conditions used in this set of experiments.

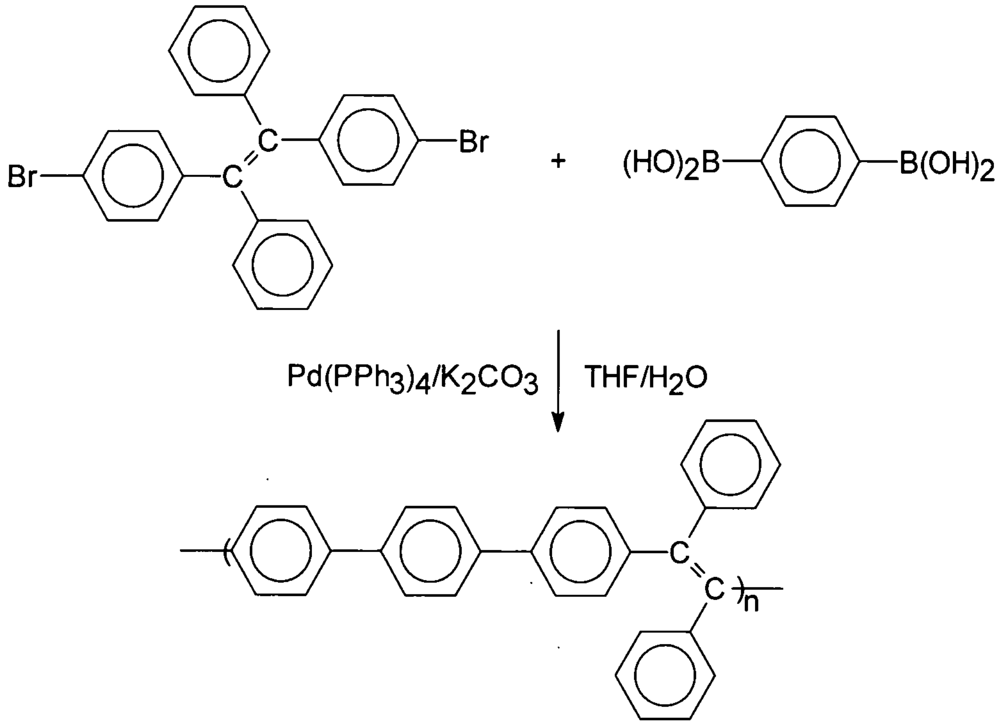
Table 4.2 Molecular weight data and reaction conditions used in the preliminary Suzuki coupling experiments with 1,2-di(4-bromophenyl)-1,2-diphenylethene and 4,4'-biphenyl diboronic acid as monomers.

run	base	solvent	$\overline{M}_n$	$\overline{M}_w$	remarks in g.p.c. trace
1	Na_2CO_3	benzene/H_2O	1300	1600	low intensity oligomeric peaks present
2	$Ba(OH)_2$	DME/H_2O	850	1300	high intensity oligomeric peaks present
3	$Ba(OH)_2$	THF/H_2O	830	960	high intensity oligomeric peaks present
4	K_2CO_3	THF/H_2O	1600	2900	low intensity oligomeric peaks present

Therefore it was decided that the reaction conditions used in run 4 in which aqueous solution of potassium carbonate in THF and two day reaction time were applied, would be used in the rest of polymerisations described in this chapter. These may not be optimal but time and starting materials were limited and this exercise was treated as a preliminary feasibility study.

4.3.2.2 *Poly(tri-p-phenylene diphenylvinylene)s*

The polymerisation procedure established in the preceding section was followed to prepare poly(tri-*p*-phenylene diphenylvinylene) from 1,4-benzene diboronic acid and 1,2-di(4-bromophenyl)-1,2-diphenylethene with various ratios of *cis* and *trans* isomers. *Scheme 4.13* shows the preparation of poly(tri-*p*-phenylene diphenylvinylene) using the *trans* dibromide monomer, in practice it was always a *cis/trans* mixture which was used.



Scheme 13 The synthesis of poly(tri-*p*-phenylene diphenylvinylene) via the Suzuki reaction.

After refluxing the reaction mixture for about two days, it was allowed to cool to room temperature and was concentrated by evaporating the solvent to about half of the original volume. This solution was poured into methanol and the resultant precipitate was recovered as a greenish yellow powder, see experimental section for details. *Table 4.3* presents the results obtained and the reaction conditions used in this set of experiments.

Table 4.3 Molecular weight data and reaction conditions used in the preparation of poly(tri-*p*-phenylene diphenylvinylene).

run	% *cis* isomer	reaction time (days)	$\overline{M}_n$[1]	$\overline{M}_w$[1]	DP[2]	mass recovery[3] (%)
1	62	2	1200	1800	3	6
2	48	4	1500	2000	4	53
3	48	2	1300	1700	3	46
4	37	2	1200	1600	3	8

[1] by GPC, "polystyrene equivalents"; [2] DP = degree of polymerisation;
[3] after reprecipitation into methanol from chloroform

It was found that the recovered material was photoluminescent. It gave a pale greenish yellow fluorescence when exposed to u.v. radiation. However, molecular weights obtained for all samples were very low with DPs of only 4 or even less. Doubling the reaction time, see runs 2 and 3, had negligible effect.

As shown in *Table 4.3*, mass recoveries of the products vary with *cis* and *trans* vinylene ratio in the dibromide monomer mixture used in the polymerisation. The maximum mass recovery was obtained from experiments using approximately 1:1 ratio.

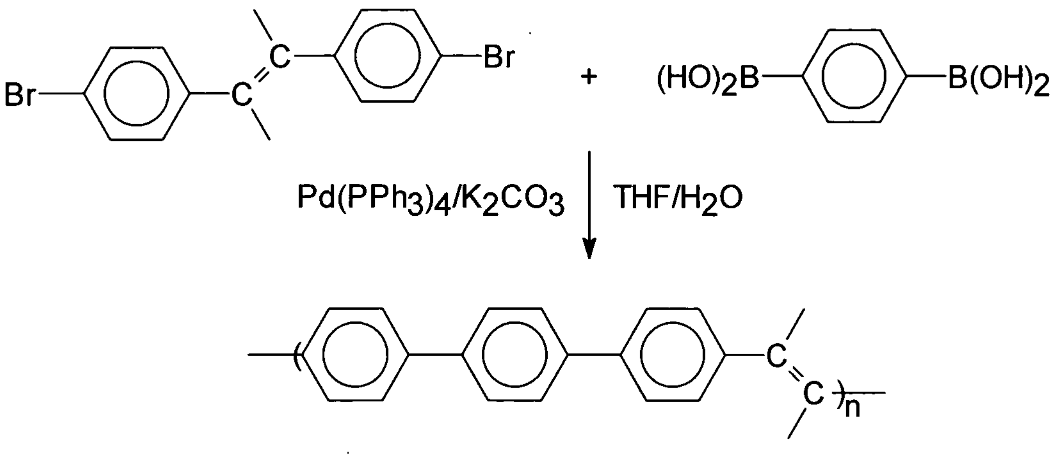
In the FTIR spectra (*Appendix 3.1.1* and *3.1.2*) the peak corresponding to an aromatic ring breathing mode can be seen at 1596cm^{-1} and both peaks at 1488cm^{-1} and 1442cm^{-1} are attributed to aryl **C-H** vibration modes. The peak at 3023cm^{-1} can be assigned to the aryl **C-H** stretching mode.

Thermogravimetric analysis (TGA) showed that the oligomer recovered from run 2 lost 2% of its weight at 300°C. It was also found that the glass transition temperature of this oligomer was 180°C as measured by DSC (*Appendix 3.5.1*).

If the "polystyrene equivalent" DPs for these polymers are realistic the average molecular chains are, never-the-less, of significant length containing nine to fifteen phenylene units and this may be sufficient to determine the luminescence properties likely for a larger polymer.

4.3.2.3 *Poly(tri-p-phenylene dimethylvinylene)s*

The polymerisation procedure outlined in the previous section was followed to prepare poly(tri-*p*-phenylene dimethylvinylene) from 1,4-benzene diboronic acid and 2,3-di(4-bromophenyl)-2-butene mixtures with various *cis*:*trans* isomer ratios. The reaction scheme for the *trans* isomer is shown in *Scheme 4.14*. Results obtained and reaction conditions used in this set of experiments are summarised in *Table 4.4*.



Scheme 4.14 The synthesis of poly(tri-*p*-phenylene dimethylvinylene) via the Suzuki reaction.

Table 4.4 Molecular weight data and reaction conditions used in the synthesis of poly(tri-*p*-phenylene dimethylvinylene).

run	% *cis* isomer	reaction time (days)	$\overline{M}_n$[1]	$\overline{M}_w$[1]	DP[2]	mass recovery[3] (%)
1	0	2	1250	1800	4	67
2	81	2	1900	2750	7	80
3	84	4	1700	2800	6	90
4	97	2	1600	2050	6	40

[1] by GPC, "polystyrene equivalents"; [2] DP = degree of polymerisation; [3] after reprecipitation into methanol from chloroform

The products were recovered as a faint orange precipitates which gave a very weak orange fluorescence when irradiated with u.v. light. In general molecular weights obtained for all samples were low, the highest $\overline{M}_n$ being 1900 which corresponding to a degree of polymerisation of 7, see run 2. However, this is a slightly higher value than that found in the preceding experiment in which similar polymers, with phenyl vinylene substituent in place of methyl, were produced. Doubling the reaction time did not result in an increase in molecular weight, see runs 2 and 3. As shown in *Table 4.4*, the mass recovery for samples from runs 1 and 4 in which virtually pure *trans* and *cis* isomers were used, were the worst, which is in agreement with earlier observations.

In the FTIR spectra (*Appendix 3.1.3* and *3.1.4*), the peak at 1604cm^{-1} is attributed to the aryl carbon skeleton breathing mode and a peak corresponding to the aryl **C-H** vibration mode can be seen at 1487cm^{-1}, with aryl **C-H** stretching at 3022cm^{-1} and methyl **C-H** stretching at 2911cm^{-1}.

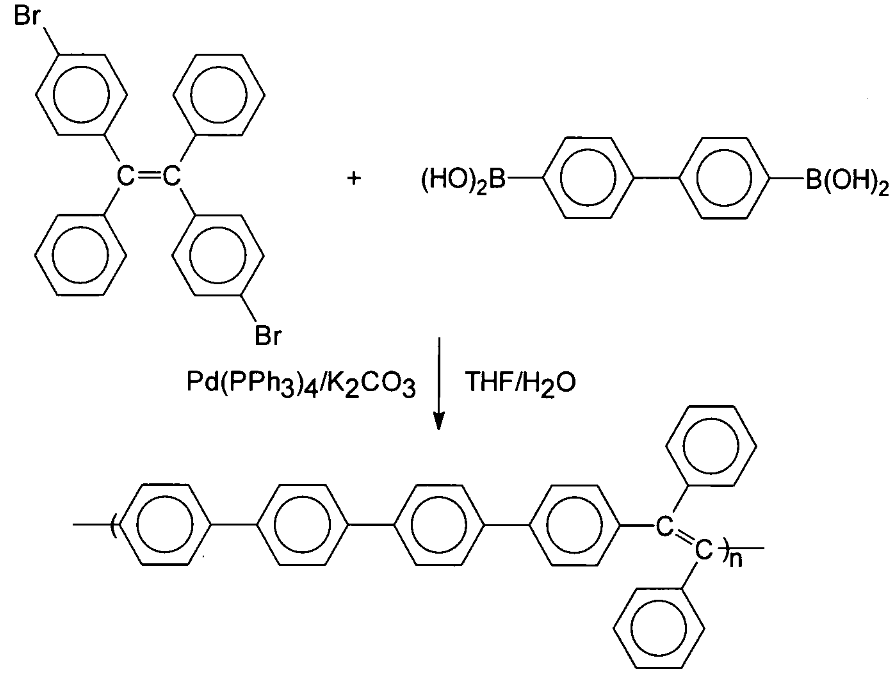
Thermogravimetric analysis (TGA) shows that the recovered polymers lose 2% of their weight at 310°C. The polymer recovered from run 2 was found to have glass transition temperature at 178°C as measured by DSC (*Appendix 3.5.2*).

Again relative low molecular weight materials have been recovered but, if the GPC data is reliable, chains of significant length (i.e. greater than 20 phenylene units) were obtained and this may be long enough for luminescence studies.

4.3.2.4 ***Poly(tetra-p-phenylene diphenylvinylene)s***

Poly(tetra-*p*-phenylene diphenylvinylene) was prepared via the Suzuki coupling reaction from 4,4'-biphenyl diboronic acid and 1,2-di(4-bromophenyl)-1,2-

diphenylethene mixtures with various *cis*:*trans* isomer ratios. The polymerisation procedure established in the earlier experiments was followed. *Scheme 4.15* illustrates the process schematically for the *trans* isomer. Results obtained and the reactions conditions used in this set of experiments are summarised in *Table 4.5*.



Scheme 4.15 The synthesis poly(tetra-*p*-phenylene diphenylvinylene) via the Suzuki reaction.

Table 4.5 Molecular weight data and reaction conditions used in the synthesis of poly(tetra-*p*-phenylene diphenylvinylene)s.

run	reaction time (days)	% *cis* isomer	$\overline{M}_n$[1]	$\overline{M}_w$[1]	DP[2]	mass recovery[3] (%)
1	2	0	2190	3350	5	78
2	2	32	3250	6200	7	51
3	2	48	4280	8300	9	50
4	2	62	2800	4500	6	62
5	2	100	2900	4800	6	85
6	4	32	3470	5850	7	90

[1] as measured on pristine samples by GPC, “polystyrene equivalents”

[2] DP = degree of polymerisation

[3] after reprecipitation into methanol from chloroform

As found in the preliminary experiments on this reaction, the polymer was recovered as a yellow precipitate and gave a strong greenish yellow fluorescence when exposed to u.v. light. In general, the molecular weights obtained for the pristine samples were higher than those found for the previous two polymers, namely poly(tri-*p*-phenylene diphenylvinylene) and poly(tri-*p*-phenylene dimethylvinylene). As shown in *Table 4.5*, a similar trend to that found in earlier experiments can be observed, in the sense that molecular weights obtained vary with the *cis*:*trans* isomer ratios. The highest number average molecular weight was obtained when a monomer mixture with an approximately 1:1 ratio of *cis* and *trans* isomers was used in the polymerisation, see run 3. This finding is in agreement with the observation of the two preceding experiments. Extending the reaction time from two to four days resulted in only a small increase in number average molecular weight, see runs 2 and 6.

In an effort to produce polymers with higher molecular weights and free from oligomers, an equilibrium fractionation similar to that described in Chapter 2 was carried out using the samples listed in *Table 4.5*. As a result, polymer fractions with higher molecular weights and relatively narrow molecular weight distributions were obtained. The fractions with the highest molecular weight from each run are tabulated below, see *Table 4.6*.

Table 4. 6 Reaction conditions and molecular weight data obtained from fractionated poly(tetra-*p*-phenylene diphenylvinylene).

run	reaction time (days)	% *cis* isomer	$\overline{M}_n$[1]	$\overline{M}_w$[1]	PDI[1] ($\overline{M}_w/\overline{M}_n$)	DP[2]
1	2	0	2750	4400	1.6	6
2	2	32	8300	13800	1.7	17
3	2	48	9550	15100	1.6	20
4	2	62	5000	9400	1.9	10
5	2	100	4350	7050	1.6	9
6	4	32	16300	27900	1.7	34

[1] as measured on the highest molecular weight fraction by GPC, "polystyrene equivalents"; [2] DP = degree of polymerisation

The same trend as that observed in pristine polymers is again found in these fractionated samples. Limiting the reaction time to two days, the sample obtained from run 3 in which the dibromide monomer mixture with a *cis* :*trans* isomer ratio of about 1:1 was used, gave the highest number average molecular weight. The degree of polymerisation for the highest molecular weight fraction of the product from run 6, in which the reaction time was extended to four days, was 34 which corresponding to a reaction conversion of 97% for the polymer in this fraction, underlining the potential of this route to poly(arylene vinylene)s if the reaction can be optimised thoroughly.

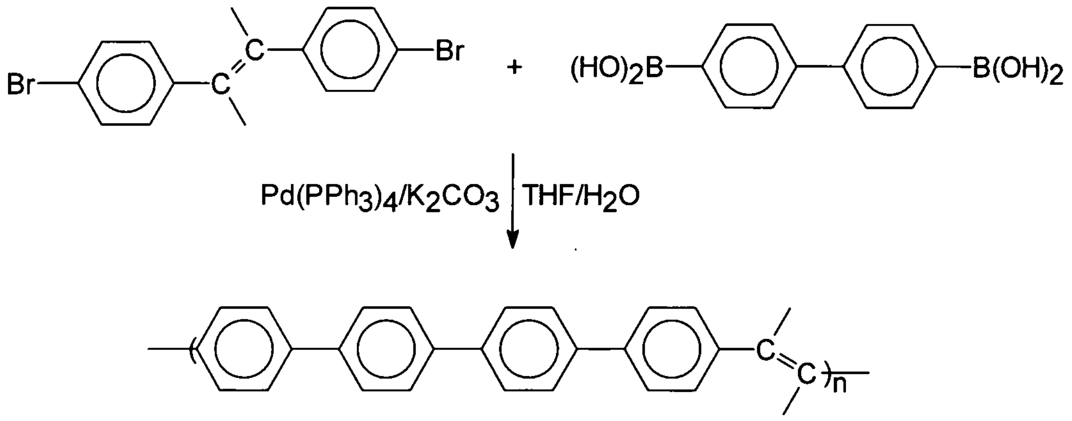
In the FTIR spectra of these material (*Appendix 3.1.5-3.1.9*), the absorption corresponding to an aryl carbon skeleton breathing mode can be seen at 1596cm^{-1} with absorptions at 1485 and 1442cm^{-1} assigned to aryl **C-H** bending modes and that attributed to the aryl **C-H** stretching mode at 3023cm^{-1}.

Thermogravimetric analysis (TGA) of the polymers recovered in runs 2 and 4 of *Table 4.6* shows that these polymers lose 2% of their weight at about 320°C.

It was also found that poly(tetra-*p*-phenylene diphenylvinylene) recovered in runs 3 and 4 of *Table 4.6* display a glass transition temperature at 220°C (*Appendix 3.5.3*).

4.3.2.5 ***Poly(tetra-p-phenylene dimethylvinylene)s***

The procedure outlined previously was followed to prepare poly(tetra-*p*-phenylene dimethylvinylene) from 4,4'-biphenyl diboronic acid and 2,3-di(4-bromophenyl)-2-butene mixtures with various *cis*:*trans* isomer ratios, see experimental section for details. *Scheme 4.16* summarises the process for poly(tetra-*p*-phenylene dimethylvinylene) preparation from the *trans* dibromide monomer.



Scheme 16 The synthesis of poly(tetra-*p*-phenylene dimethylvinylene) via the Suzuki reaction.

Products were recovered as faint yellow powders and were found to give pale yellow fluorescence under u.v. radiation. It was found that the recovered products were largely insoluble in organic solvents, thus full characterisation was not possible. Reaction conditions used in these experiments and results obtained are summarised in *Table 4.7*.

Table 4.7 Molecular weight data and reaction conditions used in the synthesis of poly(tetra-*p*-phenylene dimetylvinylene).

run	% *cis* isomer	reaction time (days)	$\overline{M}_n$ [1]	$\overline{M}_w$ [1]	mass recovery[2] (%)
1	0	2	*	*	83
2	81	2	1126	1944	77
3	97	2	1140	1179	53
4	81	4	*	*	83

[1] as analysed on soluble portion of samples by GPC, “polystyrene equivalents”
[2] after reprecipitation into methanol from chloroform
* samples are insoluble

As shown in *Table 4.7*, molecular weights for samples from runs 2 and 3 were obtained, however, the fact that only a small portion of the materials were soluble limits the value of the data obtained.

In the FTIR spectra of these materials (*Appendix 3.1.10-3.1.12*), the absorption corresponding to an aryl **C-H** stretching mode can be seen at 3022cm^{-1}, the absorption for methyl **C-H** stretching is present at 2909cm^{-1}, an aryl **C-H** bending mode is seen at 1485cm^{-1} and peak at 1605cm^{-1} is attributed to the aryl carbon skeleton breathing mode.

Thermogravimetric analysis (TGA) shows that the recovered products decompose at about 380°C. However, neither glass transition nor melting temperatures were detected in the temperature range from 30°C to 250°C.

4.4 Conclusions

In short, it has been shown that a series of poly(arylene vinylene)s, including poly(tri-*p*-pheneylene diphenylvinylene), poly(tri-*p*-phenylene dimethylvinylene), poly(tetra-*p*-phenylene diphenylvinylene) and poly(tetra-*p*-phenylene dimethylvinylene) have been synthesised via the Suzuki cross-coupling reaction with a variation of *cis* and *trans* vinylene compositions in the polymer chain.

All the polymers have been shown to be reasonably soluble in organic solvents, such as chloroform and toluene, except poly(tetra-*p*-phenylene dimethylvinylene) which was found to be largely insoluble in any organic solvents. The polymers were also found to have good thermal stability. ^{1}H and ^{13}C Nmr spectra were recorded and were consistent with the assigned structures but were not very informative apart from confirming the absence of significant structural defects or impurities.

In terms of achieving high molecular weight polymers, it was found that the use of dibromide monomer mixtures with an approximately 1:1 ratio of *cis* and *trans* isomers was required in all cases, except in the case of poly(tetra-*p*-pheylene dimethylvinylene) in which its insolubility limits the value of the molecular weight data obtained and thus no secure conclusion can be drawn. The molecular weights obtained were disappointingly low but it was possible to obtain a set of fractions of poly(tetra-*p*-phenylene diphenylvinylene)s of reasonable molecular weight and a range of *cis:trans* vinylene contents (*Table 4.6*). The lowest molecular weight fraction (run 1), the all *cis* vinylene polymer, had an average of 24 phenylenes per chain and the highest molecular weight sample had chains with 136 phenylenes per chain on average. It was considered that these samples would be suitable for examining the effect of *cis:trans* vinylene distribution on the luminescence behaviour of this family of arylene vinylene polymers.

The molecular weights obtained in these polymerisation attempts were generally rather low and the reasons for this are not clear. They are step-growth polymerisations and if either monomer was not completely pure or if an exact stoichiometric balance of both difunctional reagents was not maintained it would be impossible to reach high molecular weights. Within the limits of our analytical techniques, primarily ^{1}H and ^{13}C nmr, all the reagents were pure and difunctional but, since monomer costs and availability limited the scale on which the polymerisations were carried out it seems likely that obtaining exact stoichiometric balance in the polymerising mixture may have been the major problem. Never-the-less, this study has established the feasibility of this approach to the synthesis of poly(arylene vinylene)s with control over the arylene sequence and the distribution of *cis* and *trans* vinylenes even though a lot of optimisation work remains to be done before this approach can be regarded as a generally useful route.

One fairly consistent observation for all the systems was that highest molecular weights were obtained at a 1:1 *cis:trans* vinylene ratio. This may be a consequence of the inherent solubility of the products rather than anything else. Thus, "all-*trans*" polymers likely to be rigid rods which will tend to be rather insoluble and "all-*cis*" polymers will inevitably be very tightly coiled denying solvation and also being highly insoluble. If this is true, such polymers would precipitate at on early stage in their growth and this would explain their lower molecular weights.

4.5 **Experimental**

1,4-Benzene diboronic acid and 4,4'-biphenyl diboronic acid were purchased from Lancaster Synthesis Ltd. Tetrakis(triphenylphosphine)palladium (0), benzene, chloroform, dimethoxy ethane, potassium carbonate, sodium carbonate and barium hydroxide were purchased from Aldrich Company Ltd., and THF was purchased from BDH Chemical Company Ltd. All reagents and solvents were used without further purification except THF, benzene and dimethoxy ethane which were degassed by freeze-thaw cycle (3 times).

^{1}H and ^{13}C Nmr spectra were recorded using a Varian 400MHz spectrometer and were referenced to internal Me_4Si. IR Spectra were recorded using Perkin-Elmer 1600 series FTIR spectrometer. GPC analyses were performed using a Waters differential diffractometer as detector, three Polymer Laboratories gel columns (exclusion limits 100. 10^3, and 10^5 Å) and chloroform as eluent. Columns were calibrated using polystyrene standards (Polymer Labs). DSC measurements were performed using a Perkin-Elmer DSC7, at scanning rate of 10°C/min, the temperature scale was calibrated using the melting points of indium at 100°C and zinc at 400°C. Thermogravimetric analysis was carried out under nitrogen using a TG 760 series instrument (Rheometric Scientific Ltd.) at scanning rate of 10°C/min.

In the following sections, an example of the synthesis procedures used for every poly(arylene vinylene) prepared in this study is described. The synthesis of dibromide monomers has been already described in Chapter 3.

4.5.1 Synthesis of poly(tetra-*p*-phenylene diphenylvinylene)

Degassed THF (70ml) and degassed distilled water (10ml) were added to a mixture of 1,2-di(4-bromophenyl)-1,2-diphenylethene (1.80g, 3.7mmol), 4,4'-biphenyl diboronic acid (0.89g, 3.7mmol), tetrakis(triphenylphosphine)palladium (127mg, 3 mole % w.r.t. 1,2-di(4-bromophenyl)-1,2-diphenylethylene) and potassium carbonate (2.03g, 14.7mmol) in a two necked round bottomed flask (250ml) under a nitrogen atmosphere. The mixture was then refluxed for 48 hours with vigorous stirring. After cooling to room temperature, the whole mixture was poured into methanol. The precipitated polymer was recovered, washed with dilute hydrochloric acid and dried under vacuum. To remove the last traces of catalyst residues and inorganic salts, the polymer was extracted with chloroform in a Soxhlet apparatus for about twenty hours. The extracted solution was concentrated to about 10ml and was reprecipitated into acetone. The precipitate was recovered and dried under vacuum, giving the desired poly(tetra-*p*-phenylene diphenylvinylene) as clean granules. The polymer was characterised by GPC, FTIR, ^{1}H nmr, ^{13}C nmr, TGA and DSC (see Results and Discussion Section and Appendices).

4.5.2 Synthesis of poly(tri-*p*-phenylene diphenylvinylene)

Degassed THF (70ml) and degassed distilled water (10ml) were added to a mixture of 1,2-di(4-bromophenyl)-1,2-diphenylethene (1.80g, 3.7mmol), 1,4-benzene diboronic acid (0.61g, 3.7mmol), tetrakis(triphenylphosphine)palladium (127mg, 3 mole % w.r.t. 1,2-di(4-bromophenyl)-1,2-diphenylethylene) and potassium carbonate (2.03g, 14.7mmol) in a two necked round bottomed flask (250ml) under a nitrogen atmosphere. After refluxing the mixture for 48 hours with rapid stirring, the reaction mixture was allowed to cool to room temperature. It was then concentrated by reducing the amount of solvent to about half of the original volume and precipitated into methanol. The precipitate was collected, washed with dilute hydrochloric acid and dried under vacuum. The polymer was then extracted with chloroform in a Soxhlet apparatus for about twenty hours to remove the last traces of catalyst residues and inorganic salts which might present in the sample. The extract solution was concentrated to about 10ml and reprecipitated into acetone. The precipitate was recovered and dried under vacuum, giving the desired poly(tri-*p*-

phenylene diphenylvinylene), as a clean powder. The polymer was characterised by GPC, FTIR, ^{1}H nmr, ^{13}C nmr, TGA and DSC, see Results and Discussion Section and Appendices.

4.5.3 Synthesis of poly(tetra-*p*-phenylene dimethylvinylene)

2,3-Di(4-bromophenyl)-2-butene (1.45g, 4.0mmol), 4,4'-biphenyl diboronic acid (0.96g, 4.0mmol), tetrakis(tripheylphosphine)palladium (138mg, 3 mole % w.r.t. 2,3-di(4-bromophenyl)-2-butene) and potassium carbonate (2.19g, 16.0mmol) were placed in a two necked round bottomed flask (250ml). Degassed THF (70ml) and degassed distilled water (10ml) were then added under a nitrogen atmosphere. After refluxing the mixture with rapid stirring for 48 hours, it was allowed to cool to room temperature and concentrated to about half of its original volume and precipitated into methanol. The precipitate was collected, washed with dilute hydrochloric acid and dried under vacuum. The product was characterised by GPC, FTIR, TGA and DSC (see Results and Discussion Section and Appendices) without further purification since it was hardly soluble in any organic solvents.

4.5.4 Synthesis of poly(tri-*p*-phenylene dimethylvinylene)

2,3-Di(4-bromophenyl)-2-butene (1.24g, 3.4mmol), 1,4-benzene diboronic acid (0.56g, 3.4mmol), tetrakis(triphenylphosphine)palladium (117mg, 3 mole % w.r.t. 2,3-di(4-bromophenyl)-2-butene), and potassium carbonate (1.87g, 13.6mmol) were placed in a two necked round bottomed flask (250ml). Degassed THF (70ml) and degassed distilled water (10ml) were then added under a nitrogen atmosphere. The mixture was refluxed for 48 hours with vigorous stirring. The reaction mixture was concentrated by evaporating the solvent to about half of the original volume and precipitated into methanol. The precipitate was collected, washed with dilute hydrochloric acid and dried under vacuum. The product was extracted with chloroform in a Soxhlet apparatus and the resultant extract solution was concentrated to about 10ml and reprecipitated into acetone. The precipitate was collected and dried under vacuum, giving the desired poly(tri-*p*-phenylene dimetylvinylene) as a clean faint orange powder. The polymer was characterised by GPC, ^{1}H nmr, ^{13}C nmr, TGA, FTIR, and DSC, see Results and Discussion section and Appendices.

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Chapter 5

The optical and electro-optical properties of poly(arylene vinylene)s

5.1 Introduction

The first part of this chapter presents a brief review of the application of organic polymers, particularly poly(arylene vinylene)s, in light emitting diodes and includes a discussion of how the devices work, established chemical and physical procedures for colour tuning, and device efficiency. This chapter is concerned primarily with the author's work in characterising the polymers produced throughout the course of this study in terms of optical and electro-optical properties including UV-visible absorption, photoluminescence and electroluminescence characteristics of the polymers. The study of the latter two properties was a joint project with Professor Friend's group at the Cavendish Laboratory, Cambridge University. All measurements associated with photoluminescence and electroluminescence were carried out at the Cavendish Laboratory and results reported in this chapter were obtained through collaboration with workers in Professor Friend' group. The author visited Cambridge to participate in a part of this experimental work.

5.2 Application of UV-visible absorption study in poly(arylene vinylene)s

The UV-visible absorptions recorded using a spectrometer arise as a consequence of electronic excitation of electrons involved in bonds within the polymer molecule. Electrons involved in σ bonds absorb high energy radiation in the UV region, whereas π electrons absorb radiation at longer wavelengths, often in the visible region. One application of UV-visible absorption spectroscopy is in determining the band gap of the polymer which is the energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). This energy gap is a function of the conjugation length in unsaturated polymers. The π electrons in a conjugated system are delocalised, thus they move freely within the conjugated region which arises from overlapping p_z orbitals of adjacent carbon atoms forming the polymer backbone.[1] The greater the conjugation length the smaller the band gap, so measurements of UV-visible spectra provide a means of establishing the conjugation length of the polymer.

It is important to note that when dealing with a polymer, the conjugation length will not take a characteristic single value, instead there will be a characteristic distribution of conjugation lengths.[2] The shape and the position of the lowest energy absorption are determined by the distribution and the length of the uninterrupted conjugation sequences in the polymer. In general, the observation of sharp and well resolved bands indicates the presence of a relatively narrow distribution of conjugation lengths and the observation of a low energy for the onset of the absorption peak indicates a high degree of delocalisation.

5.3 Photoluminescence and electroluminescence of poly(arylene vinylene)s

Photoexcitation of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) generates an electronically excited species which can decay radiatively with emission of light in the visible region, this process is called photoluminescence.[3] Although the energy of the photoluminescence depends on the size of band gap in the polymer, it usually occurs at longer wavelengths than that absorbed in the process of photoexcitation. This phenomenon is called 'Stokes shift' and can be due to a combination of several factors.[4] For example, emission may take place from an electronically excited state that is different from the one formed in the excitation process; for instance, in intersystem crossing the singlet excited state undergoes a spin inversion to give a lower energy triplet excited state before decaying radiatively. Also, absorption to form the excited species can take place anywhere in the polymer. However, within a polymer with a distribution of conjugation lengths, the excited species may migrate among the different polymer segments and may be trapped on those chains with the longest conjugation length (lowest energy), or at a "defect" in the chain, and emission then occurs from these trapped species.

In a similar process, when holes and electrons are injected into polymer film from anode and cathode respectively, they can travel through the polymer film under an applied electric field and may combine to form an electronically excited species which can relax radiatively with emission of light.[3] The emission is called electroluminescence and it is this process which is the strong driving force behind the current interest in poly(arylene vinylene)s. This was discussed in Chapter 1.

5.4 Organic polymer light emitting diodes

5.4.1 What is an organic polymer light emitting diode?

Organic light emitting diodes were first fabricated from small organic molecules.[5] These systems have a serious disadvantage in that the emissive molecules can recrystallise during operation of the device, leading to poor device stability[5] and also to a decrease in emission efficiency.[6] The use of conjugated polymers, particularly poly(arylene vinylene)s in such devices was realised in the early 1990s.[7,8] The devices typically consist of one or more thin organic polymer films sandwiched between electron- and hole-injecting electrodes.[7] Indium tin oxide (ITO) was used as a transparent hole-injecting anode and aluminium or calcium as an electron-injecting cathode. When the current flows through the device the emitted light can be seen through the transparent ITO and the glass substrate. A schematic diagram of the device is shown in *Figure 5.1.* Additional layers may be applied between the emissive layer and cathode or/and the emissive layer and anode to enhance the device performance.

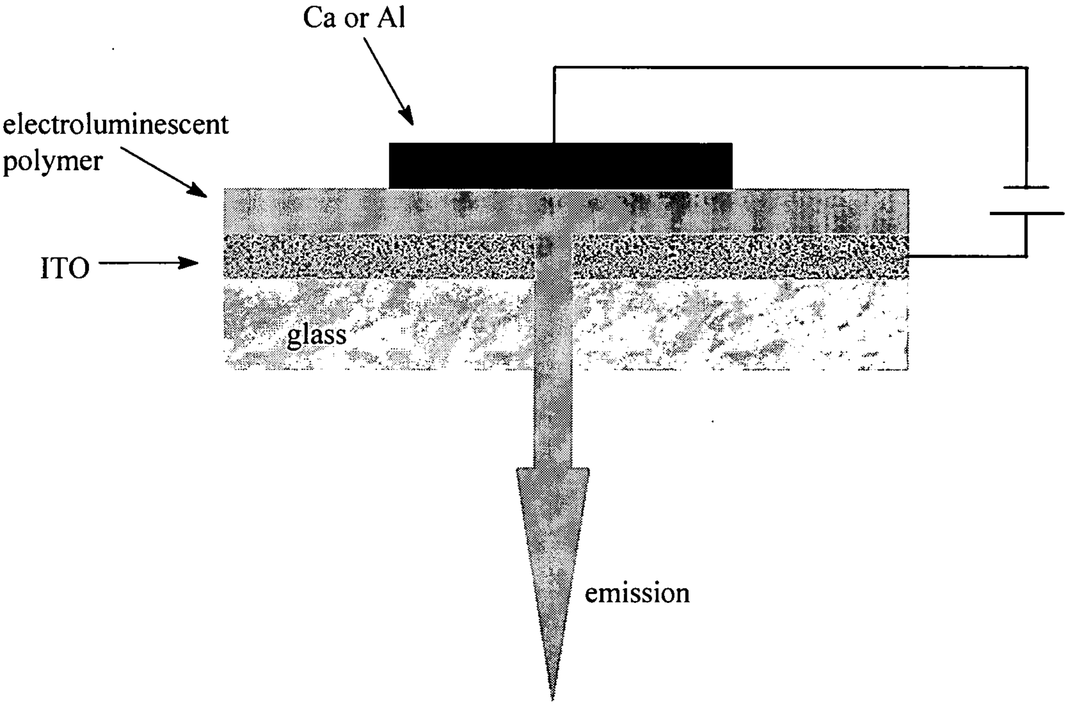

Figure 5.1. Schematic diagram of an LED.

5.4.2 How does an organic polymer light emitting diode work?

Conjugated polymers possess extensive networks of delocalised π-electrons distributed in molecular orbitals formed by the overlap of carbon p_z orbitals along the polymer chains.[2,9] Typical structures are shown in *Figure 5.2*, all the structures contain an alternating sequence of single and double bonds.

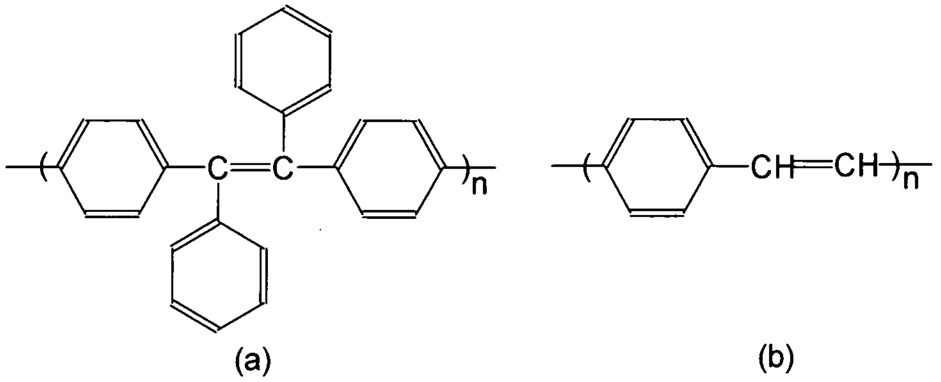

Figure 5.2 Some conjugated polymers, (a) poly(4,4′-diphenylene diphenylvinylene), (b) poly(*p*-phenylene vinylene).

These conjugated polymers are organic semiconductors with variable band gaps between the valence and conduction bands.[10] Electroluminescence in these materials is achieved by injection of electrons into the lowest unoccupied molecular orbital (LUMO), of the conduction band and holes into the highest occupied molecular orbital (HOMO), of the valence band.[11] The electronic structure relaxes to give the positive and negative charge carriers which travel through the polymer film under the influence of the applied electric field. A pair of carriers can combine to form an excited species (exciton) which can then decay radiatively. The process is depicted in *Figure 5.3.*

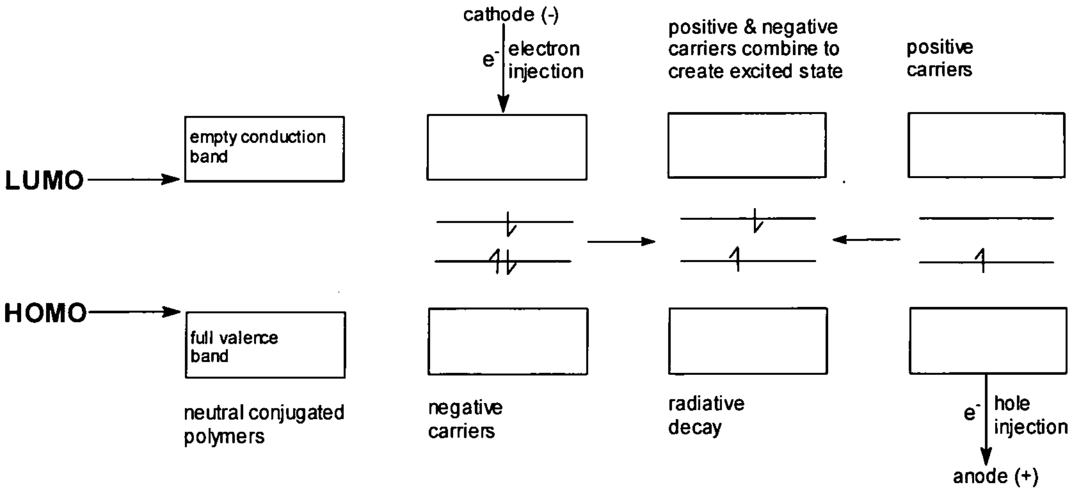

Figure 5.3. π-Band structures involved in creation and radiative recombination of charge carriers.

5.4.3 Challenges in developing organic polymer light emitting diodes

5.4.3.1 *Colour tuning*

Control of the emission colour is clearly a requirement for the achievement of full-colour displays. The colour of emission is determined by the energy gap, which is a function of the effective conjugation length.[12] Polymers with short conjugation lengths or relatively poor π-overlap have a larger band gap and show a blue shift in their electroluminescence with respect to polymers with longer conjugation lengths and good π-overlap.[13]

In the first discovery of electroluminescence from an organic polymer, namely poly(*p*-phenylene vinylene), emission in yellow-green region was produced which corresponds to a band gap of 2.5eV.[7] To date, control of emission colour has been achieved via several different routes. The incorporation of large aromatic units such as anthracene into arylene vinylene chains has been proven to be valuable in this context since they posses smaller band gaps as compared to that of the 1,4-phenylene unit. Thus, it was reported that the poly(9,10-anthrylene butadienylene) shown in *Figure 5.4* gave a red shifted emission in comparison to that reported for poly(*p*-phenylene vinylene).[14] Similarly, the poly(1,4-naphthylene vinylene) (*Figure 5.4*) was reported to have an approximately 0.4eV smaller band gap than that for poly(*p*-phenylene vinylene) and a red shifted electroluminescence.[10]

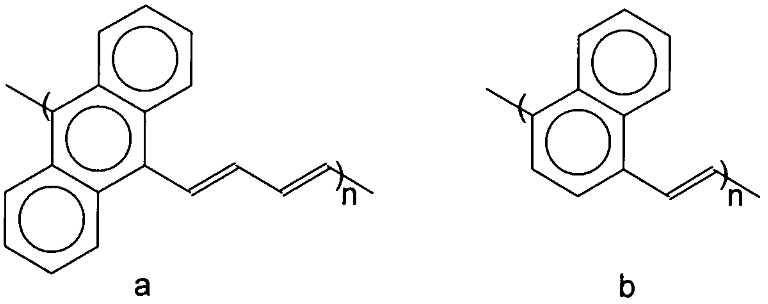

Figure 5.4 a) Poly(9,10-anthrylene butadienylene) and b) poly(1,4-naphthylene vinylene).

The emission colour may be controlled by attachment of either electron-donating or electron-withdrawing groups to the polymer backbone. The application of electron-donating methoxy groups in poly(2,5-dimethoxy-*p*-phenylene vinylene) was shown to lower the band gap with respect to that for poly(*p*-phenylene vinylene),[15] this was attributed to a shift in oxidation potential of the polymer in a positive direction. By contrast, the attachment of electron-withdrawing groups, exemplified by the case of cyano substituted poly(arylene vinylene), in *Figure 5.5*, resulted in an increase in band gap as compared to that of poly(*p*-phenylene vinylene).[15]

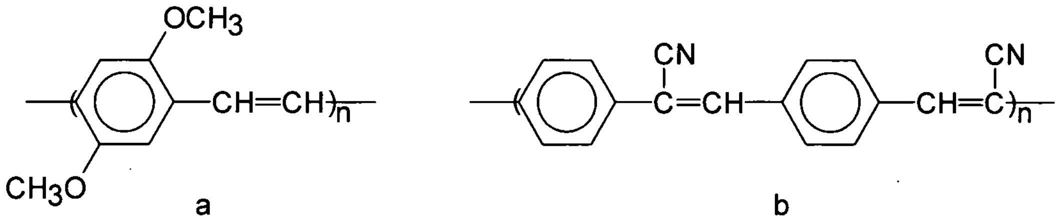

Figure 5.5 a) Poly(2,5-dimethoxy-*p*-phenylene vinylene) and b) cyano substituted poly(*p*-phenylene vinylene) derivative.

Substituents can also cause changes in the size of band gap through steric hindrance. Enhanced steric hindrance from side groups leads to a decrease in planarity of the main chain which reduces the conjugation and increases the band gap,[16,17] this phenomenon was illustrated by poly(*p*-phenylene diphenylvinylene), *Figure 5.6*.

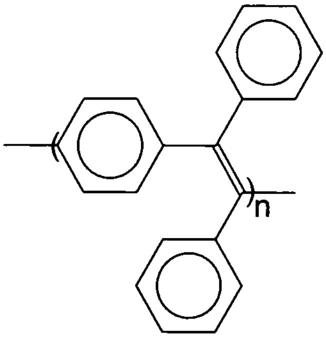

Figure 5.6 Poly(*p*-phenylene diphenylvinylene).

It was observed that the external applied voltage could control the emission colour to some extent.[16] This was demonstrated in the application of poly(1,4-phenylene vinylene-co-1,4-naphthylene vinylene), *Figure 5.7*, as an emissive layer in a light emitting diode where higher voltage resulted in red-shifted emission compared to that found when lower voltage was used.[18]

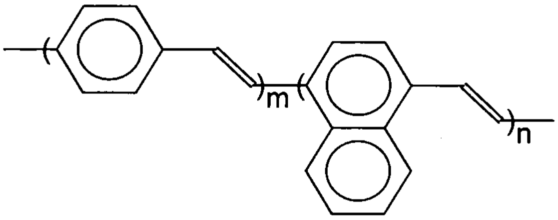

Figure 5.7 Poly(1,4-phenylene vinylene-co-1,4-naphthylene vinylene).

Friend *et al.* reported that the colour of the emission could be tuned by constructing multilayer devices using several layers of different polymers.[3,19] Such devices have been constructed and some of the results of their work are shown in *Table 5.1*.

Table 5.1 Characteristics of the four multilayer electroluminescent devices.

	Sample Number			
	$I^{1,2,3}$	$II^{1,2,3}$	$III^{1,2,3}$	$IV^{1,2}$
layer 1	copolymer	MEHPPV	copolymer	copolymer
layer 2	PPV	PPV	MEHPPV	PPV
layer 3	MEHPPV	copolymer	PPV	copolymer
layer 4	-	-	copolymer	-
colour of emission	red	orange	orange	yellow

[1] copolymer = partially converted poly(2,5-dimethoxy-*p*-phenylene vinylene) with band gap of 2.6 eV

[2] PPV = poly(*p*-phenylene vinylene) with band gap of 2.5 eV

[3] MEHPPV = poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene) with band gap of 2.2 eV

It was found that such devices emitted light from more than one polymer layer. There are several possible explanation for this phenomenon.[19] The first being the existence of a broad electron-hole capture region extending over several layers. This could be attributed to the fact that in different polymer layers, the mobilities of electrons are different and in common with many organic semiconductors, the mobilities of electrons can be significantly lower than hole mobilities. The second explanation is that excited species, once formed, can diffuse into other layers.

Another method of tuning the emission colour is the application of copolymers as emissive layers. The copolymer shown in *Figure 5.8* was prepared in such a way that a non-conjugated unit was introduced statistically in the polymer chain and was reported to emit in the blue-green region of the spectrum, showing a blue shift with respect to poly(*p*-phenylene vinylene).[20]

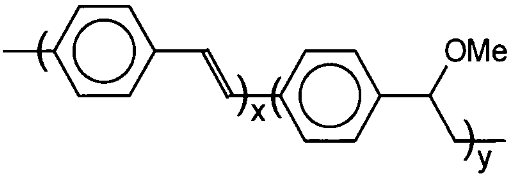

Figure 5.8 Poly(*p*-phenylene vinylene) based copolymer.

In another example two conjugated segments, namely phenylene vinylene and dimethoxyphenylene vinylene were incorporated into the copolymer, *Figure 5.9.* The individual homopolymers were known to emit different colours and varying the proportion of dimethoxyphenylene vinylene in the polymer allowed control over emission colour from blue-green to orange-red.[20]

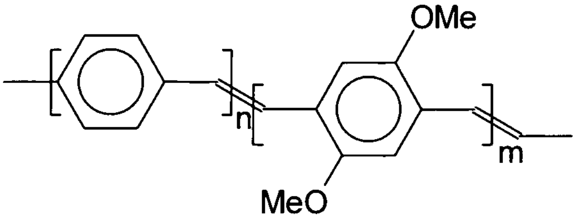

Figure 5.9 Poly(*p*-phenylene vinylene-co-2,5-dimethoxy-*p*-phenylene vinylene).

A similar method of tuning the emission colour was applied in the synthesis of the blue-emitting copolymer presented in *Figure 5.10.* In this case, although the repeat unit is fully conjugated the bulky substituted terphenylene spacer interrupts the conjugation by decreasing the planarity of the conjugated backbone hence increasing the band gap of the polymer.[21]

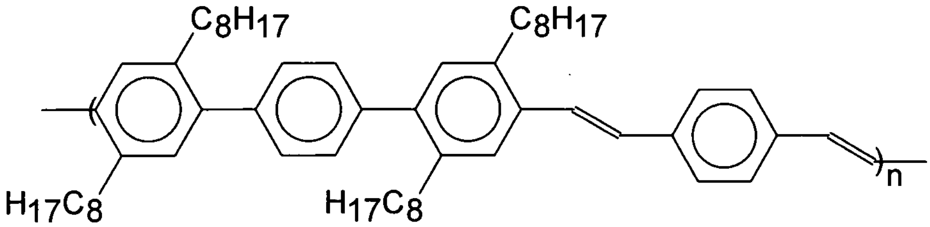

Figure 5.10 Poly(*p*-phenylene vinylene) based copolymer.

It was reported that introduction of the in-chain phenyl ring with *meta* linkage in the conjugated backbone decreases the planarity required for conjugation, hence increasing the band gap of the polymer. Varying the proportion of this *meta* linkage in the polymer chain allows control over the emission colour.[22,23]

5.4.3.2 *Emission efficiency*

Another challenging task in developing organic polymer LEDs is achieving high enough internal electroluminescence efficiency (i.e. the ratio of the total number of photons produced in the emissive layer to the number of charge carriers injected).[24,25] The efficiencies of devices based on PAVs have improved greatly from only 0.01% when PPV was used for the first time as an emissive layer[7] to about 4% recently.[26] This is a subject of intense development work in industry and the real figure is being increased constantly. This problem has been addressed primarily through device engineering which includes varying the type of metal used as electrodes, the thickness of emissive layers, the use of charge transport layers, and the use of random copolymers.[8,27,28,29]

Once the excited species has been formed, it may also decay non-radiatively by processes which include migration of excited species to quenching sites.[9] Friend *et al.* reported that random copolymers having spacer units with slightly wider band gaps than the emissive part of the polymer restricts the possible migration to quenching sites and enhances radiative decay.[30]

A partial replacement of conjugated segments in conjugated polymers by non-conjugated units also shortens the conjugation length and decreases the mobility of excited species reducing the possibility of interaction between excited species and quenching sites. Consequently this may also contribute to the enhancement of device efficiency.[20]

Another strategy to improve device efficiency is to balance the rates of injection of electrons and holes into the devices, electron injection has proved more difficult than hole injection.[11] The use of additional organic charge-transporting layers between the emissive layer and one or both of the electrodes introduces energy barriers to transport of either electrons or holes between the layers, and thus confines and controls the charge carriers. The confined charges at the interface act to redistribute the electric field within the devices so as to improve the balance of electron and hole injection at the emissive layer.

The choice of the correct electrode combination is crucial to the operation of LEDs and as was noted earlier most conjugated polymers have a tendency to transport holes in preference to electrons.[20] Burn *et al.* reported that while keeping the hole injecting electrode (ITO) fixed, the efficiency of an LED depends critically on the type of electron injecting electrodes. Low work function metals such as calcium yielded higher efficiencies due to their better electron injecting characteristics.[20]

5.5 **Results and Discussion**

5.5.1 **UV-visible studies of poly(arylene vinylene)s.**

5.5.1.1 ***Poly(4,4'-diphenylene diphenylvinylene)s***

A series of fractionated poly(4,4'-diphenylene diphenylvinylene) prepared via McMurry reaction with various molecular weights were examined for their UV-visible absorption characteristics. The UV-visible absorption spectra were recorded for chloroform solutions of the polymer fractions. A representative set of the spectra recorded is shown in *Figure 5.11.*

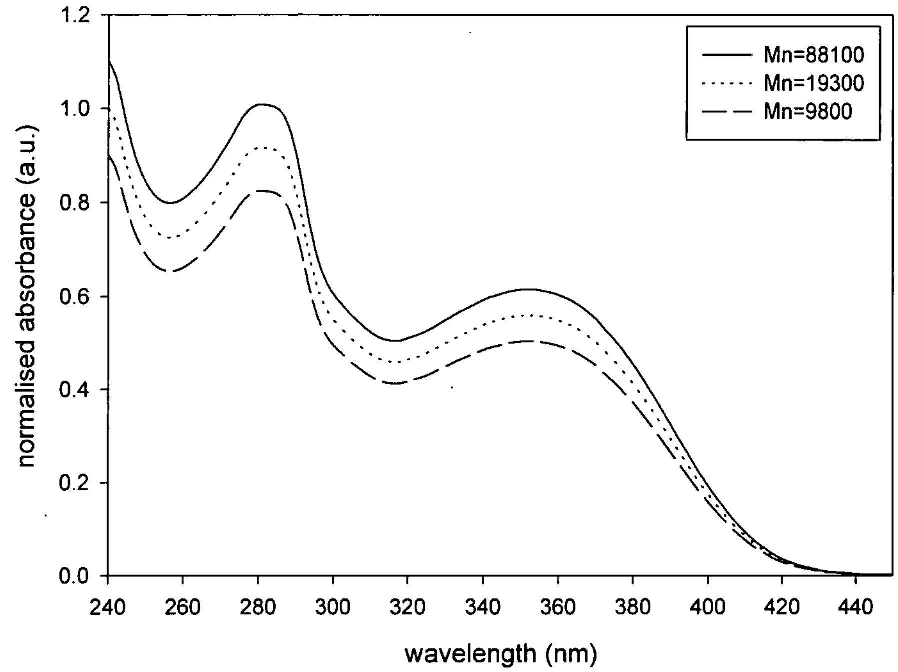

Figure 5.11 A representative set of UV-visible spectra of poly(4,4'-diphenylene diphenylvinylene).

Generally the spectra show two resolved peaks with broad bands indicating that polymers examined have a wide distribution of conjugation lengths. The absorption bands at shorter wavelengths are possibly due to the π-π* transitions associated with the pendant phenyl groups and the absorption bands at longer wavelengths can be attributed to the π-π* transitions for π electrons delocalised along conjugated polymer backbone. Maximum absorptions at longer wavelengths (1^{st} λ_{max}) of every sample were recorded and are tabulated together with the molecular weight data in *Table 5.2*.

***Table** 5.2* Molecular weight data and results from UV-visible absorption for poly(4,4'-diphenylene diphenylvinylene)s.

Samples	$\overline{M}_n$[1]	$\overline{M}_w$[1]	DP[2]	1st λ_{max} (nm)
fraction 1	88100	211000	266	356
fraction 2	49900	225400	151	356
fraction 3	42900	78100	130	356
fraction 4	19300	28100	58	356
fraction 5	16500	22400	50	356
fraction 6	13600	16600	41	356
fraction 7	9800	11600	29	356
fraction 8	7000	8800	21	354
fraction 9	5700	7100	17	352
fraction 10	4200	5900	12	352
fraction 11	3800	5200	11	352
fraction 12	3600	5000	10	350
fraction 13	3100	4100	9	350
fraction 14	2500	3260	7	350
fraction 15	2000	2500	6	350
fraction 16	1800	2330	5	344
fraction 17	1200	1560	3	330
fraction 18	790	800	2	326

[1] 'polystyrene equivalent' values

[2] DP = degree of polymerisation

As shown in *Table 5.2*, on going from fraction 17 to fraction 7 the value of the first absorption peak, λ_{max}, increases as the molecular weight increases, this is as expected and correlated with increasing conjugation length. However, going from fraction 7 to fraction 1 the absorption spectrum remains unchanged even though the molecular weight increases indicating that, within this range the effective conjugation length does not increase with the increasing molecular weight. Thus it is possible to conclude that the effective conjugation length is achieved in poly(4,4'-diphenylene diphenylvinylene) prepared via McMurry reaction at values for the degree of polymerisations between 29 and 21. As was commented earlier molecular weights in excess of $\overline{M}_n$ ~20,000 are required for good mechanical properties and film formation, and these results show that there is no correlation between the absorption spectra and film formation. This is unsurprising but useful knowledge since it allows us to make spectroscopic measurements of relatively low molecular weight polymers and so to screen a range of structures without the necessity of optimising the synthesis for high molecular weight.

Fraction 18 was a special case and, as shown in Chapter 2, was the pure cyclic trimer. The absorption maximum occurs at the lowest wavelength of all samples and this probably a consequence of the steric inhibition of planarity in this compound. The low value for fraction 17 may indicate some cyclic oligomers in this material although no purification and identification was achieved in this case.

5.5.1.2 *Poly(1,3-phenylene diphenylvinylene)s*

The UV-visible absorption characteristics of a series of polymer fractions with various molecular weights obtained from the fractionation experiment carried out on poly(1,3-phenylene diphenylvinylene) prepared via the McMurry reaction were measured. The spectra were recorded for chloroform solutions of the polymer. *Figure 5.12* presents some of the spectra recorded.

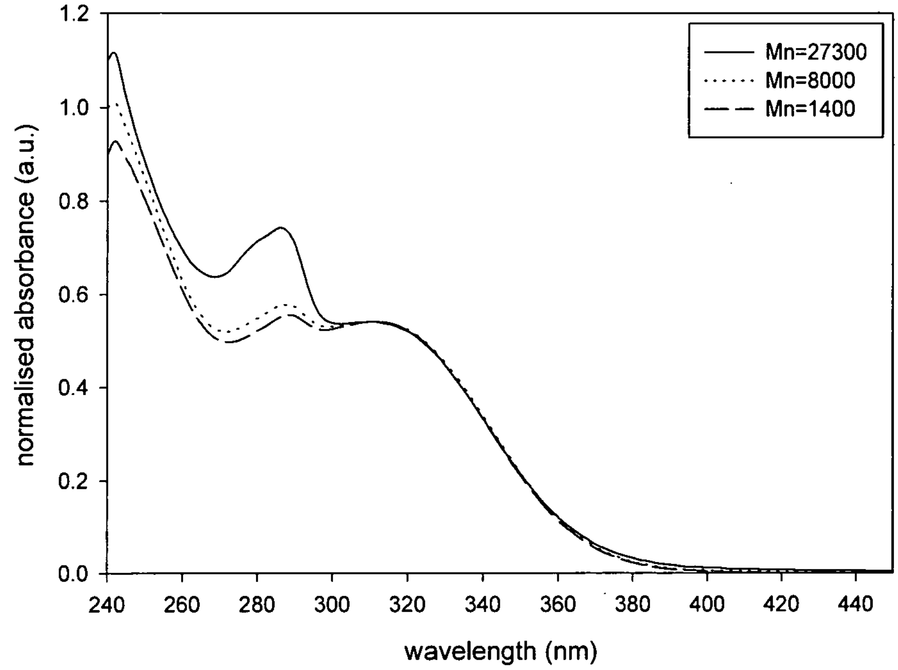

Figure 5.12 A representative set of UV-visible spectra for poly(1,3-phenylene diphenylvinylene).

Similar spectra to those of poly(4,4'-diphenylene diphenylvinylene) were obtained in the sense that broad absorption bands were observed. As mentioned earlier, the presence of broad absorption bands in the spectra suggests that the polymers examined have a wide distribution of effective conjugation lengths. The wavelength maxima for the absorptions at lower energy, which correspond to the effective conjugation length in the polymer, were recorded and are summarised in *Table 5.3* together with the molecular weight data of the polymer fractions examined.

Table 5.3 Molecular weight data and results from UV-visible absorption of poly(1,3-phenylene diphenylvinylene)s.

Samples	$\overline{M}_n$[1]	$\overline{M}_w$[1]	DP[2]	1st λ_{max} (nm)
fraction 1	27300	70800	107	310
fraction 2	19000	53700	75	310
fraction 3	17400	49900	69	310
fraction 4	14600	35000	57	310
fraction 5	12700	29300	50	310
fraction 6	8000	15400	32	310
fraction 7	5200	6800	20	310
fraction 8	2500	3370	10	310
fraction 9	2000	2580	8	310
fraction 10	1700	2250	7	310
fraction 11	1400	1010	6	310

[1] 'polystyrene equivalent' values
[2] DP = degree of polymerisation

In contrast to the case of poly(4,4'-diphenylne diphenylvinylene), within the range of molecular weight examined, the values of the first λ_{max} recorded do not exhibit any change at all with molecular weight. This observation suggests that the longest effective conjugation sequence for this polymer is out of the molecular weight range used in this experiment, and most probably it lies lower than the degree of polymerisation of 6 which is the shortest polymer chain in the range tested. If this was the case, it would probably due to the presence of in-chain phenyl ring with *meta* linkage in the polymer repeat unit which might have prevented the planarity of the conjugated backbone required for the extension of conjugation length in the polymer.

5.5.1.3 *Poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene)s*

Samples of poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene) with three different molecular weights were examined for their UV-visible absorption characteristic by recording the spectra for polymer solutions in chloroform. *Figure*

5.13 presents the spectra obtained and wavelengths at the first maximum absorption are recorded in *Table 5.4*.

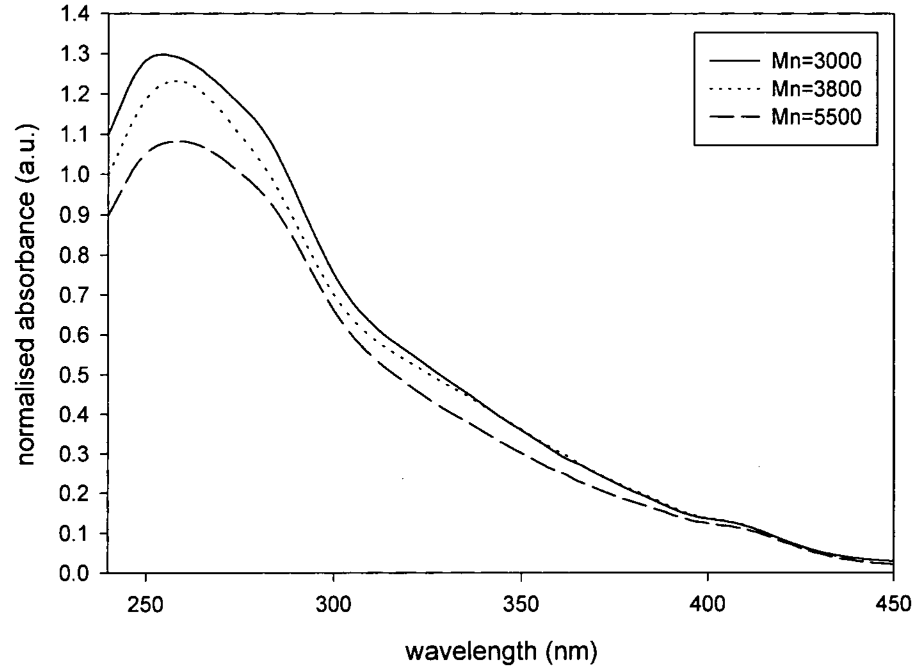

Figure 5.13 UV-visible absorption spectra of poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene).

The result obtained was quite unexpected in the sense that the overall appearance of the spectrum was different to that of the hydrocarbon analogue. The first absorption maximum occurred at relatively low energy indicating the presence of a relatively small band gap whereas it was anticipated that fluorination would increase the band gap. It is also clear that the intensity of the first absorption peak is lower than that for the hydrocarbon analogue. The luminescence of this polymer (see later) was also weak. These observations are not immediately amenable to explanation, since we did not obtain the effect we were seeking (i.e. a blue shifted luminescence) we abandoned further work on this polymer, the observation are clearly unusual and this topic merits further study which was not possible because of time constraints.

Table 5.4 Molecular weight data and results from UV-visible absorption of poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene).

samples	$\overline{M}_n$[1]	$\overline{M}_w$[1]	DP[2]	1st λ_{max} (nm)
1	3000	13400	6	400
2	3800	16000	7	403
3	5500	20400	11	405

[1] 'polystyrene equivalent' values
[2] DP = degree of polymerisation

As shown in *Table 5.4*, the position of the first absorption maximum increases with molecular weight as expected for the case of increasing conjugation length, although the effect is small.

5.5.1.4 **Poly(tetra-*p*-phenylene diphenylvinylene)s**

UV-visible absorption spectra for samples of poly(tetra-*p*-phenylene diphenylvinylene)s with various *cis:trans* vinylene ratios and molecular weights were recorded from polymer films which were prepared by spin casting polymer solutions in chloroform onto a quartz disc. *Figure 5.14* shows a representative set of the spectra recorded for samples with 68% *trans* vinylenes.

The spectra obtained show two broad absorption bands, the absorption band with shorter λ_{max} may be attributed to the π-π^* transitions of electrons of the pendant phenyl rings and the other absorption band can be assigned to the π-π^* transitions of electrons delocalised along the conjugated polymer backbone which corresponds to the band gap transition of the polymer. Wavelengths at the maximum absorption of the latter band were recorded and summarised in *Table 5.5*.

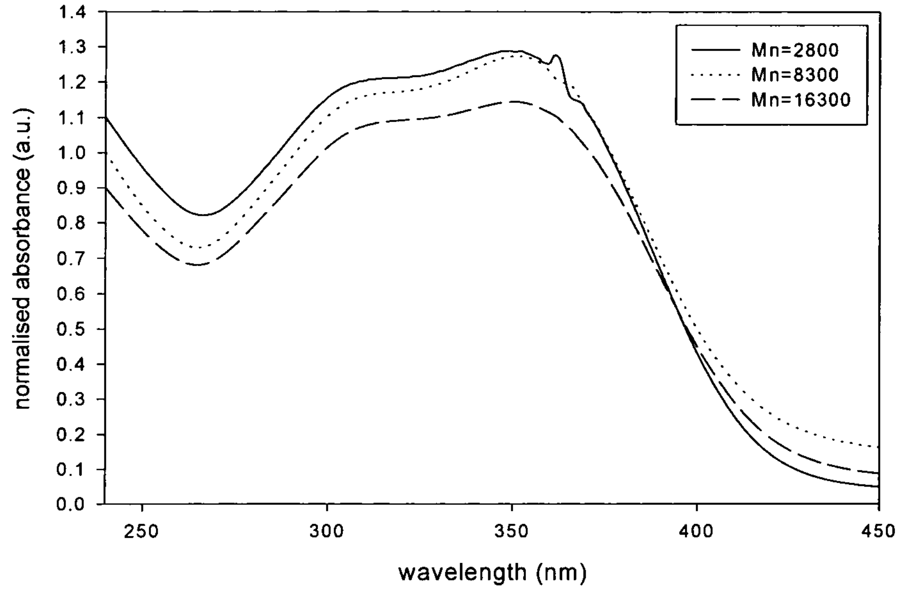

Figure 5.14 UV-visible absorption spectra of poly(tetra-*p*-phenylene diphenyvinylene)s with 68% *trans* vinylenes.

Table 5.5 Molecular weight data and results from UV-visible absorption of poly(tetra-*p*-phenylene diphenylvinylene)s.

samples	% *cis* isomer	$\overline{M}_n$[1]	$\overline{M}_w$[1]	DP[2]	1st λ_{max} (nm)
1	97	3850	9630	8	319
2	32	2800	5000	6	349
3	32	8300	13800	17	351
4	32	16300	27900	34	351
5	2	1810	2950	4	354

[1] 'polystyrene equivalent' values

[2] DP = degree of polymerisation

Samples 1, 2 and 5 have respectively 97, 32 and 2% *cis* vinylenes and are of similar molecular weight. Qualitatively we can see that the higher the *cis* content the higher the bad gap. A high *cis* vinylene content might result in a highly coiled chain structure; chain planarity, which is required for conjugation, is clearly inhibited in such structures and this may explain why the high *cis* polymer had a bigger band gap than those with lower *cis* vinylenes content. By contrast the virtually all *trans* vinylenes in the polymer sample 5 was expected to facilitate the formation of a rigid rod-like structure and a highly ordered conjugated polymer with a smaller band gap as observed. For samples 2, 3 and 4 which all have about 32% *cis* vinylene content, the wavelength at first absorption maximum increases with molecular weight as expected on going from sample 2 to sample 3. However, going from samples 3 to 4, does not result in further change. Thus it seems that the effective conjugation length is achieved for this polymer between degree of polymerisations of 6 and 17. In another set of measurements, UV-visible absorption spectra were recorded for polymer solutions in chloroform using samples with various molecular weights and about 1:1 *cis:trans* vinylene ratios. The values of the first absorption maximum were recorded and are tabulated in *Table 5.6* below.

Table 5.6 Molecular weight and UV-visible absorption data for poly(tetra-*p*-phenylene diphenylvinylene)s.

samples	$\overline{M}_n$	$\overline{M}_w$	DP	1st λ_{max} (nm)
1	1300	1600	2	341
2	1350	2050	3	344
3	2800	4500	6	348
4	4500	10200	9	351
5	6000	9400	12	351

As can be seen from the *Table 5.6*, it is possible to conclude that the effective conjugation length is achieved in this polymer at a DP of about 6 to 9 which is equivalent to a chain containing on average 24 phenylene and 6 vinylene units. These figures are about half of those found for poly(4,4'-diphenylene diphenylvinylene), but here the repeat unit has twice the number of phenylene rings and it would seem that a chain sequence of 30 to 40 phenylene and vinylene units is long enough to accommodate an effective conjugation length for these kinds of polymer.

5.5.1.5 *Summary of UV-visible absorption studies of poly(arylene vinylene)s*

A summary of the UV-visible absorption data of all polymers prepared throughout the course of this study, namely poly(4,4'-diphenylene diphenylvinylene) (**PDPV**), poly(tri-*p*-phenylene diphenylvinylene) (**P3PV-DP**), poly(tetra-*p*-phenylene diphenylvinylene) (**P4PV-DP**), poly(4,4'-diphenylene dimethylvinylene) (**PDMeV**), poly(tri-*p*-phenylene dimethylvinylene) (**P3PV-DMe**), poly(tetra-*p*-phenylene dimethylvinylene) (**P4PV-DMe**), poly(1,3-phenylene diphenylvinylene) (**m-PPV-DP**), poly(1,3-phenylene dimesitylvinylene) (**m-PPV-DM**) and poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene) (**PDPV-DF**) is given in *Table 5.7* below.

As shown in *Table 5.7* it was found that among the polymers produced, PDPV has the smallest band gap. Increasing the number of phenyl rings in the polymer repeat unit was shown to increase the band gap of the resultant polymer, see PDPV, P3PV-DP and P4PV-DP. An increase in the size of band gap was observed when in-chain phenyl ring with *meta* linkage was introduced in the polymer repeat unit, see PDPV and m-PPV-DP. However, rather an unexpected result was obtained from fluorinated PDPV; in that the polymer was anticipated to have a larger band gap than that of the non-fluorinated analogue, see PDPV and PDPV-DF but did not, this remains as an unexplained result. Replacing phenyl with methyl as pendant group also resulted in an increase in band gap, see for example PDPV and PDMeV. However, although all these effects (except the fluorinated case) are in the directions expected the total effect is relatively small, the limited blue shift with increasing phenylene sequence was particularly disappointing.

Table 5.7 Summary of molecular weight and UV-visible absorption data of poly(arylene vinylene)s examined.

samples	synthetic routes	% *cis* isomer[1]	$\overline{M}_n$[2,3]	λ_{max} (nm)[4]
PDPV	McMurry		2000	350
PDPV	Yamamoto	48	1900	352
P3PV-DP	Suzuki	48	1530	347
P4PV-DP	Suzuki	48	2050	344
PDMeV	Yamamoto	80	1300	290
P3PV-DMe	Suzuki	80	1890	309
P4PV-DMe	Suzuki	80		314
m-PPV-DP	McMurry		2000	310
m-PPV-DM	McMurry		1000	377
PDPV-DF	McMurry		3000	400

[1] only polymers prepared via Yamamoto and Suzuki routes could be structurally defined

[2] 'polystyrene equivalent' values

3 molecular weight of P4PV-DMe could not be determined by GPC due to poor solubility

[4] λ_{max} = peak of first absorption

5.5.2 Photoluminescence studies of poly(arylene vinylene)s

5.5.2.1 *Poly(4,4'-diphenylene diphenylvinylene)s*

Photoluminescence characteristics of samples with various molecular weights of poly(4,4'-diphenylene diphenylvinylene) prepared via McMurry reaction were measured. This part of the work was a joint project with Professor Friend's group, at the Cavendish Laboratory, Cambridge University, where all these measurements were carried out. Measurement were carried by photoexciting the samples with an Argon-ion laser which lases in the UV to green region of the spectrum with two dominating lines at 351 and 364nm.

Figure 5.15 presents the spectra of PDPV of two different molecular weights, the wavelengths at peak emission are recorded in *Table 5.8*. The sharp peaks are overtones of the strong laser lines. The spectra obtained showed identical shape for all samples with no vibronic structure. The position of the peak of the emission (λ_{max}) seems to vary slightly with molecular weight; as the molecular weight increases λ_{max} increases as expected but the effect is relatively small.

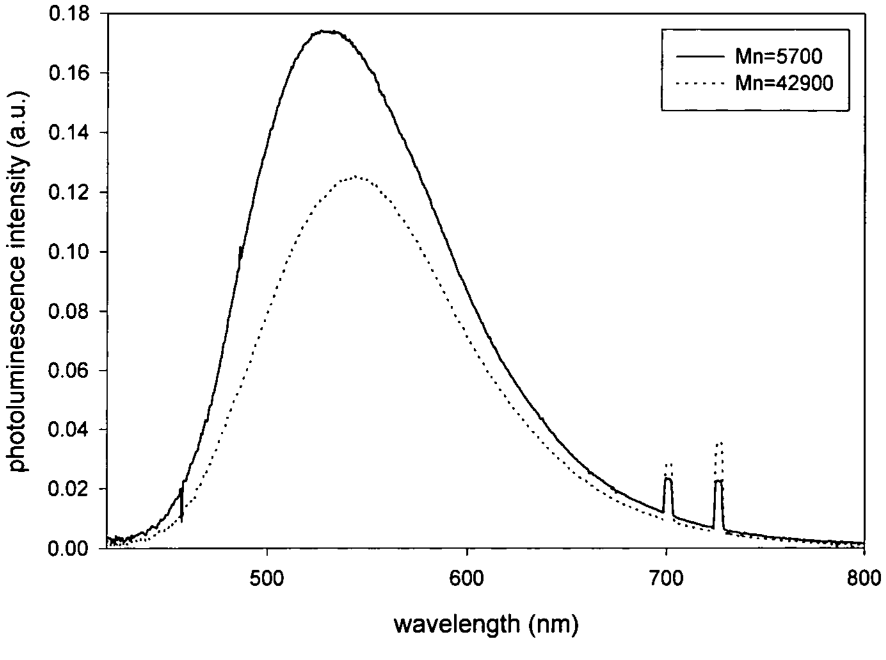

Figure 5.15 Photoluminescence spectra of poly(4,4'-diphenylene diphenylvinylene)s.

Table 5.8 Molecular weight and photoluminescence data of poly(4,4'-diphenylene diphenylvinylene)s prepared via the McMurry reaction.

samples	$\overline{M}_n$ [1]	photoluminescence	
		efficiency (%)	λ_{max} (nm)
1	5700	52.5	528
2	9800	53.0	533
3	16500	58.7	533
4	42900	50.2	543

[1] 'polystyrene equivalent' values

Generally the photoluminescence efficiencies recorded were relatively high in comparison to that first reported for poly(*p*-phenylene vinylene) of 8%.[7] In *Table 5.8*, in samples 1 to 4, the molecular weight increases by a factor of about 7, never-the-less no significant decrease in photoluminescence efficiency was observed underlining the purity of the polymers examined, the structural regularity and the absence of significant concentration of defects. Photoluminescence efficiency was expected to decrease with increasing molecular weight since more structural defects might be expected to be present in high molecular weight polymer; such defects may act as quenching sites for photoluminescence. In addition, generally the higher the molecular weight the more difficult it becomes to purify the polymer. Thus the efficiencies obtained in this experiment may also reflect the effectiveness of fractionation carried out not only as a procedure to isolate high molecular weight fractions from the as made polymer but also as a polymer purification method.

In another set of measurements, samples with variation of molecular weights and *cis:trans* vinylenes ratios of poly(4,4'-diphenylene diphenylvinylene)s prepared via Yamamoto polycondensation were examined for their photoluminescence characteristics, the results obtained are summarised in *Table 5.9*.

Table 5.9 Photoluminescence data of poly(4,4'-diphenylene diphenylvinylene)s prepared via Yamamoto polycondensation.

samples	% *cis* isomer	$\overline{M}_n$[1]	photoluminescence	
			efficiency (%)	λ_{max} (nm)
1	59	1200	35.0	522
2	48	1900	41.4	515
3	37	2900	35.2	523

[1] 'polystyrene equivalent' values

Interestingly, it was shown that photoluminescence efficiency varied with the *cis:trans* isomer ratios of the monomer mixture used in the polymerisation. For samples of similar molecular weight the maximum efficiency was obtained from the polymer prepared using a monomer mixture with an approximately 1:1 *cis:trans* isomer ratio.

5.5.2.2 *Poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene)s*

Photoluminescence characteristics of samples with different molecular weights of poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene) prepared via the McMurry reaction were measured in the same way as described earlier. *Figure 5.16* shows the spectra recorded and the results obtained are summarised in *Table 5.10.*

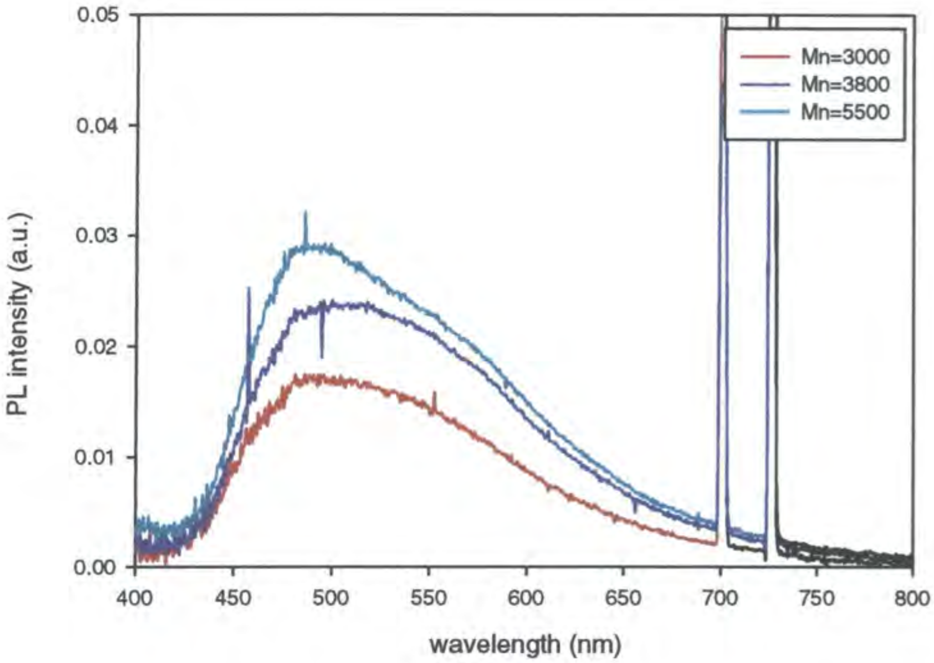

Figure 5.16 Photoluminescence spectra of poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene)s.

Table 5.10 Photoluminescence data of poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene)s.

samples	$\overline{M}_n$[1]	photoluminescence	
		efficiency (%)	λ_{max} (nm)
1	3000	9.5	492
2	3800	13.1	505
3	5500	16.1	489

[1] 'polystyrene equivalent' values

Spectra obtained showed an identical shape for all samples examined with no vibronic structure. The maximum emission occurred at lower energy than that of poly(4,4'-diphenylene diphenylvinylene). The photoluminescence efficiencies recorded increased with increasing molecular weight which is unusual. The fact that these polymers do not have high extinction coefficients at the main excitation wavelengths might have contributed to the limited efficiency values obtained.

5.5.2.3 *Poly(1,3-phenylene diphenylvinylene)s*

Samples with various molecular weights of poly(1,3-phenylene diphenylvinylene) prepared via McMurry reaction were examined for their photoluminescence properties and the spectra obtained are recorded in *Figure 5.17*. The emission peaks for all samples were recorded and are summarised in *Table 5.11*.

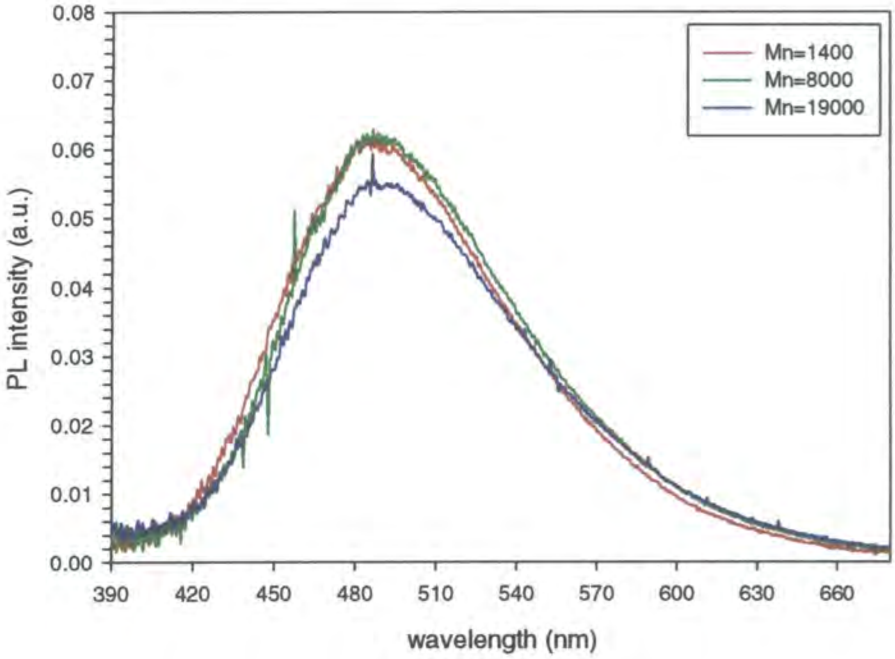

Figure 5.17 Photoluminescence spectra of poly(1,3-phenylenediphenylvinylene)s.

Table 5.11 Photoluminescence data of poly(1,3-phenylene diphenylvinylene)s.

samples	$\overline{M}_n$[1]	photoluminescence	
		efficiency (%)	λ_{max} (nm)
1	1400	27.3	482
2	8000	24.3	487
3	19000	22.2	489

[1] 'polystyrene equivalent' values

Generally the maximum emission occurred at higher energy than that of poly(4,4'-diphenylene diphenylvinylene). This is possibly be due to the presence of in-chain phenyl ring with *meta* linkage in the polymer repeat unit which was expected to inhibit the planarity required for conjugation and consequently increase the band gap of the polymer.

It was shown in *Table 5.11* that the λ_{max} for the photoluminescence peak increases with increasing molecular weight as expected. The photoluminescence efficiencies obtained were about half of those found for poly(4,4'-diphenylene diphenylvinylene), however, these figures were three times higher than the first reported for poly(*p*-phenylene vinylene).[7] Going from samples 1 to 3 where molecular weight increases by a factor of more than 13, the photoluminescence efficiencies obtained showed a drop of only 5%, this consistency of observation again underlines the purity and structural uniformity of the samples examined.

5.5.2.4 *Poly(tetra-p-phenylene diphenylvinylene)s*

Photoluminescence characteristics of poly(tetra-*p*-phenylene diphenylvinylene)s with various *cis:trans* vinylenes contents and molecular weights prepared via Suzuki coupling reaction were measured. A representative set of the spectra recorded is shown in *Figure 5.18*. Results obtained are tabulated in *Table 5.12*.

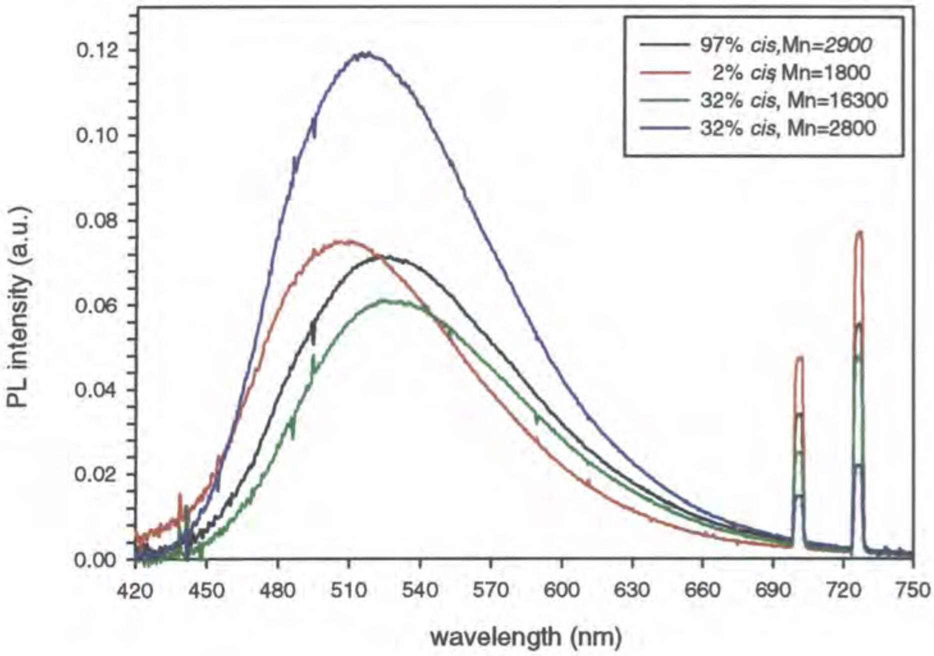

Figure 5.18 Photoluminescence spectra of poly(tetra-*p*-phenylene diphenylvinylene)s.

Table 5.12 Photoluminescence data of poly(tetra-*p*-phenylene diphenylvinylene)s.

samples	% *cis* isomer	$\overline{M}_n$[1]	photoluminescence	
			efficiency (%)	λ_{max} (nm)
1	97	2900	28.6	524
2	62	5000	30.1	533
3	48	4200	53.5	520
4	32	2800	35.8	517
5	32	8300	32.5	521
6	32	16300	21.7	523
7	2	1800	30.7	496

[1] ‘polystyrene equivalent’ values

Generally the photoluminescence spectra obtained showed that the maximum emission occurred at a slightly higher energy than that found for poly(4,4'-diphenylene diphenylvinylene) as expected. In *Table 5.12*, going from samples 4 to 6 which contained the same ratio of *cis:trans* vinylenes the emission peak recorded increases with increasing molecular weight; this is consistent with the hypothesis that increasing molecular weight extends the conjugation length hence decreases the band gap of the polymer; however, the effect is rather small.

A similar trend to that found in the case of poly(4,4'-diphenylene diphenylvinylene) prepared via Yamamoto polycondensation was observed in the sense that the photoluminescence efficiencies obtained varied with the *cis:trans* isomer ratios of the monomer mixture used in the polymerisation. The highest efficiency was observed in the polymer prepared using a monomer mixture with an approximately 1:1 *cis:trans* isomer ratio. This is also in agreement with the observation made earlier in the case of poly(4,4'-diphenylene diphenylvinylene). The relatively low efficiency observed in sample 7 can be attributed to the virtually all *trans* vinylene structure in this polymer chain which we postulate leads to the formation of a highly ordered conjugated polymer. In such an ordered polymer the mobility of electrons and excited species will be enhanced and this results in a higher possibility of excited species meeting photoluminescence quenching sites before decaying radiatively.

It was shown in *Table 5.12* that photoluminescence efficiency decreases with increasing molecular weight, see samples 4 to 6. This suggests that more photoluminescence quenching sites are present in the higher molecular weight polymers which might arise from structural defects or impurity. However, no such structural defects or significant impurity was observed in the polymer by using our analytical techniques (^{1}H nmr and ^{13}C nmr).

5.5.3 **Electroluminescence studies of poly(arylene vinylene)s**

As mentioned earlier this part of the work was a joint project with Professor Friend's group. All measurements were carried out at Cavendish Laboratory, Cambridge University and the author played no experimental part. The results reported here were obtained through collaboration with workers in Professor Friend's group and are included for completion. However, only one polymer, namely poly(4,4'-diphenylene diphenylvinylene) prepared via McMurry reaction has been used in the study so far.

In a preliminary attempt to apply poly(4,4'-diphenylene diphenylvinylene) (PDPV) as the emissive material in a light emitting diode, the polymer film was incorporated in between calcium as the cathode and indium-tin oxide (ITO) as the anode. The polymer was spun cast onto ITO from either chloroform or toluene solution. As a result, an emission in yellow-green region of the spectrum was observed with an efficiency of 0.035%.

Balanced injection and transport of electrons and holes are prerequisites for achieving highly efficient light emitting diodes.[28] In order to meet these prerequisites a multi-layer device structure was constructed using poly(*p*-phenylene vinylene) (PPV) and poly(vinylcarbazole) (PVK) as complement layers. Poly(*p*-phenylene vinylene) was shown to be compatible with ITO in terms of hole-injecting characteristics[31] and poly(vinylcarbazole) was applied recently as hole-injecting layer as well.[32] It was shown that for organic semiconductors the transport of holes is favoured in comparison to electrons. However, due to difference in ionisation potential of poly(*p*-phenylene vinylene) and poly(vinylcarbazole) the incorporation of poly(vinylcarbazole) between the emissive layer and poly(*p*-phenylene vinylene) was expected to form a hole barrier at the interface of poly(*p*-phenylene vinylene) and poly(vinylcarbazole) this would slow the transport of holes and consequently more balanced transport of holes and electrons could be achieved.

In order to implement this idea a three layer device structure was constructed consisting of ITO/PPV/PVK/PDPV/Ca. As a result, the same emission colour to that obtained earlier was observed with efficiency of 0.8%, showing a more than twenty-fold increase. The role of poly(vinylcarbazole) is evident when comparing diodes which incorporated a poly(vinylcarbazole) layer with single-layer ITO/PDPV/Ca and double-layer ITO/PPV/PDPV/Ca in which efficiencies up to 0.04% in the former and 0.25% in the latter were observed. *Figure 5.19* shows an example of the electroluminescence spectra obtained. This work in the Cambridge group is continuing at the time of writing.

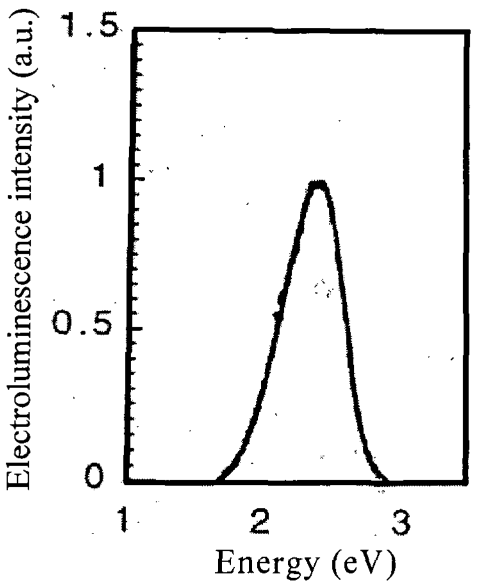

Figure 5.19 Electroluminescence spectrum of poly(4,4'-diphenylene diphenylvinylene) obtained from an ITO/PPV/PVK/PDPV/Ca device structure.

5.6 Conclusions

In this study it was shown that the size of the band gap in poly(arylene vinylene)s can be controlled chemically i.e. by varying the pendant groups, the number of phenyl rings in the polymer repeat unit and also by introducing different in-chain phenyl ring linkages in the polymer chain.

It was found that photoluminescence efficiency varies with the *cis:trans* vinylene contents in the polymer, in the case of poly(4,4'-diphenylene diphenylvinylene) and poly(tetra-*p*-phenylene diphenylvinylene), maximum photoluminescence efficiencies were obtained from polymers with an approximately 1:1 ratio of *cis* and *trans* vinylene contents.

Poly(arylene vinylene)s produced in this study, particularly poly(4,4'-diphenylene diphenylvinylene), poly(tetra-*p*-phenylene diphenylvinylene) and poly(1,3-phenylene diphenylvinylene) have been shown to have potential in light emitting diode applications due to their high photoluminescence efficiencies and good solubilities in common organic solvents.

Poly(4,4'-diphenylene diphenylvinylene) has been proved to be suitable for application in light emitting diodes and it was shown that this polymer gives yellow-green electroluminescence with an efficiency of 0.8% in a three layer device structure.

5.7 References

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Chapter 6

Overall conclusions and proposals for future work

6.1 Overall conclusions

The work performed during the course of this study into the synthesis of poly(arylene vinylene)s has highlighted several interesting features. The synthesis of poly(4,4'-diphenylene diphenylvinylene) via the McMurry reaction which was reported to be erratic in terms of yields and molecular weights,[1] has been optimised significantly. Polymerisation with reproducible and high yields has been achieved and high molecular weight polymer was produced by fractionating the as made polymer, although the *cis/trans* vinylene distribution in the polymer chain was not controllable in this step-growth synthesis. The McMurry reaction has been shown to be a feasible route to other poly(arylene vinylene)s as well, particularly poly(1,3-phenylene diphenylvinylene).

In other attempts, the so-called Suzuki and Yamamoto polycondensations were applied in the synthesis of poly(arylene vinylene)s with a view to producing structurally defined (controllable *cis/trans* vinylene distribution) polymers and expanding the structural variety of the polymers accessible. It was shown that to produce high molecular weight polymers the application of monomer mixtures with about 1:1 *cis:trans* ratios was most effective under the experimental conditions investigated.

The polymers produced in this study have been shown to have potential in light emitting device applications since they have high photoluminescence brightness and efficiency and good solubility in organic solvents, particularly poly(1,3-phenylene diphenylvinylene), poly(tetra-*p*-phenylene diphenylvinylene) and poly(4,4'-diphenylene diphenylvinylene). In fact the latter has been proved to be a suitable material for application in light emitting diodes and it was shown that this polymer gives yellow-green electroluminescence with an efficiency of 0.8%. Further work on electroluminescence on this and related polymers produced in this study is continuing in the Cavendish Laboratory, Cambridge.

The content of *cis/trans* vinylenes in the polymer was found to be correlated with photoluminescence efficiency. In the case of poly(4,4'-diphenylene diphenylvinylene) and poly(tetra-*p*-phenylene diphenylvinylene), maximum photoluminescence efficiencies were obtained from polymers with an approximately 1:1 ratios of *cis* and *trans* vinylenes content. By correlating spectra of poly(4,4'-diphenylene diphenylvinylene) with known *cis/trans* vinylene ratios with those from materials produced by the McMurry route it was possible to show that the McMurry route gave polymers with a *cis/trans* ratio close to 50:50 with a slight *trans* dominance.

Although the feasibility of the approaches used during the course of this study has been established, there is room for optimisation especially in the application of the Suzuki and Yamamoto polycondensation. In these methods the optimum reaction conditions leading to high molecular weight polymers have yet to be found and results obtained in this study should be considered as preliminary observations.

However, in summary the synthesis of relatively high molecular weight poly(arylene vinylene)s has been achieved and in a few cases the distribution of *cis/trans* vinylene content could be controlled.

6.2 Proposals for future work

Since it was shown that the fluorinated analogue of PDPV had an unexpected and so far unexplained property in terms of the size of the band gap, studies on other fluorinated analogues would seem to be necessary in order to find an explanation for this observation. Despite the presence of reports in the literature discussing the effect of electron donating and electron withdrawing substituents on polymer properties, particularly the electrooptical properties,[2,3,4,5] none of them involved fluorine substituted directly on the unsaturated carbons of poly(arylene vinylene)s. This adds to the need of the study on fluorinated poly(arylene vinylene)s.

In this study the photoluminescence efficiency was found to vary with the *cis/trans* vinylene content in the polymer. Since the approaches used throughout this synthesis work did not result in high molecular weight polymer, an alternative procedure might be the application of the so-called Heck reaction.[6] It was reported that such a reaction leads to the formation of predominantly *trans* double bonds.[7] *Figure 6.2.1* shows a hypothetical polymerisation scheme in which substituents may be introduced on either monomer while maintaining the regularity of the *cis/trans* vinylenes. Variation of *cis/trans* vinylene contents could be achieved by controlling the *cis/trans* ratio of the dibromide monomer mixture, this route would allow a maximum *cis* content of 33% if the Heck reaction gives all *trans* vinylenes.

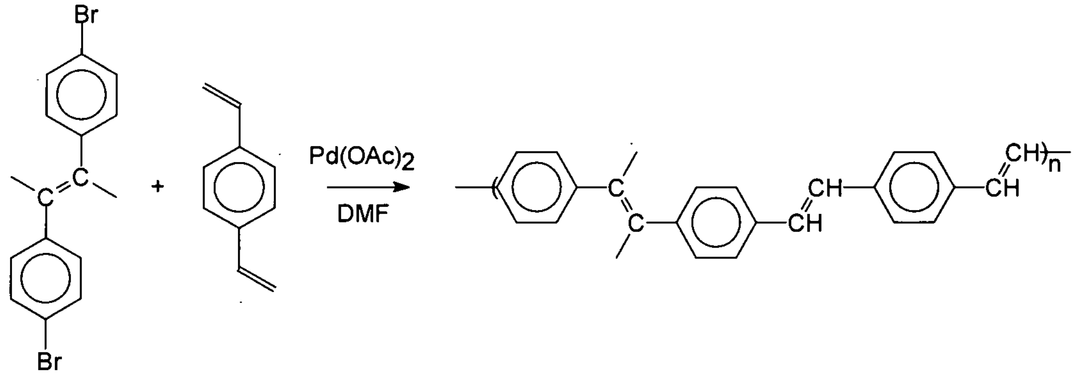

Figure 6.2.1 The synthesis of hypothetical poly(*p*-phenylene vinylene) derivative via Heck reaction.

The Yamamoto and Suzuki approaches, when optimised, will allow a virtually infinite range of well controlled arylene vinylene polymers to be made and from the synthetic chemists point of view it would be nice if theory and modelling predicted the best candidates for investigations. There is clearly much interdisciplinary work remaining to be done in this field of research.

6.3 References

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Appendix 1 Analytical data for Chapter 2

Appendix 1.1 FTIR spectra

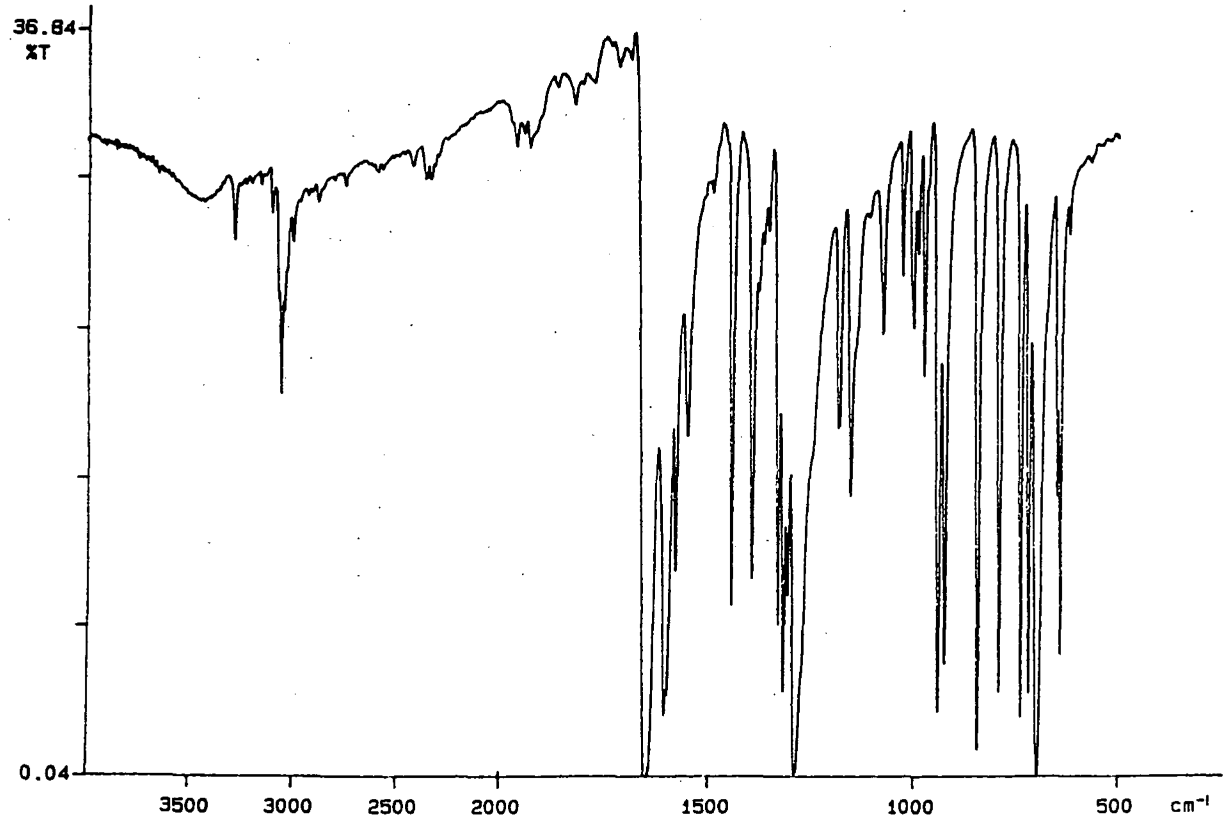
Appendix 1.2 ^{1}H Nmr spectra

Appendix 1.3 ^{13}C Nmr spectra

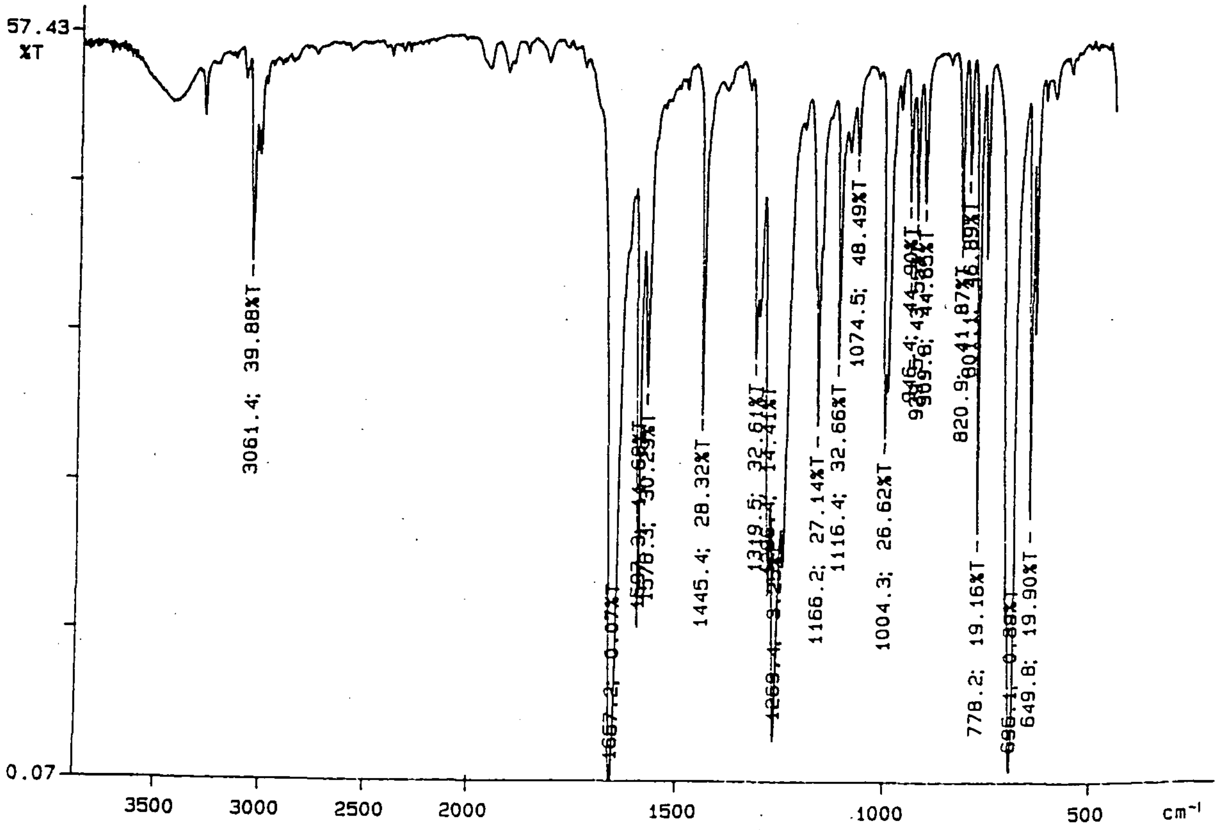
Appendix 1.4 Mass spectra

Appendix 1.5 GPC traces

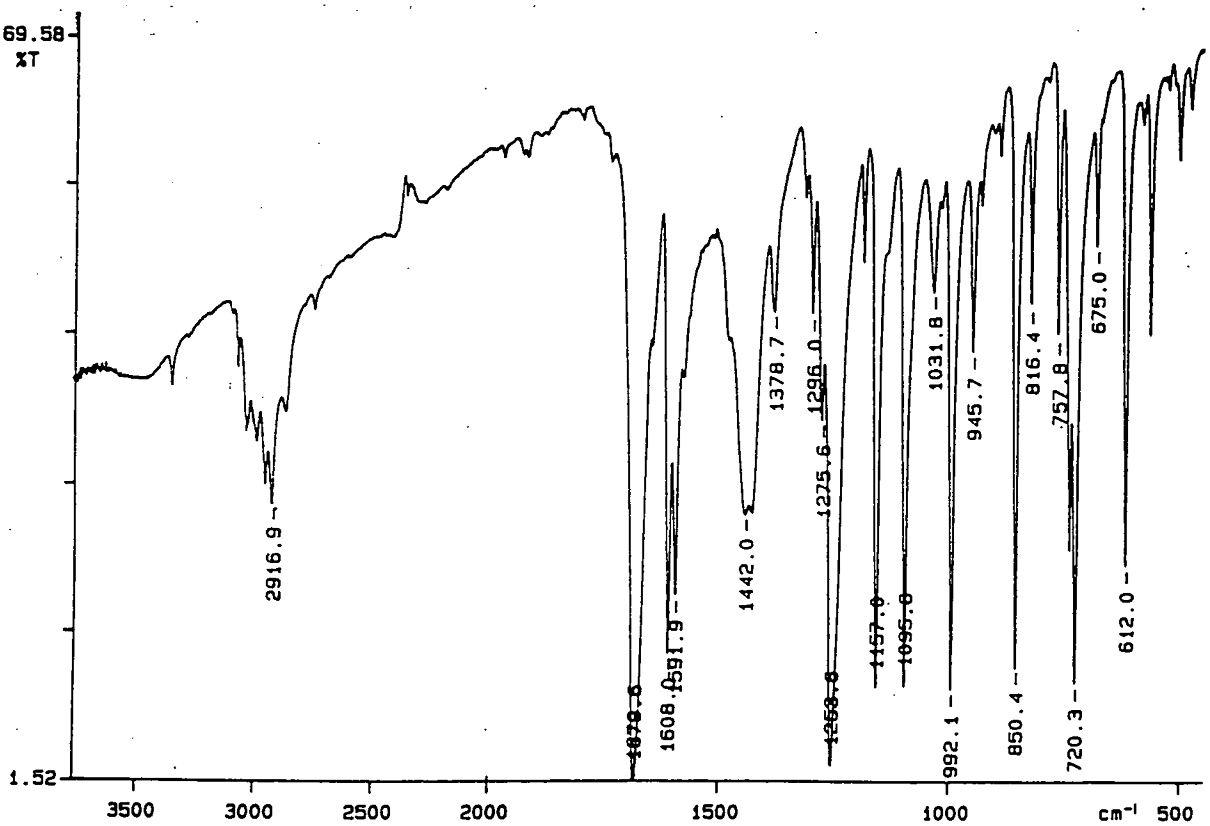
Appendix 1.6 DSC traces



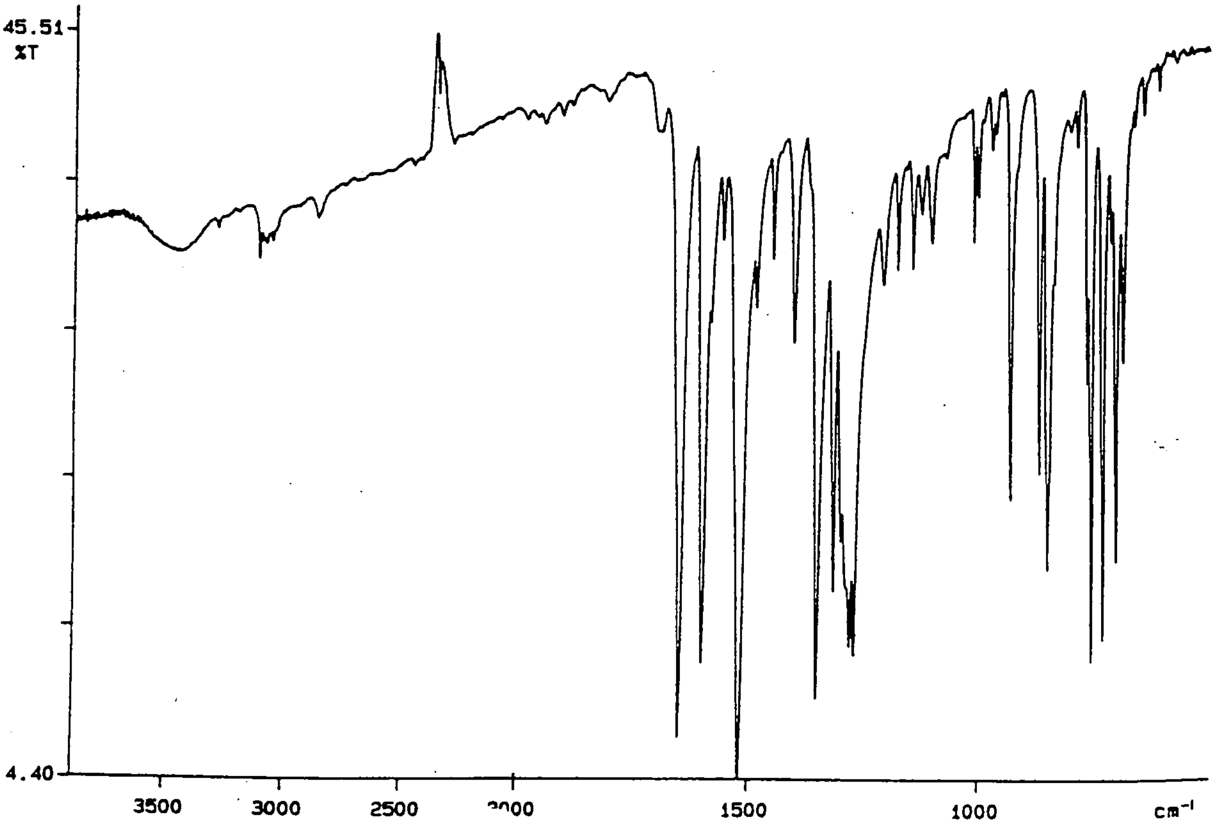
Appendix 1.1.1 FTIR spectrum of 4,4'-dibenzoylbiphenyl.



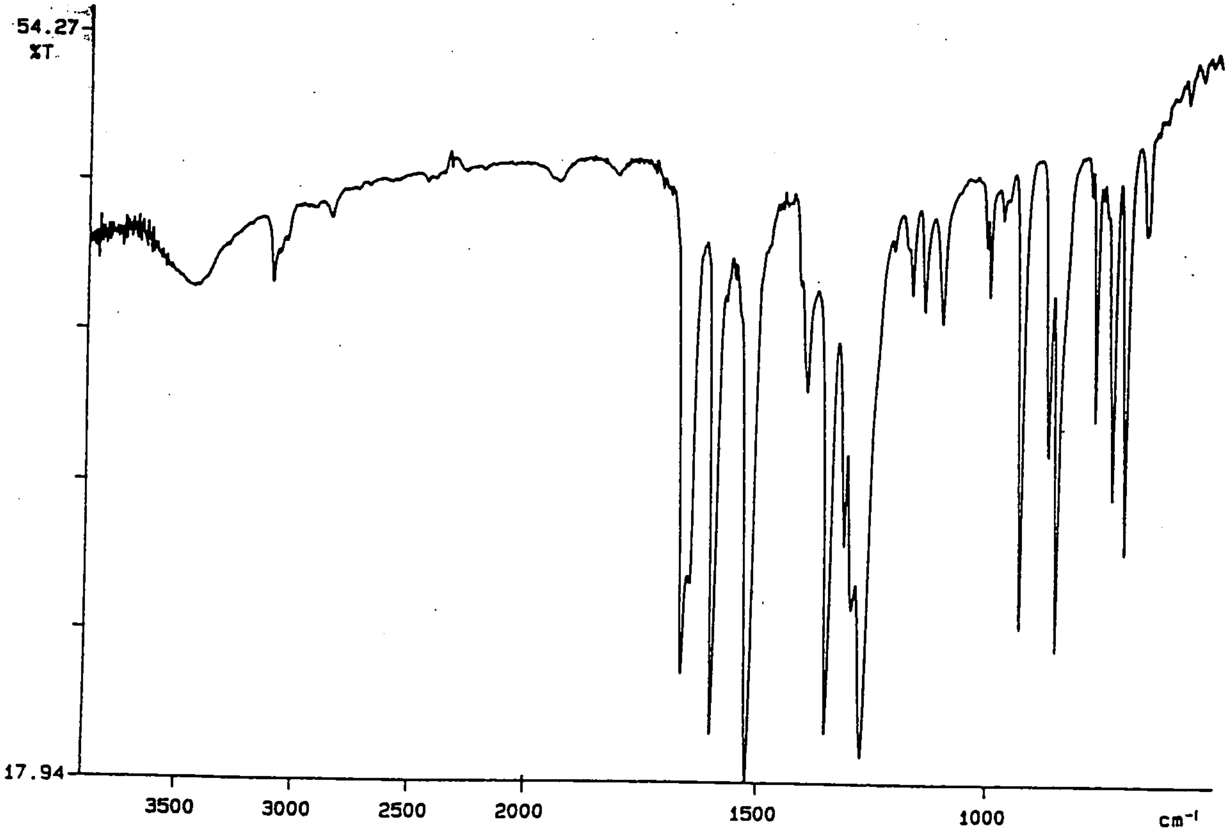
Appendix 1.1.2 FTIR spectrum of 1,3-dibenzoylbenzene.



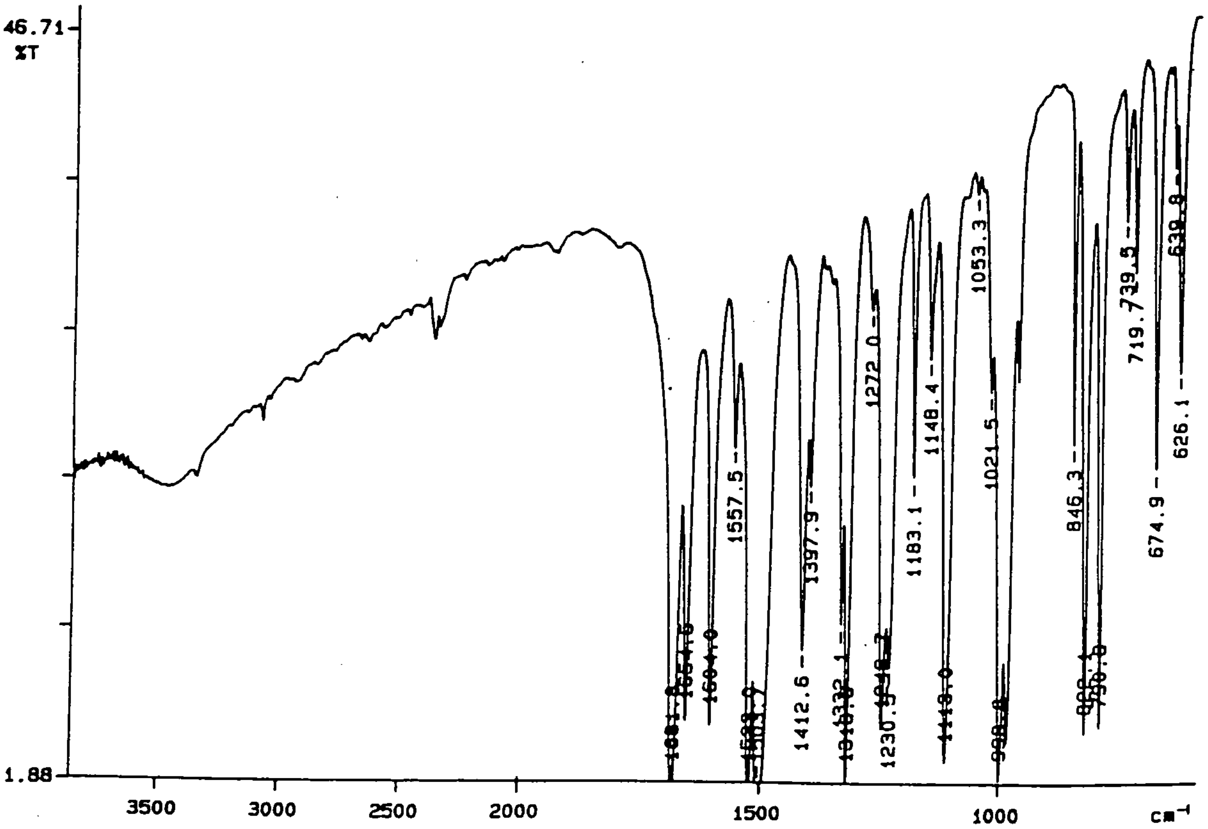
Appendix 1.1.3 FTIR spectrum of 1,3-dimesitoylbenzene.



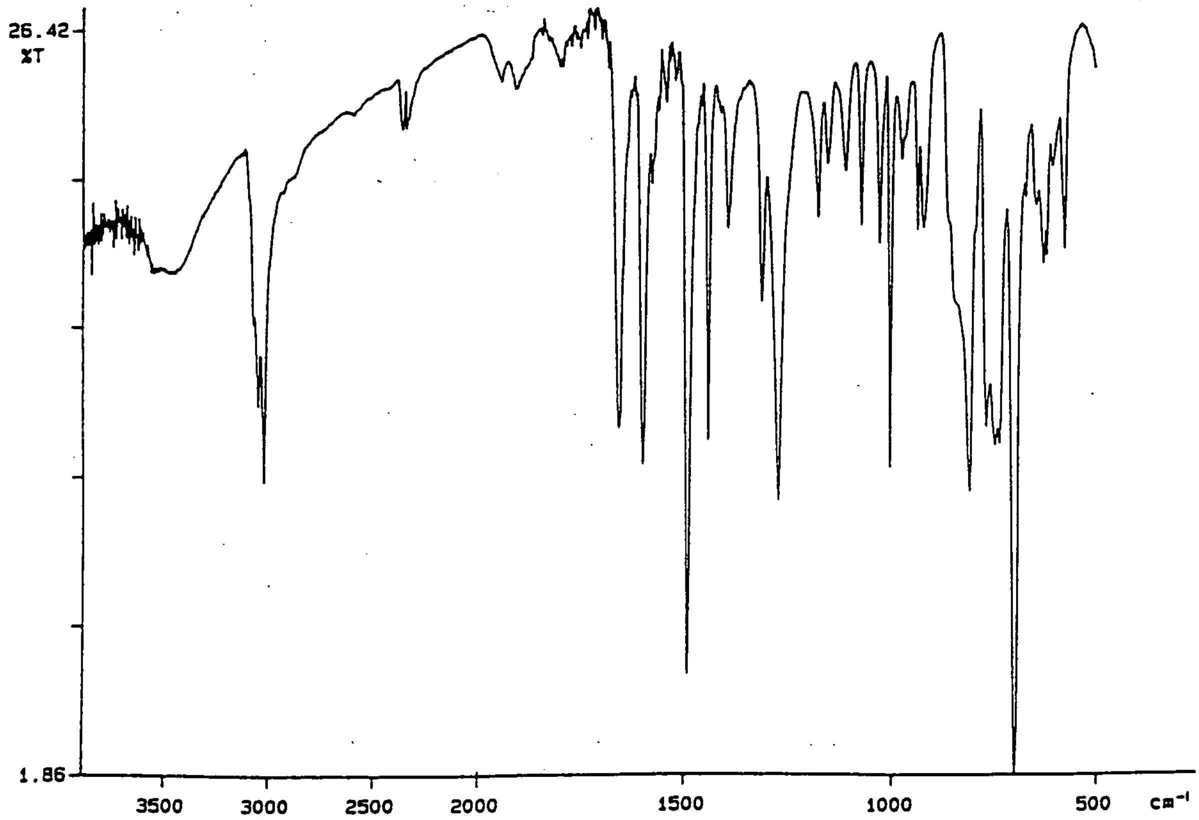
Appendix 1.1.4 FTIR spectrum of 4-nitrobenzoylbiphenyl.



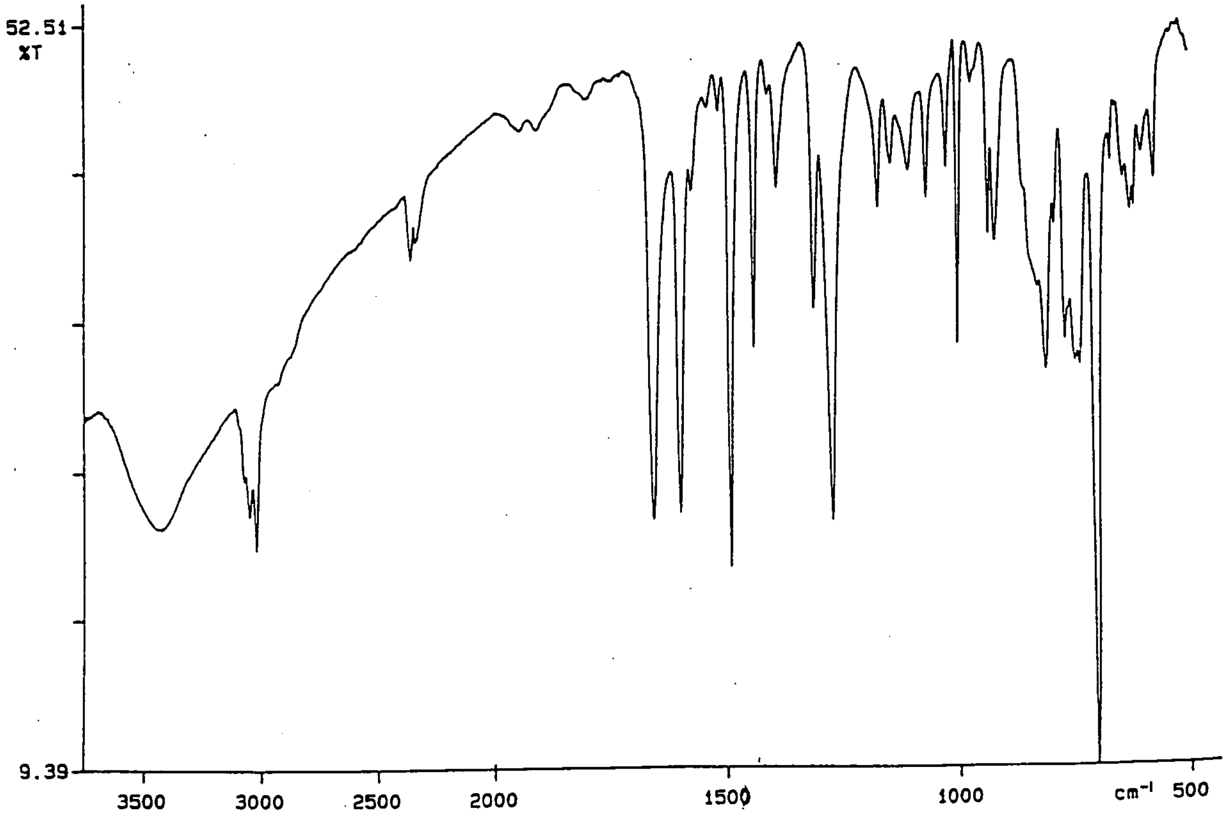
Appendix 1.1.5 FTIR spectrum of 4,4'-di(4-nitrobenzoyl)biphenyl.



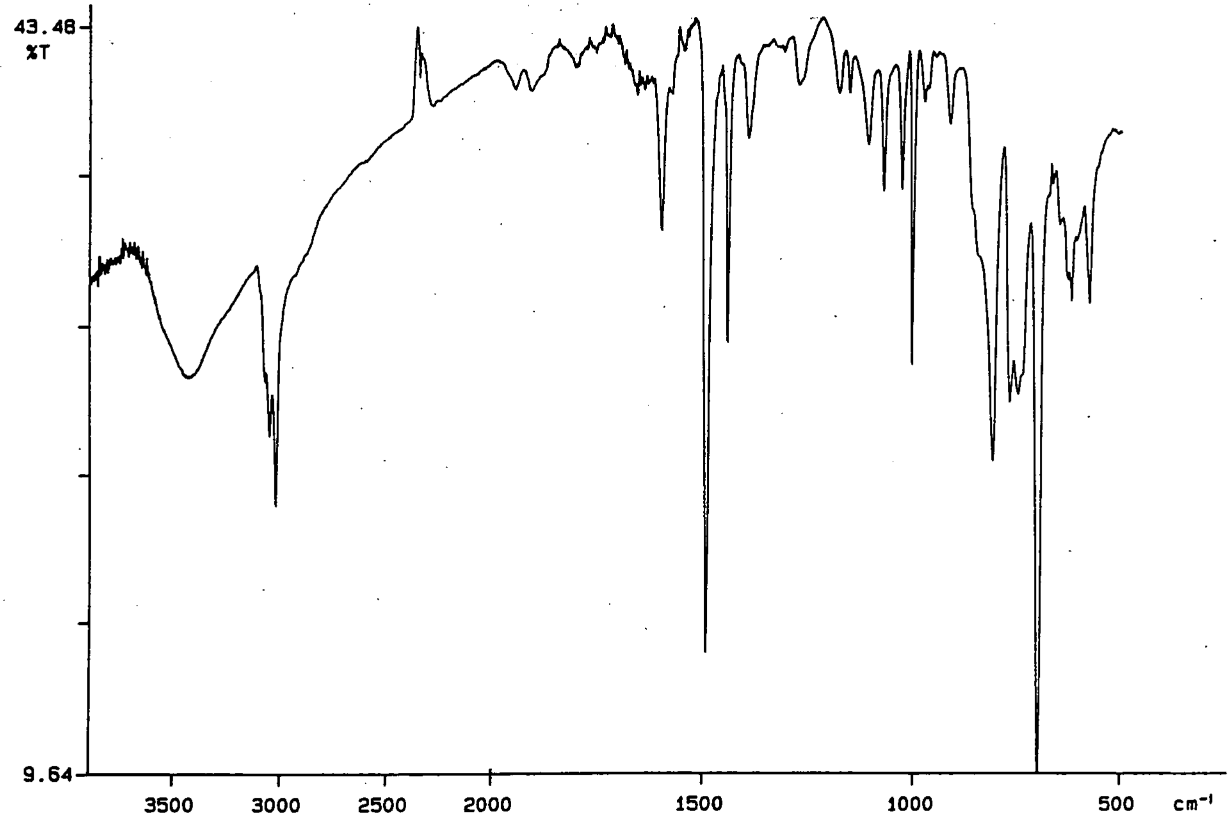
Appendix 1.1.6 FTIR spectrum of 4,4'-bis(pentafluorobenzoyl)biphenyl.



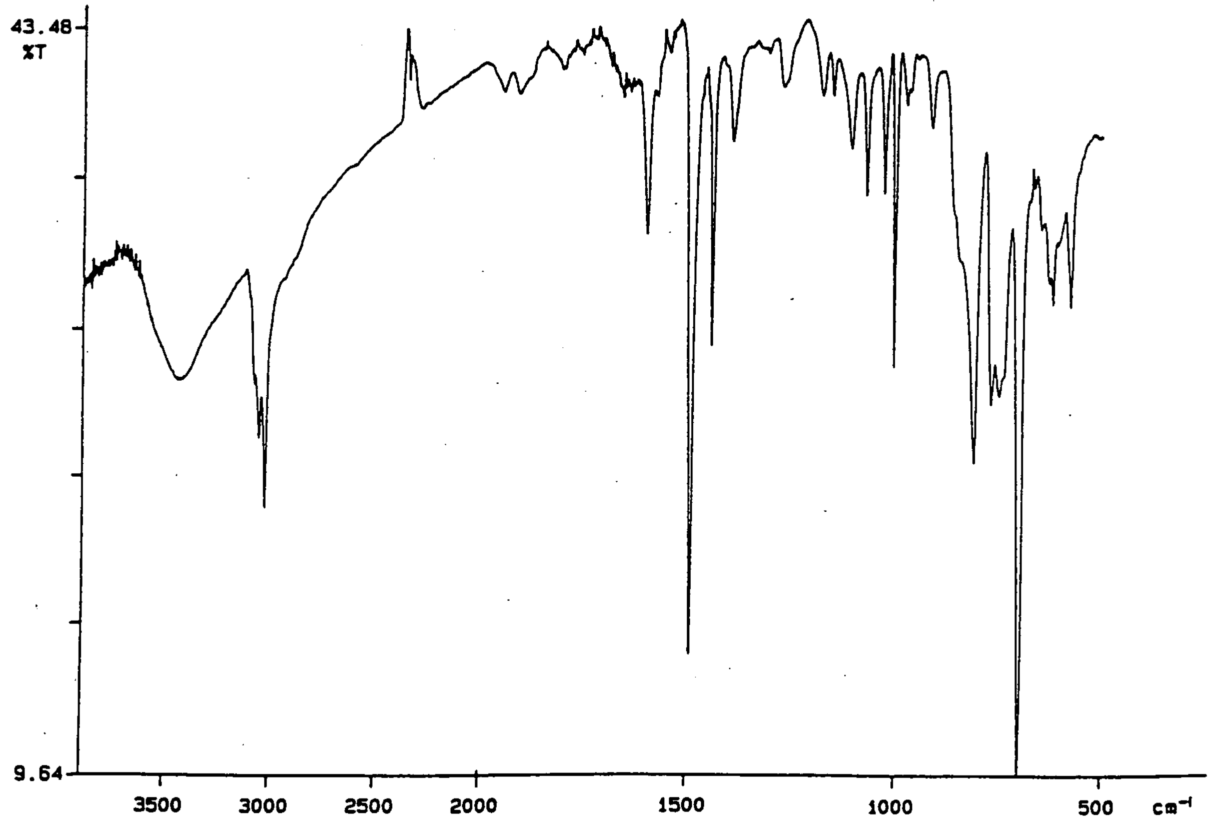
Appendix 1.1.7 FTIR spectrum of PDPV prepared in the preliminary experiment.



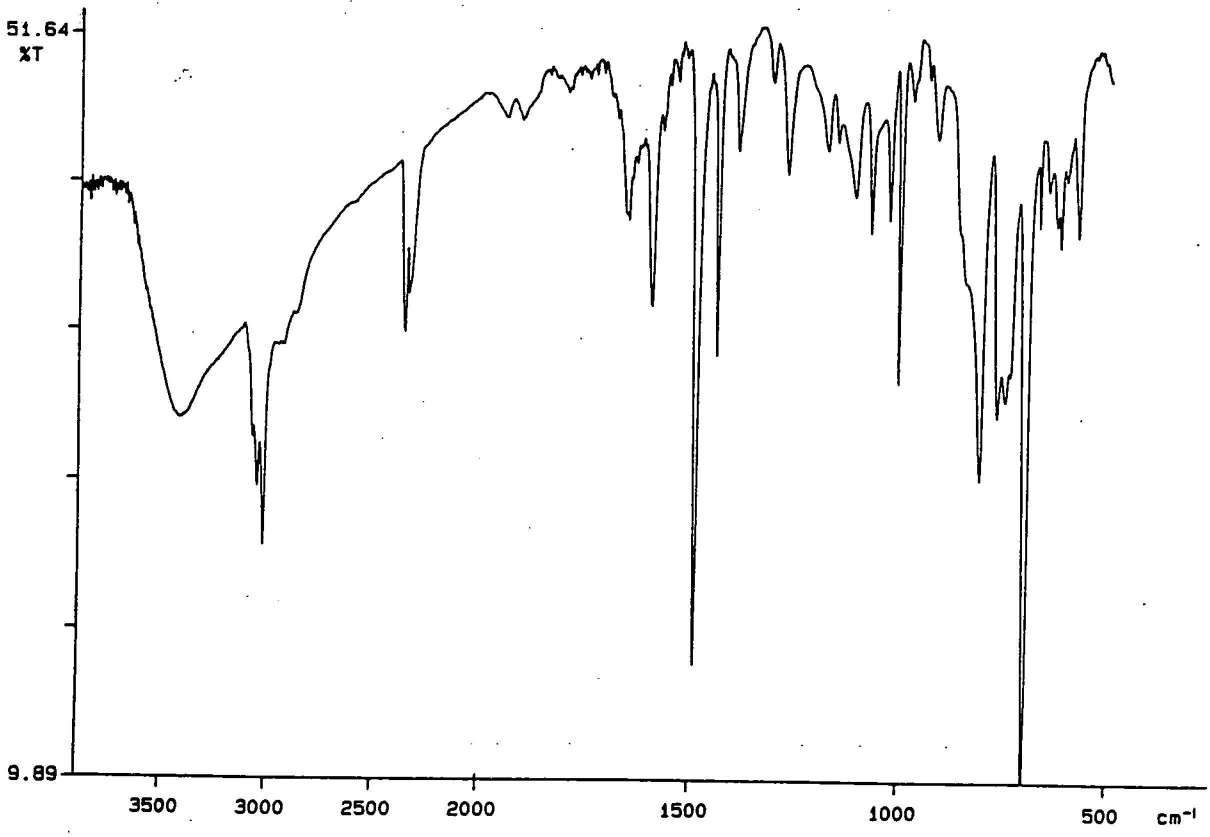
Appendix 1.1.8 FTIR spectrum of PDPV (4 hrs reaction time).



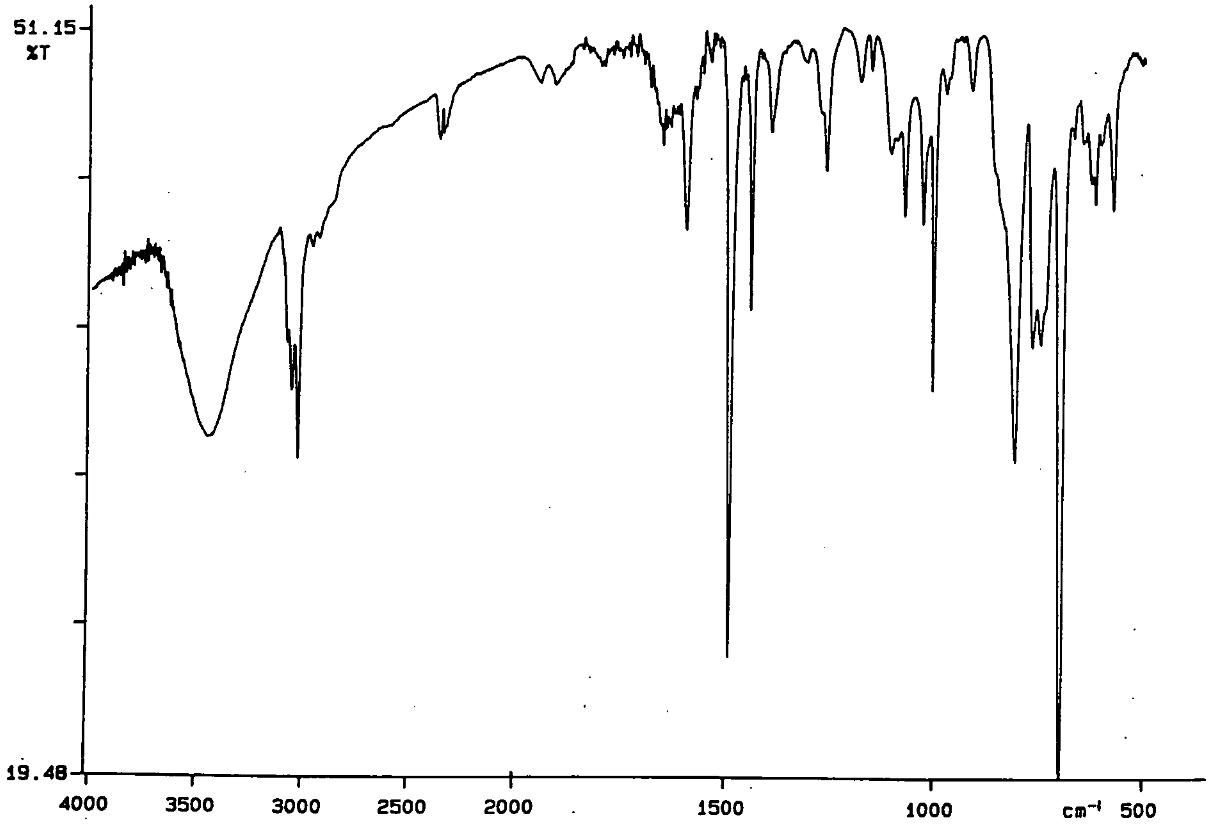
Appendix 1.1.9 FTIR spectrum of PDPV (20 hrs reaction time).



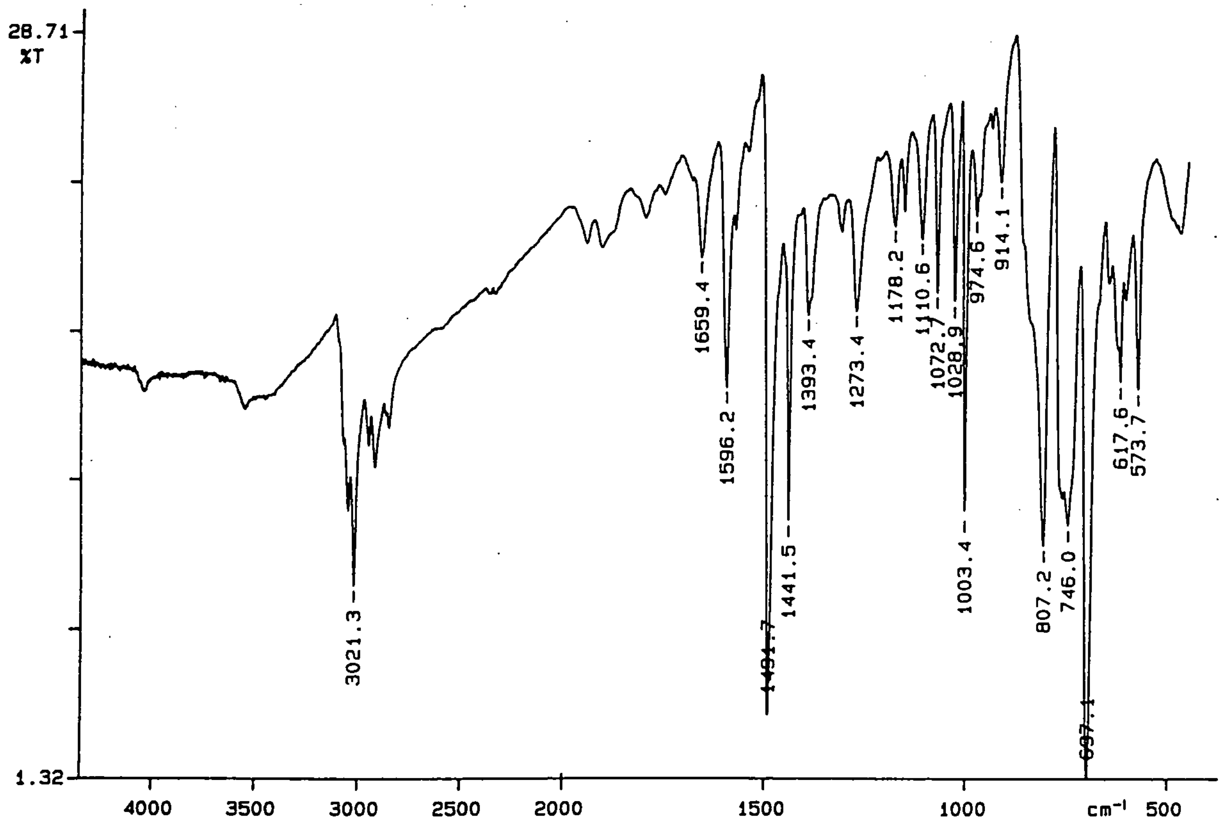
Appendix 1.1.10 FTIR spectrum of PDPV (44 hrs reaction time).



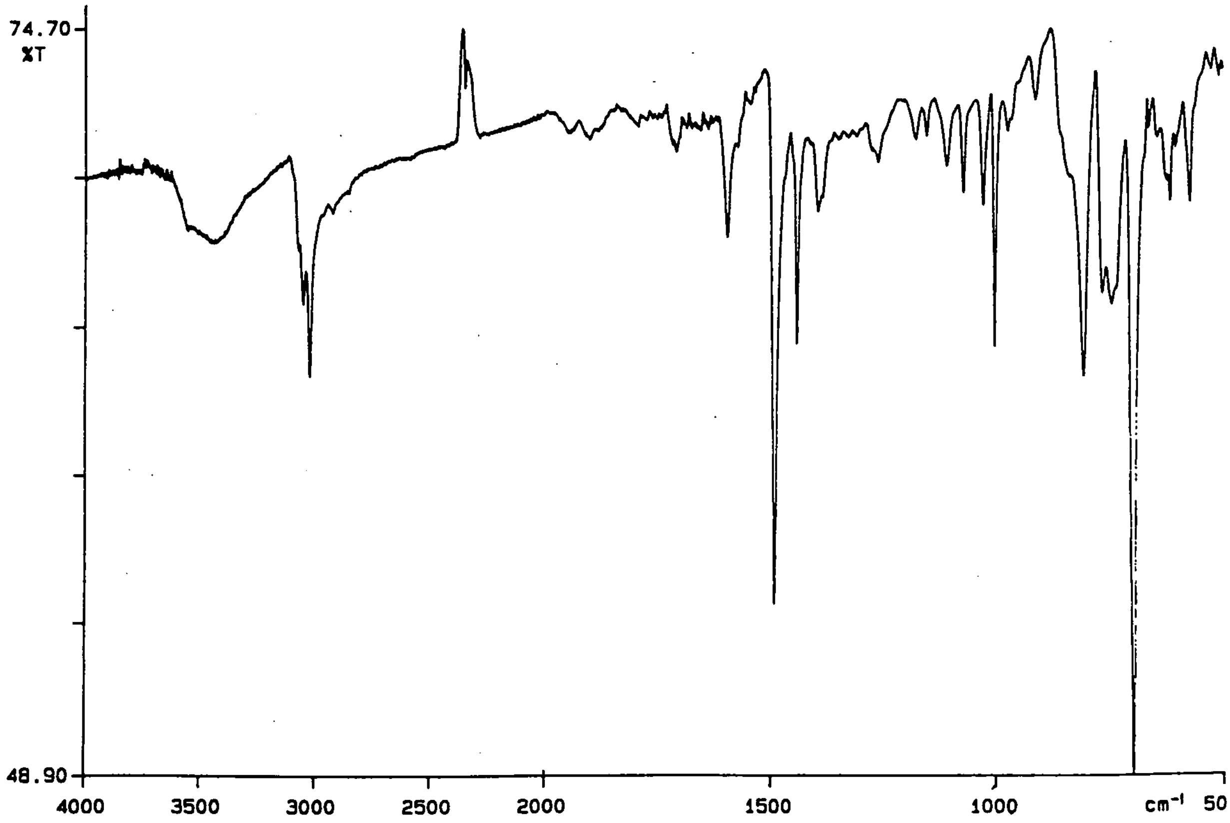
Appendix 1.1.11 FTIR spectrum of PDPV (168 hrs reaction time).



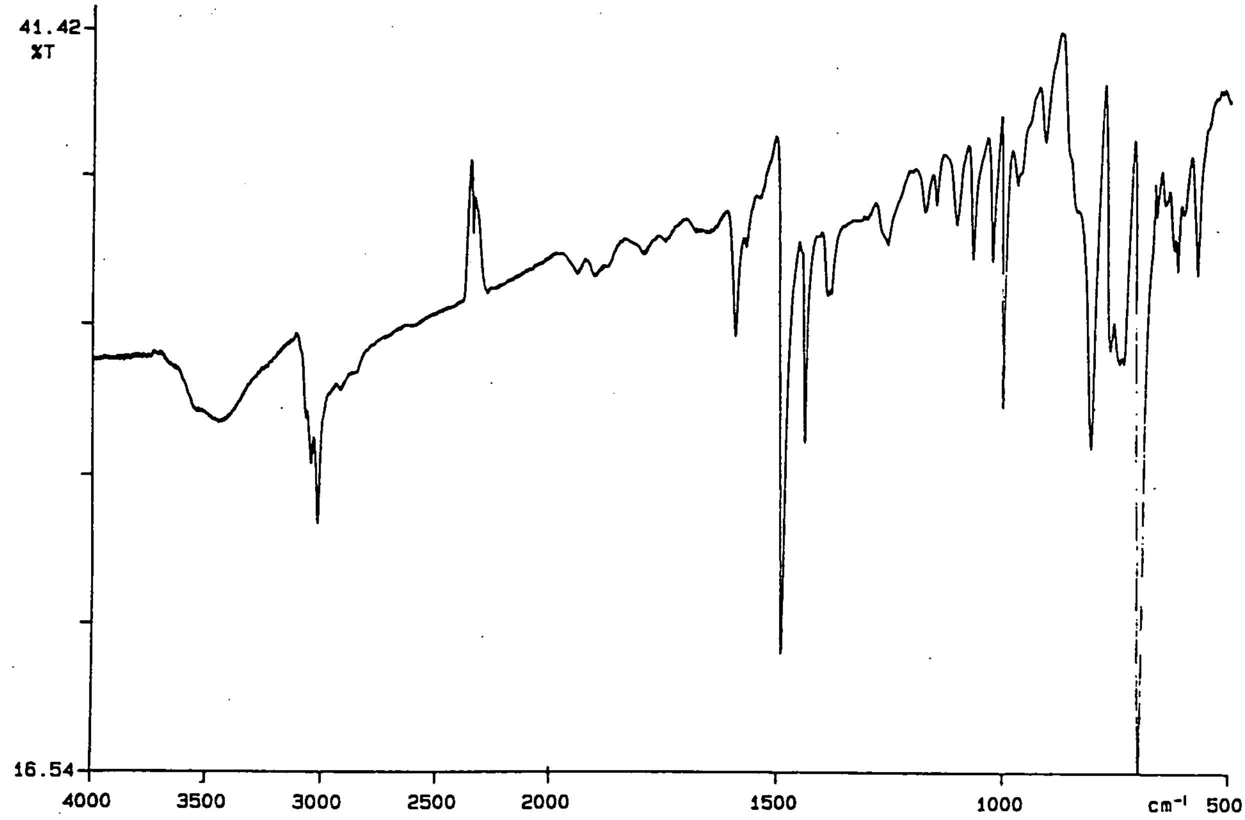
Appendix 1.1.12 FTIR spectrum of PDPV produced in recoupling experiment.



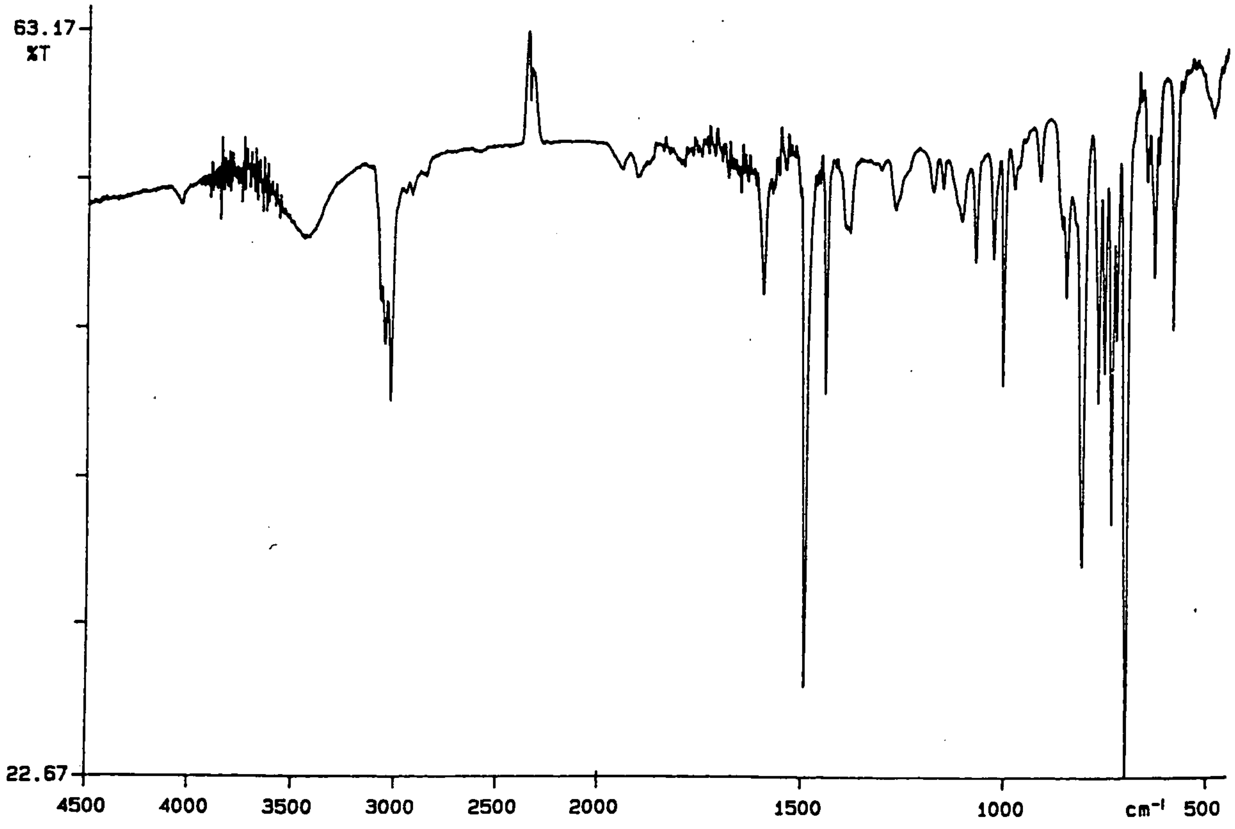
Appendix 1.1.13 FTIR spectrum of PDPV (4.43% monomer concentration).



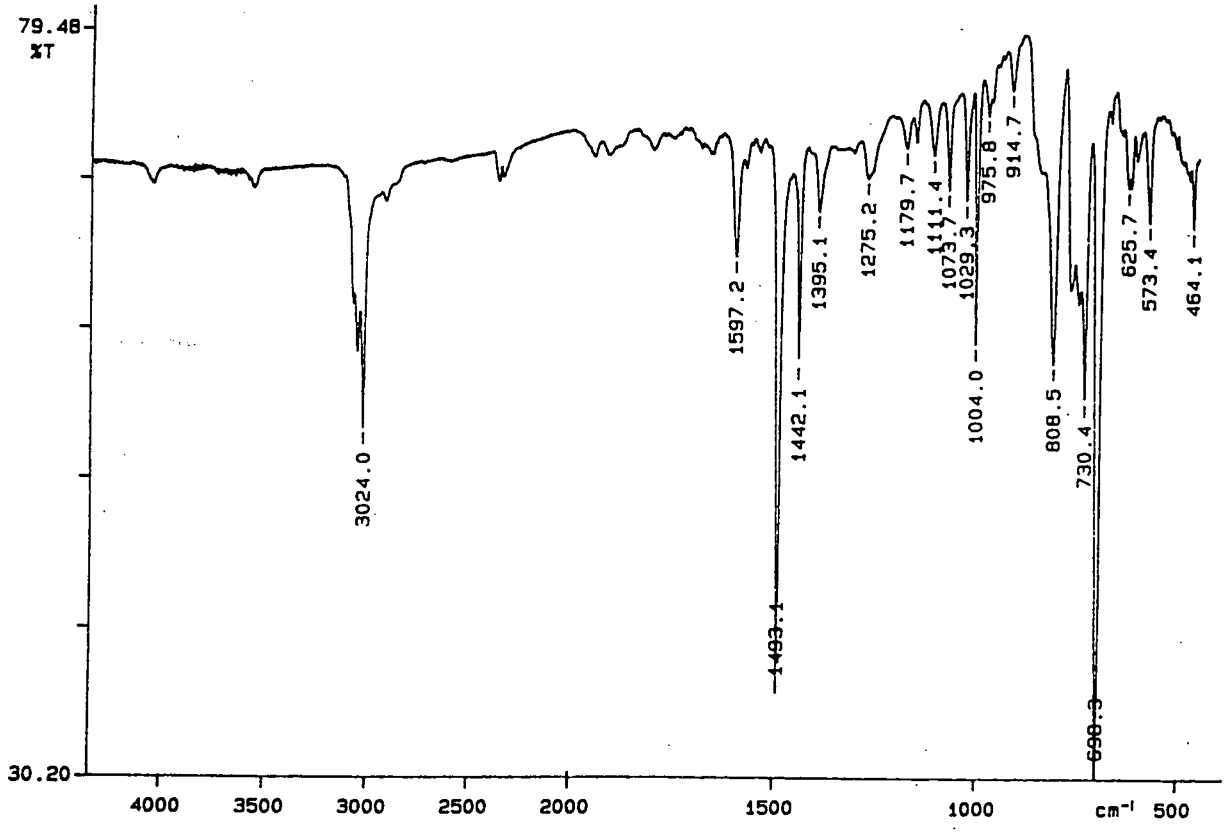
Appendix 1.1.14 FTIR spectrum of PDPV (7.10% monomer concentration).



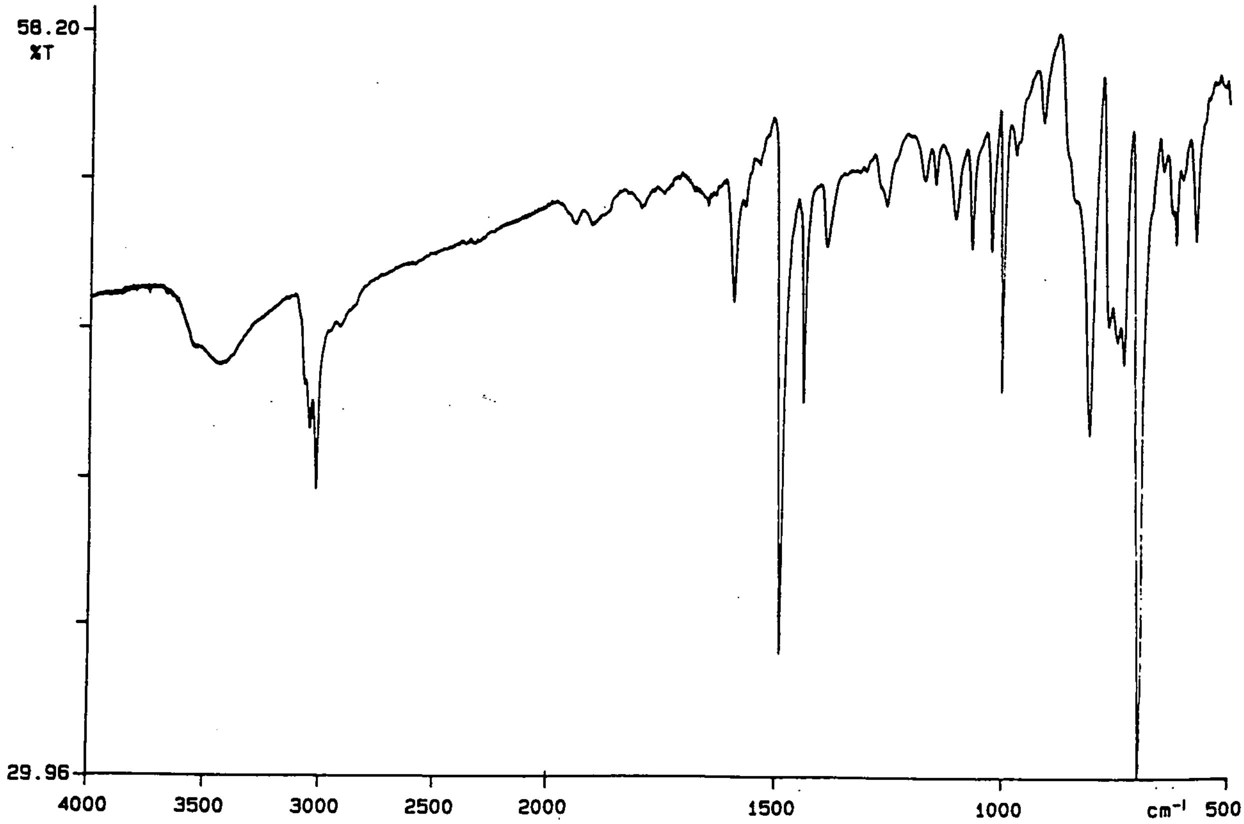
Appendix 1.1.15 FTIR spectrum of PDPV (10.00% monomer concentration).



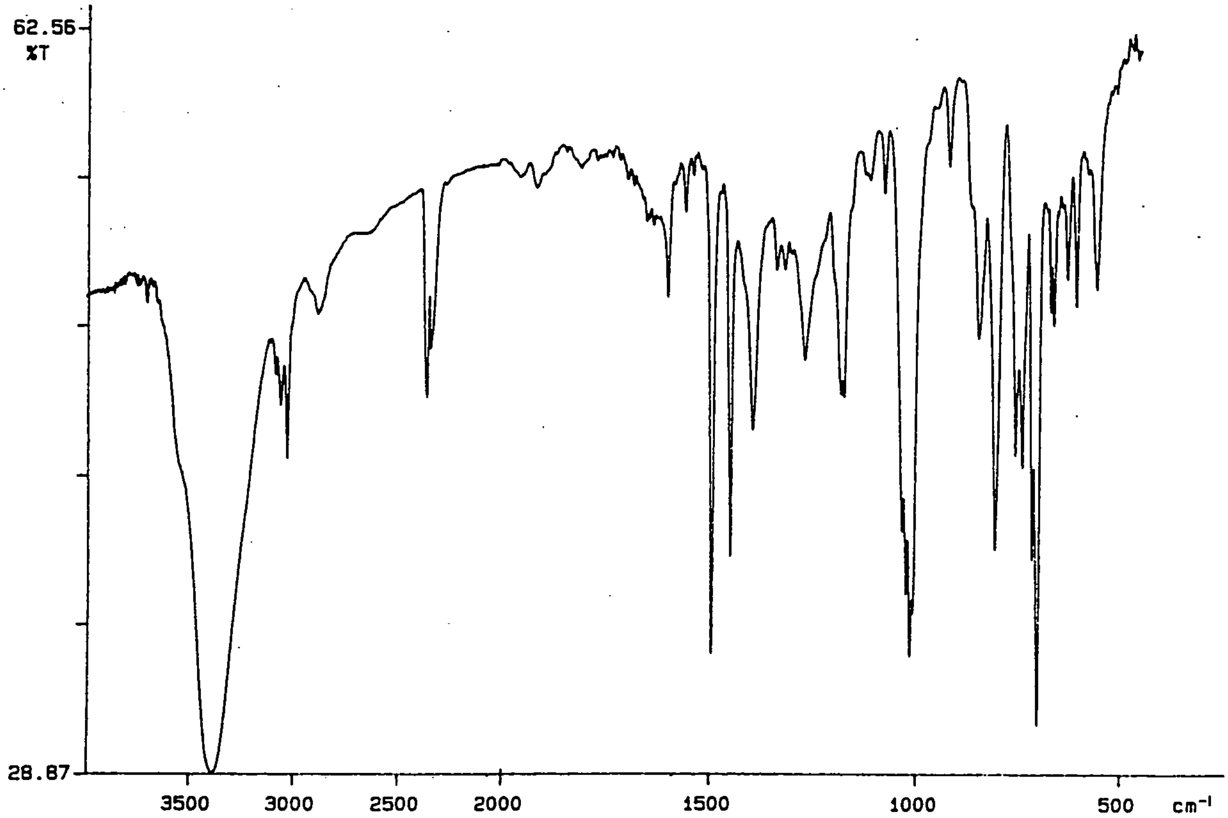
Appendix 1.1.16 FTIR spectrum of the cyclic trimer.



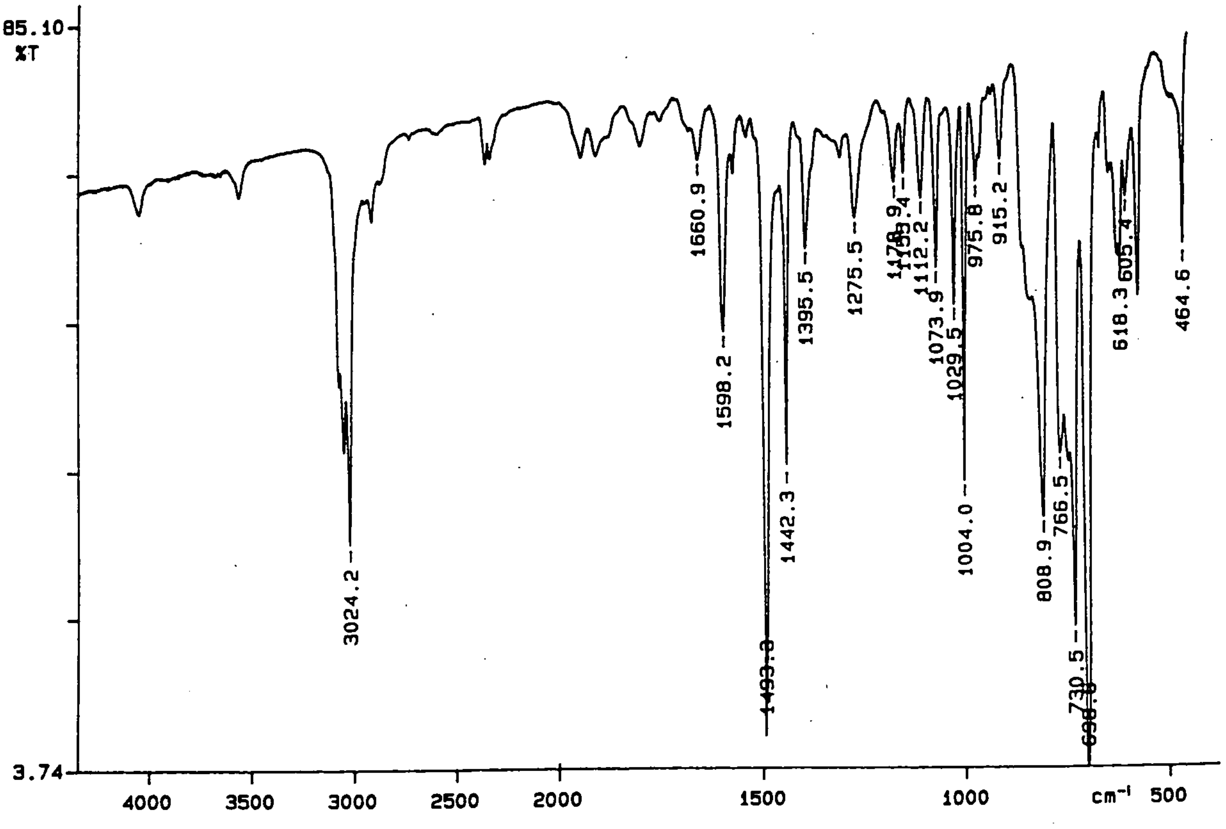
Appendix 1.1.17 FTIR spectrum of the fractionated PDPV (fraction 1).



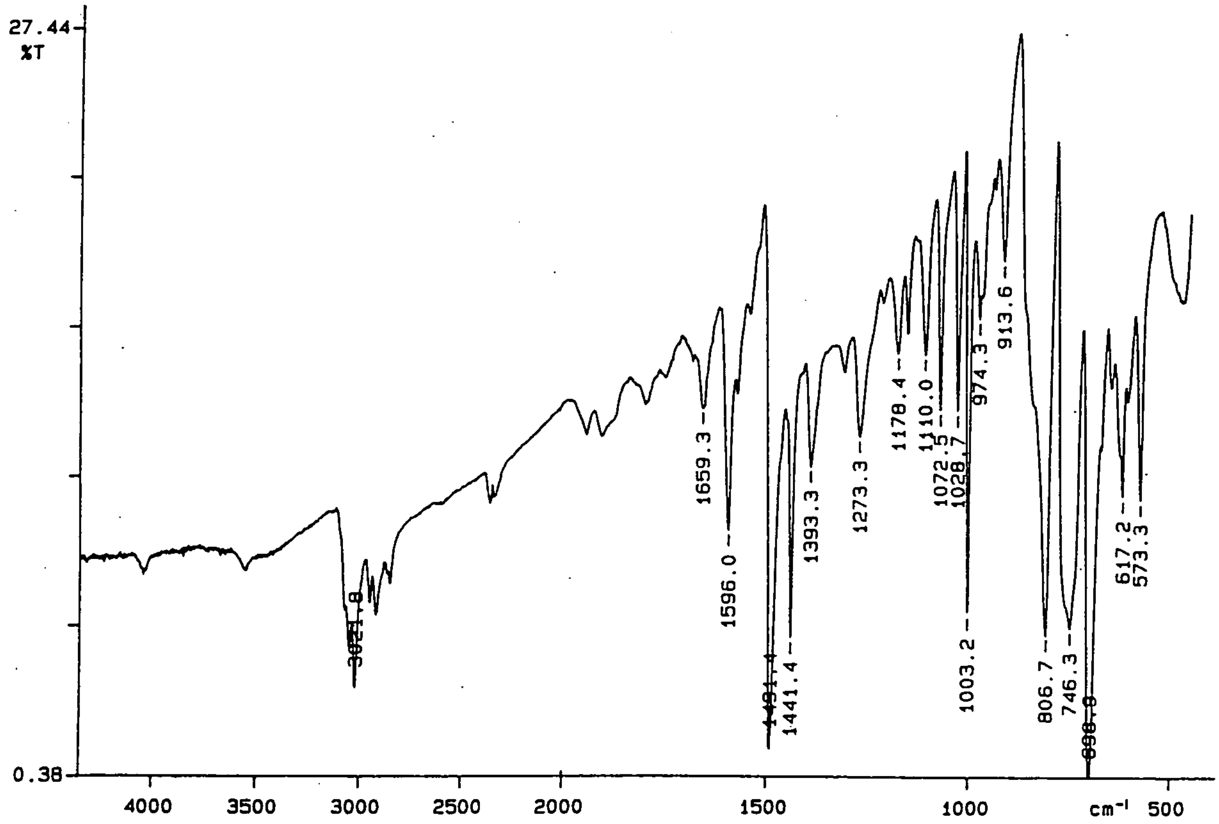
Appendix 1.1.18 FTIR spectrum of the fractionated PDPV (fraction 2).



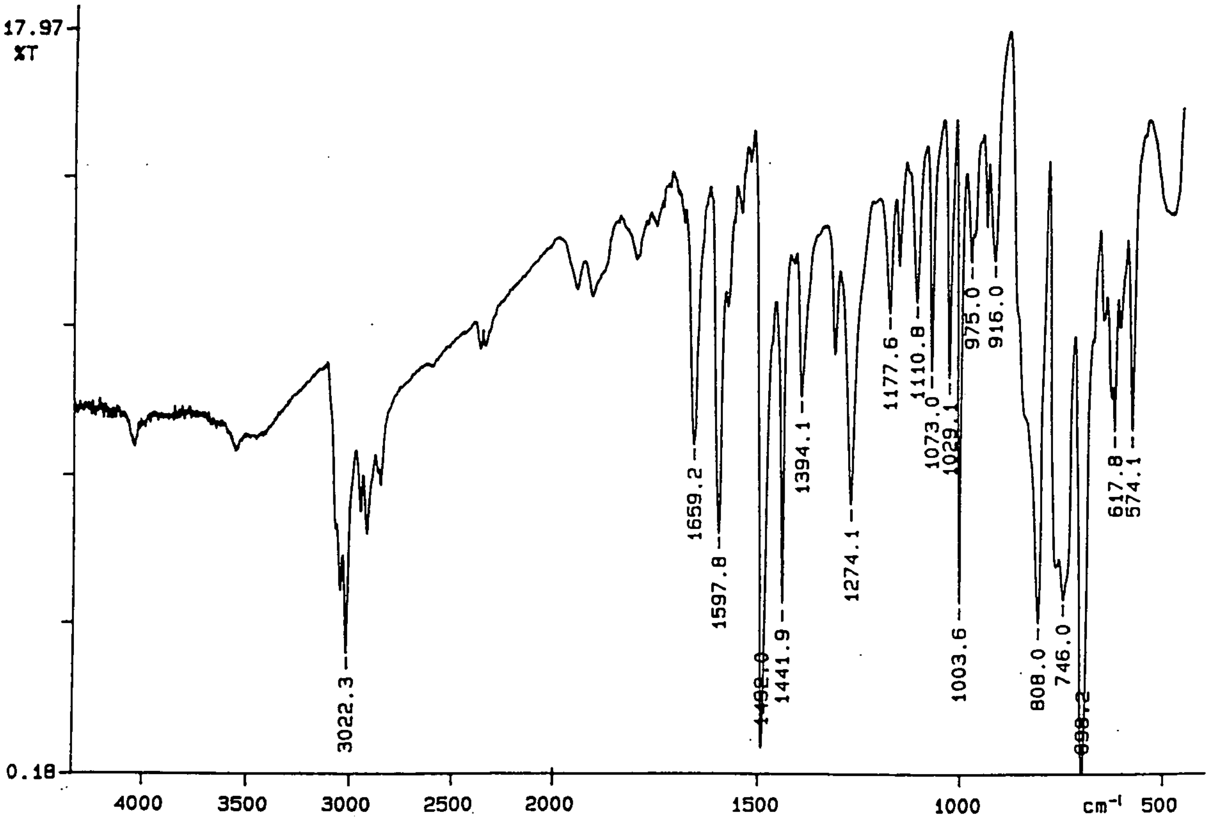
Appendix 1.1.19 FTIR spectrum of the fractionated PDPV (fraction 3).



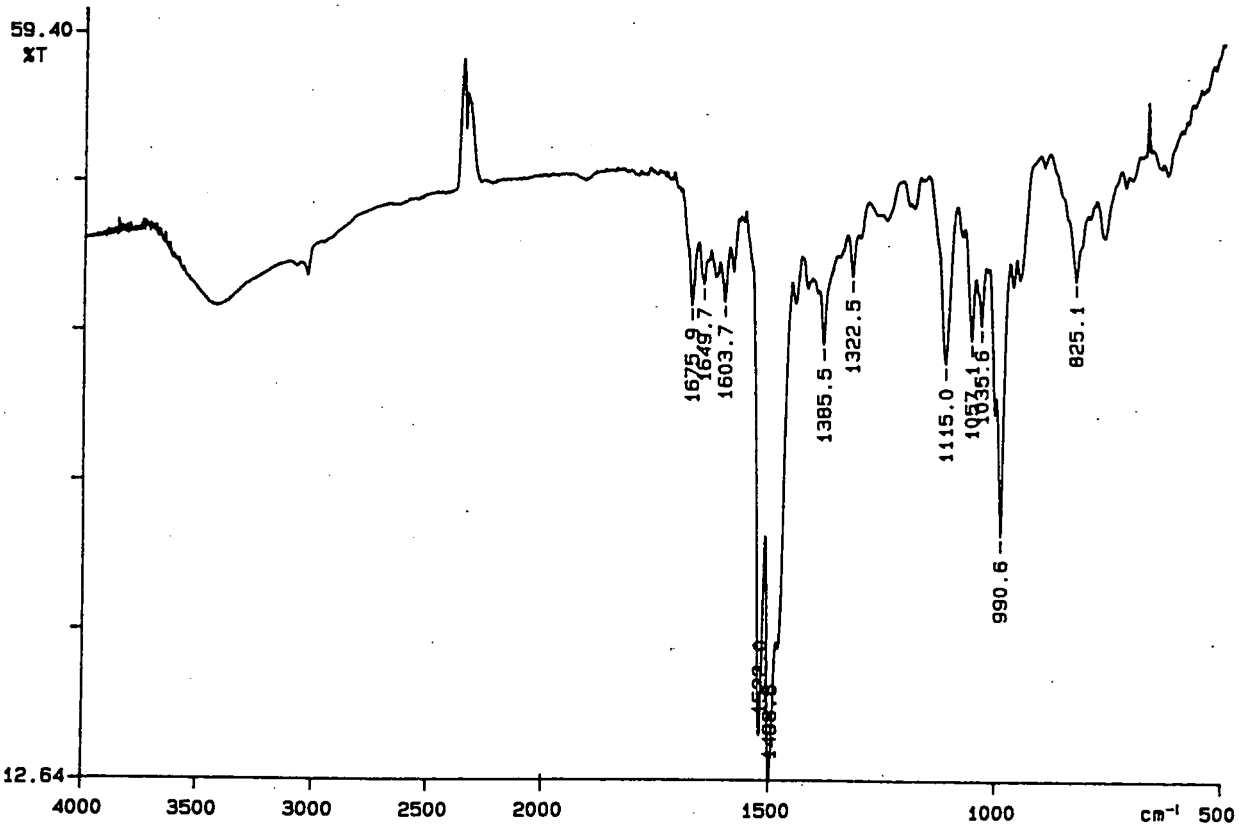
Appendix 1.1.20 FTIR spectrum of the fractionated PDPV (fraction 4).



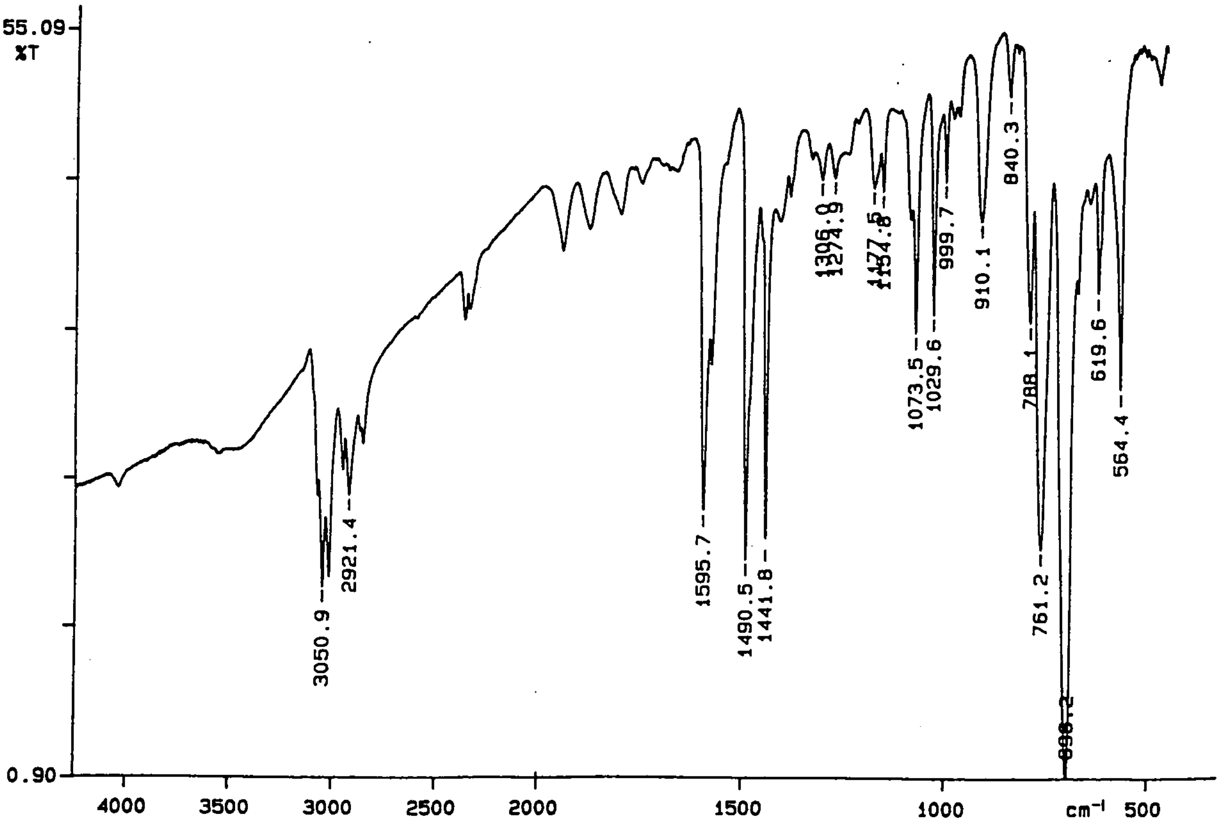
Appendix 1.1.21 FTIR spectrum of the fractionated PDPV (fraction 6).



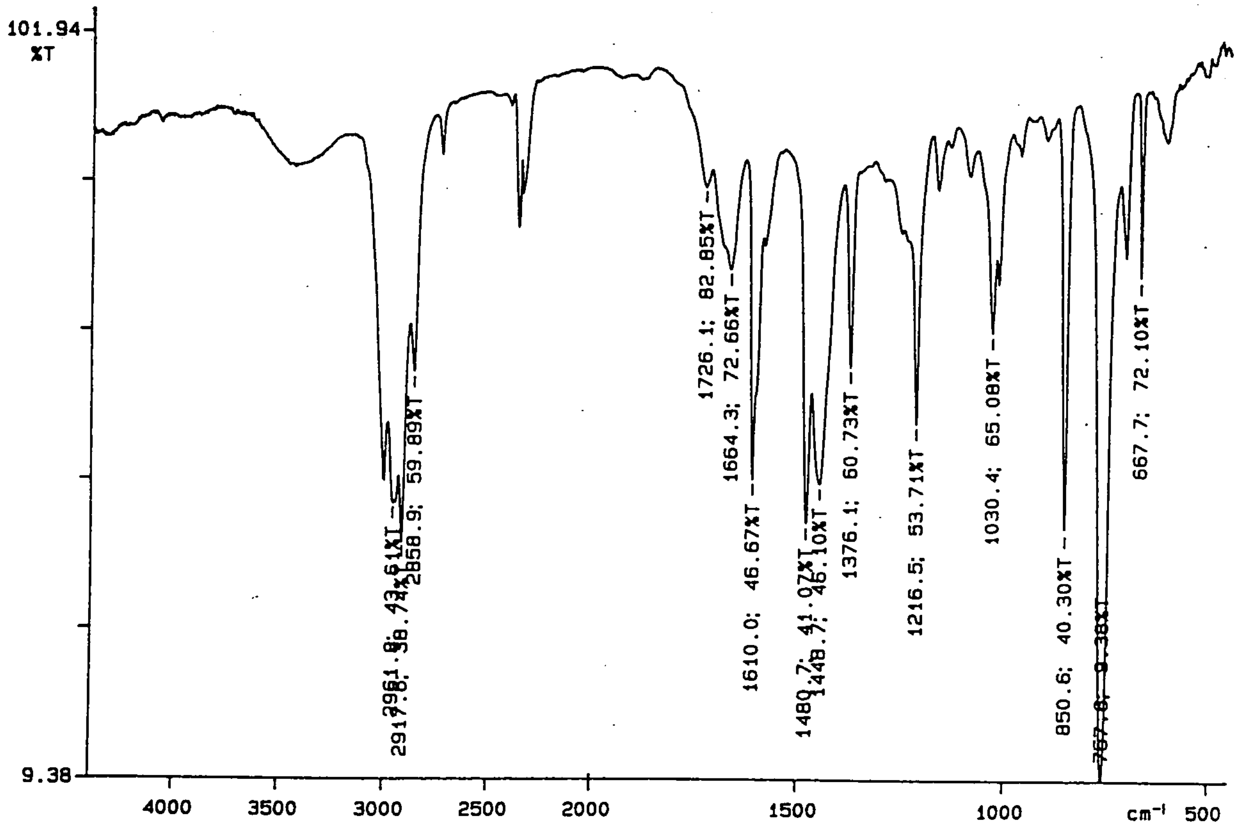
Appendix 1.1.22 FTIR spectrum of the fractionated PDPV (fraction 11).



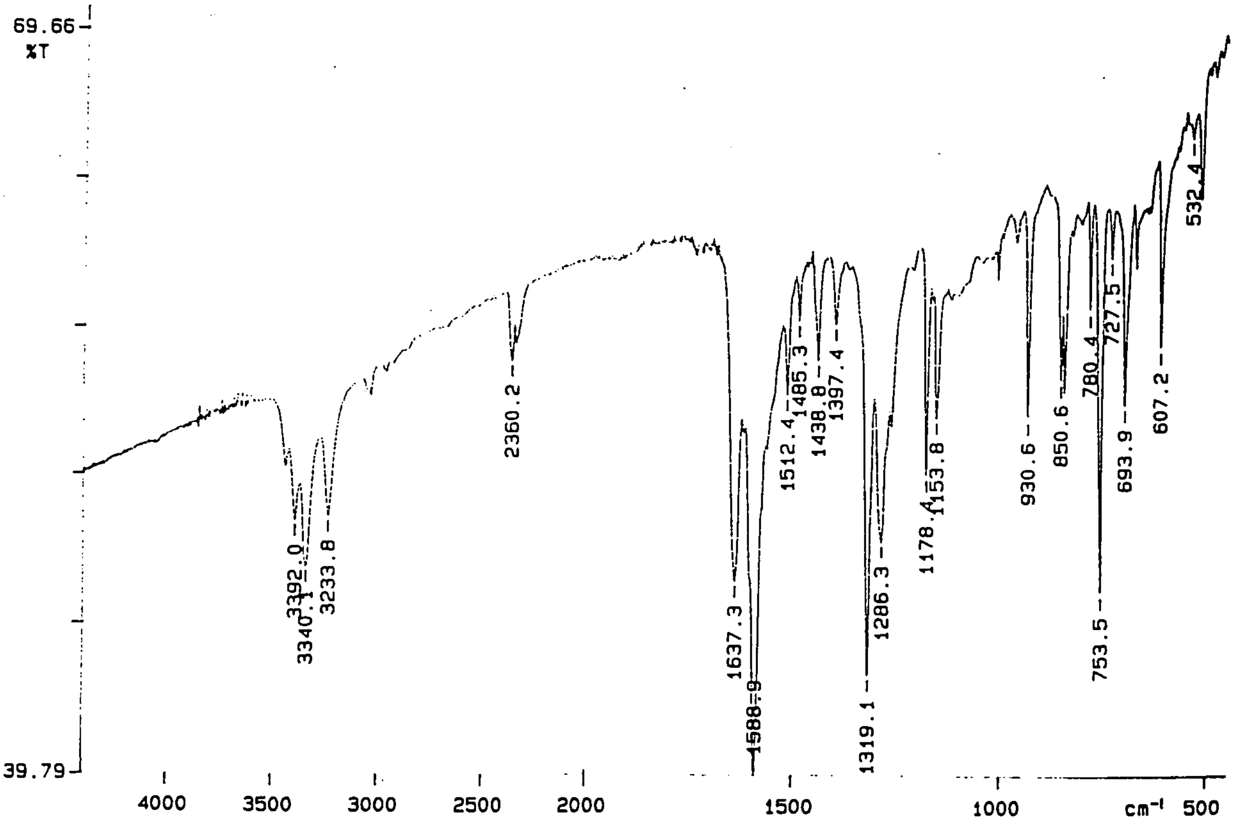
Appendix 1.1.23 FTIR spectrum of PDPV-DF.



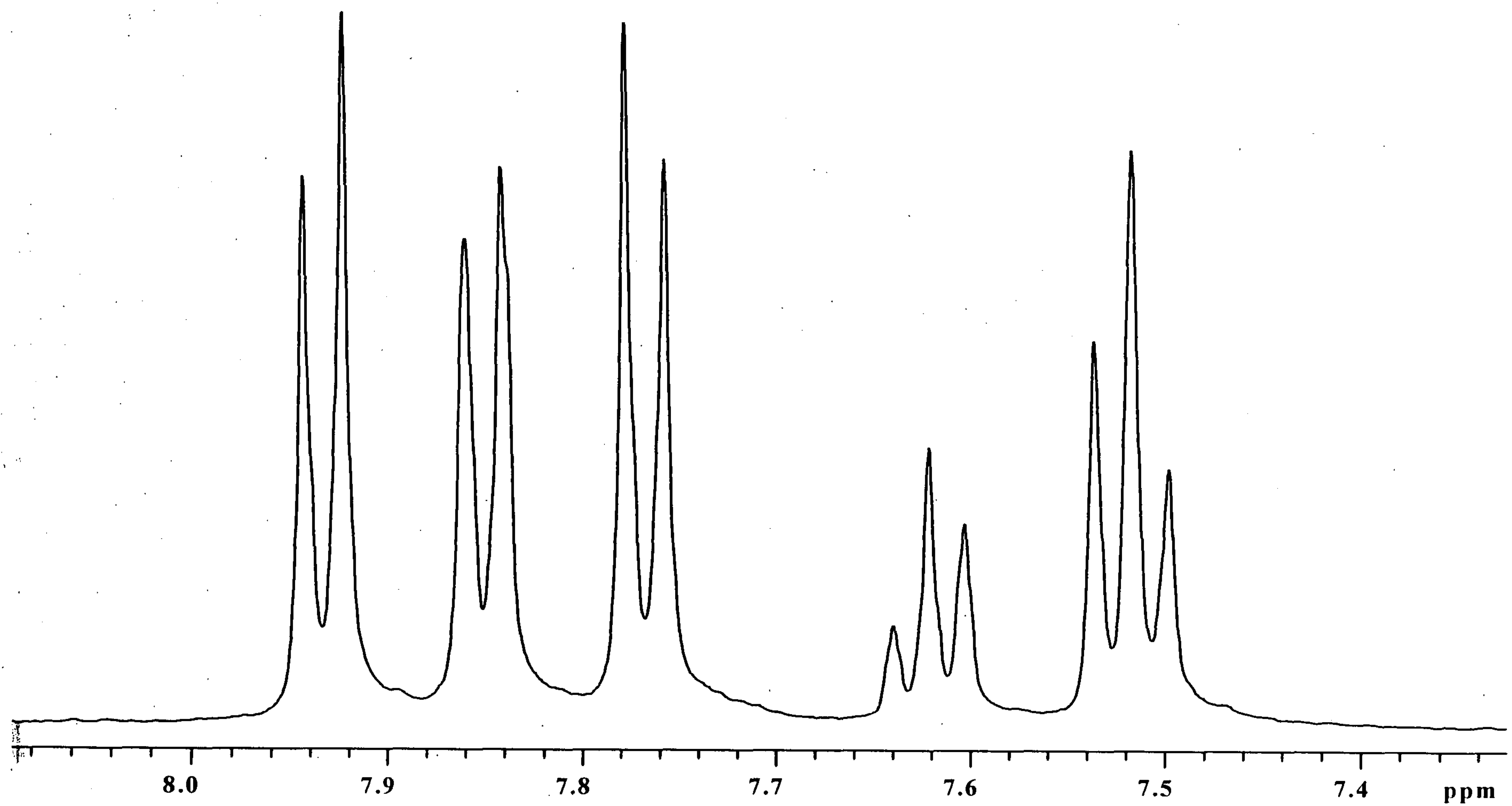
Appendix 1.1.24 FTIR spectrum of m-PPV-DP.



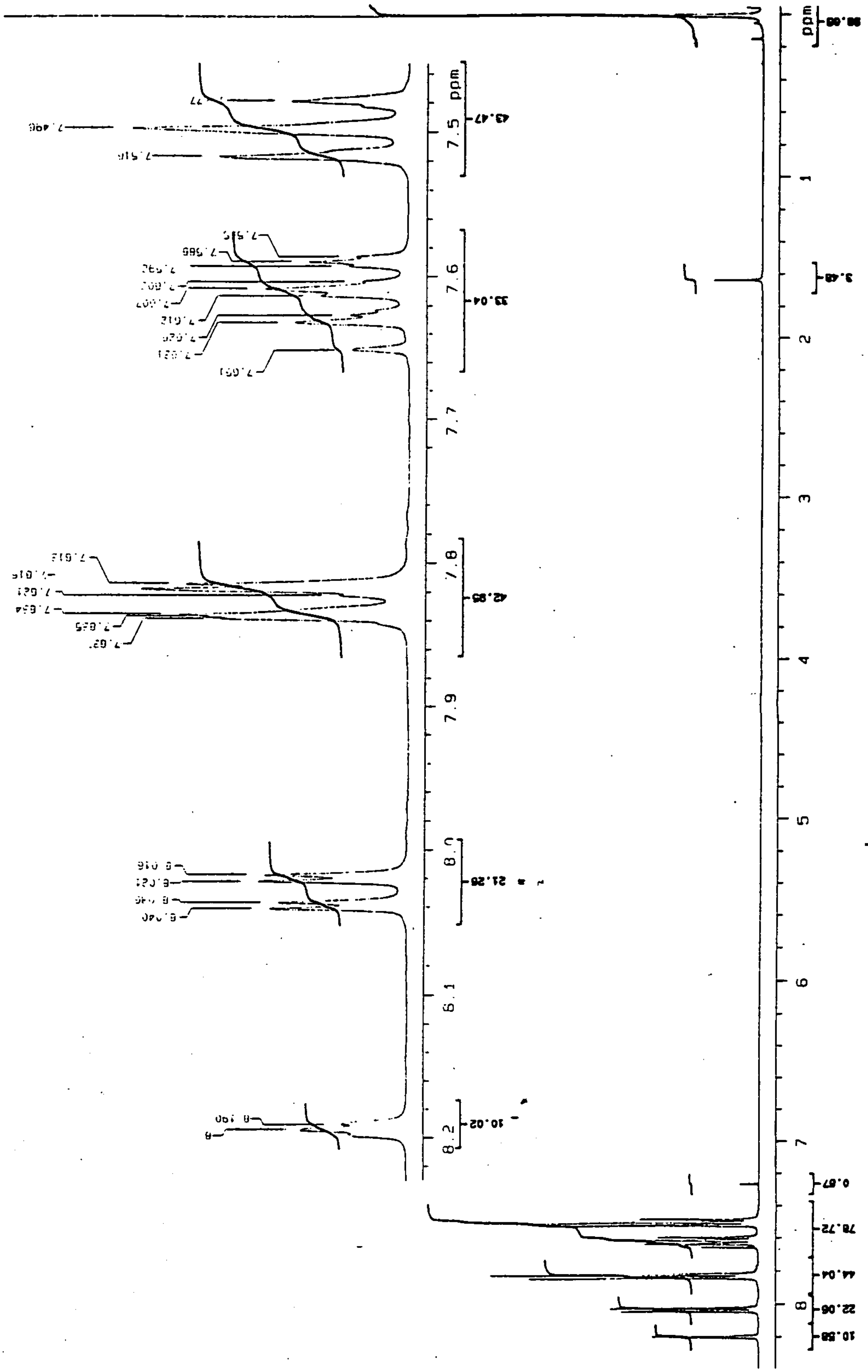
Appendix 1.1.25 FTIR spectrum of m-PPV-DM.



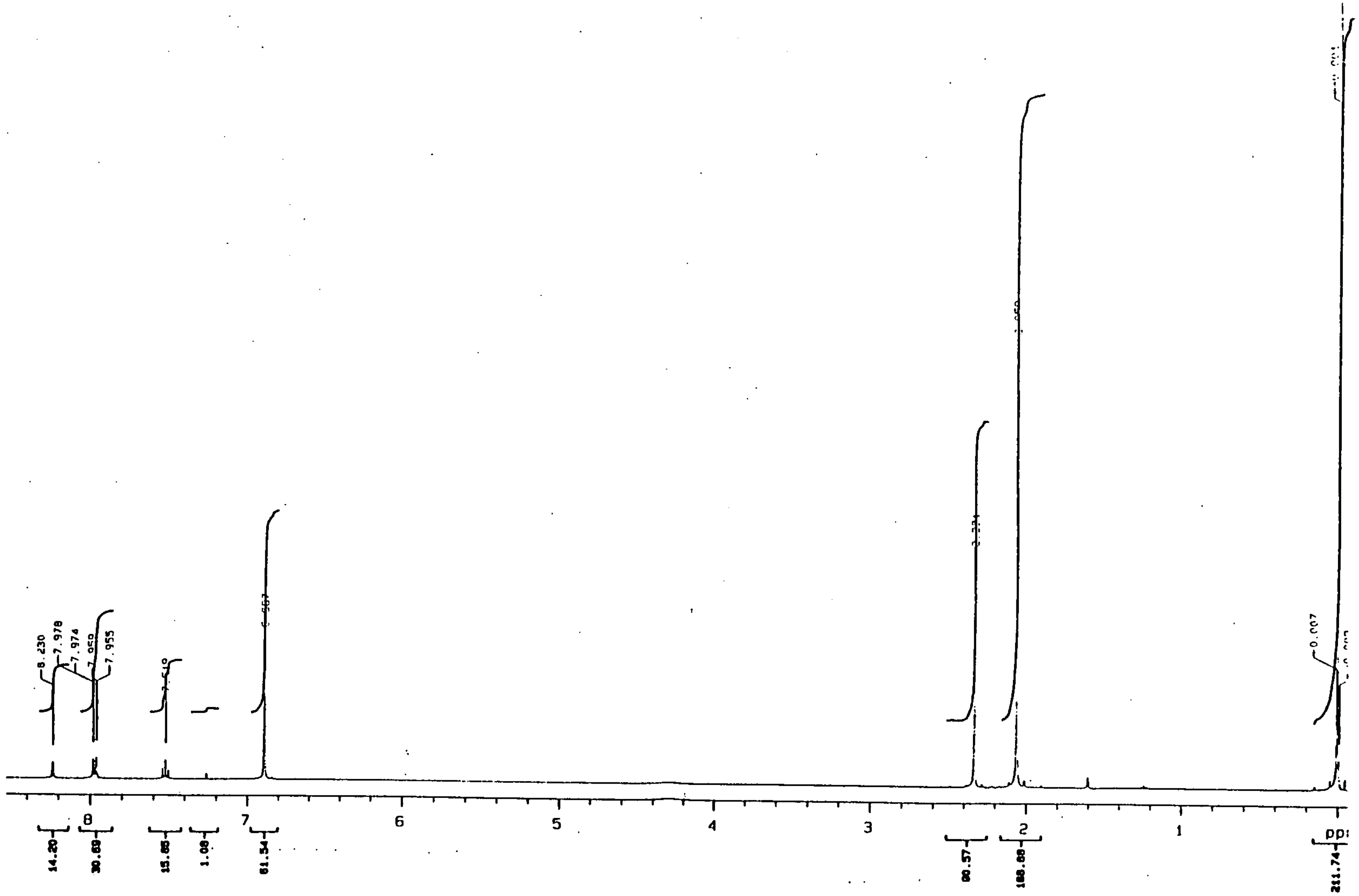
Appendix 1.1.26 FTIR spectrum of material produced in coupling reaction of 4-nitrobenzoyl biphenyl.



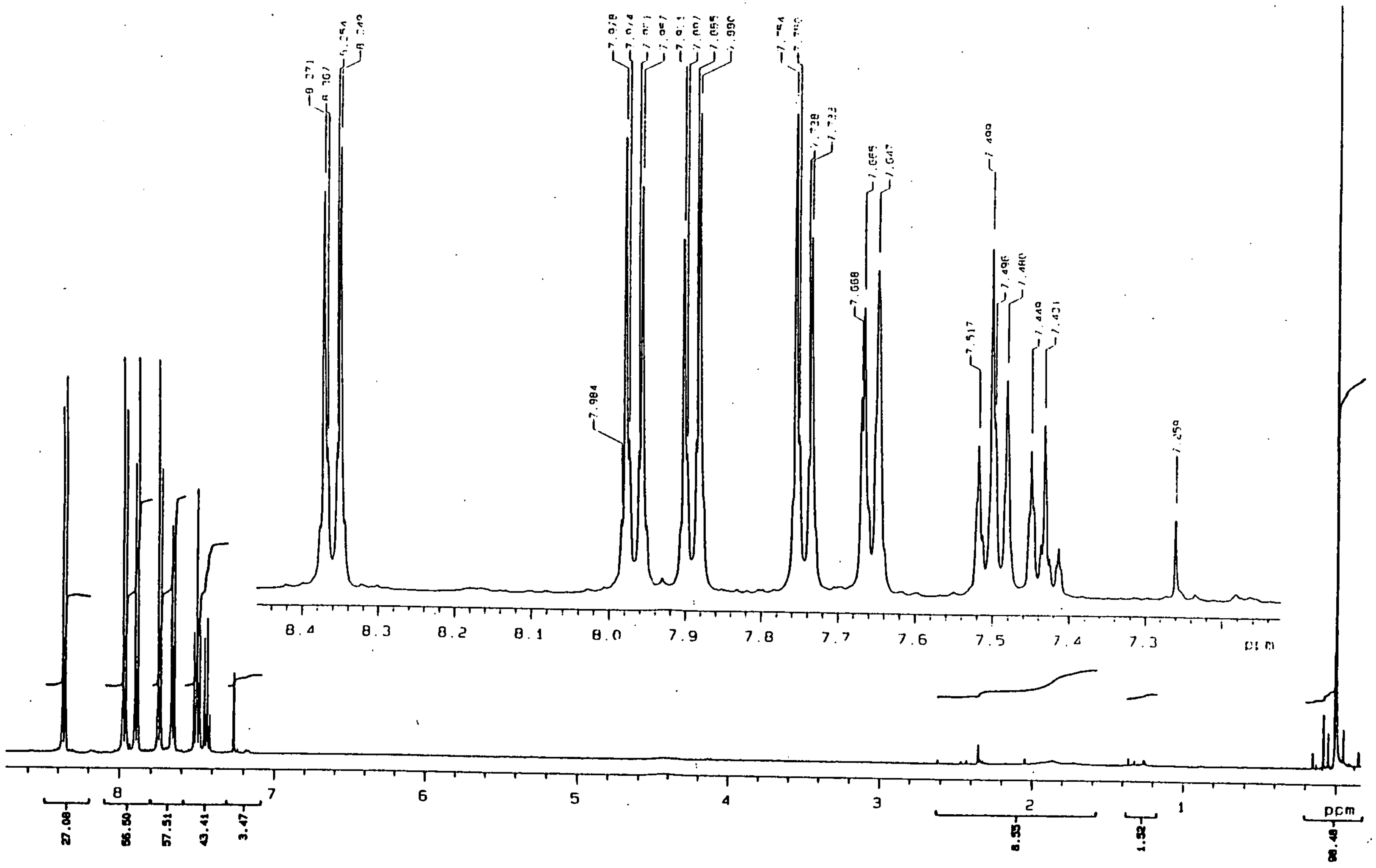
Appendix 1.2.1 ^{1}H Nmr spectrum of 4,4'-dibenzoylbiphenyl.



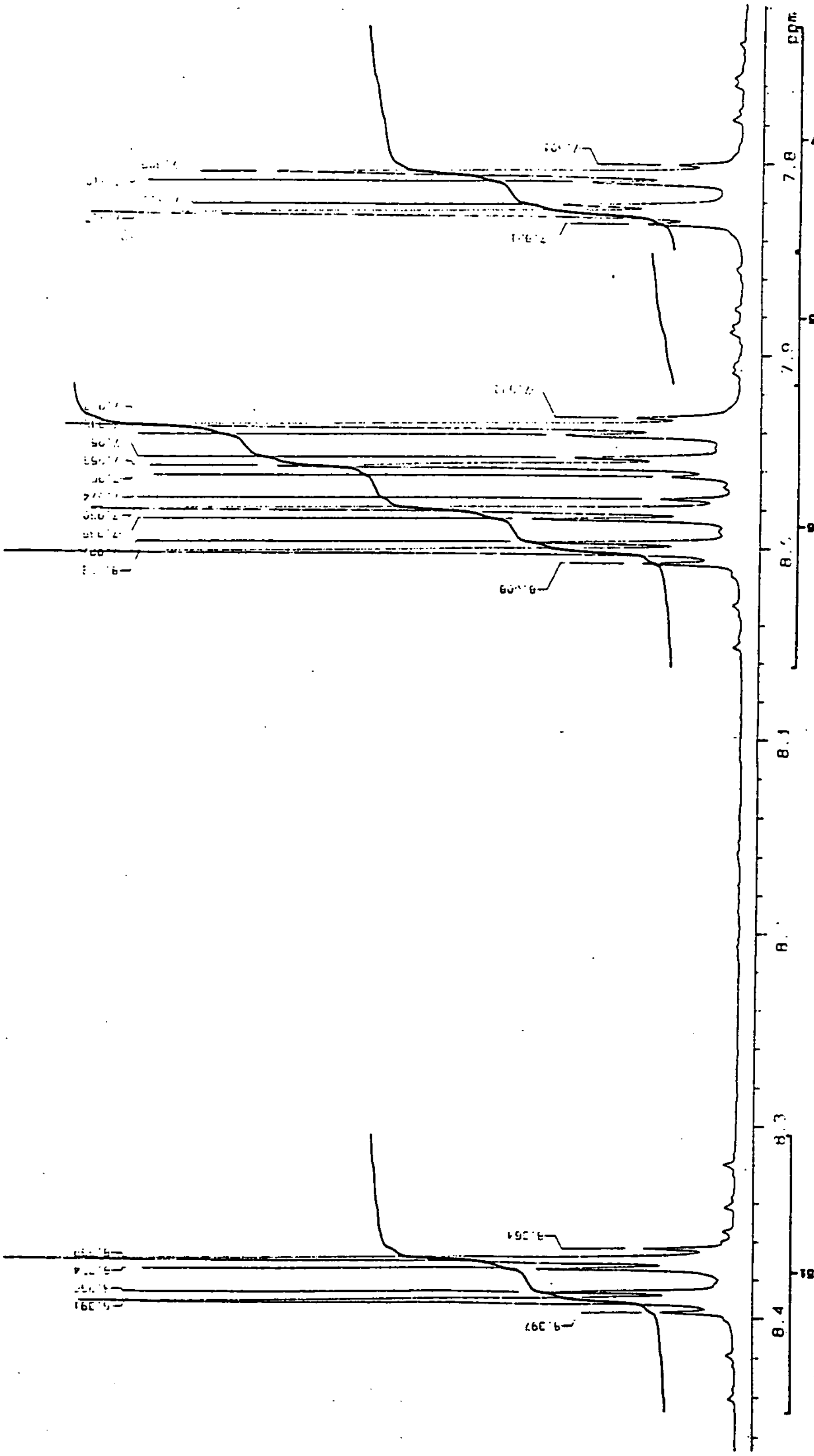
Appendix 1.2.2 ^{1}H Nmr spectrum of 1,3-dibenzoylbenzene.



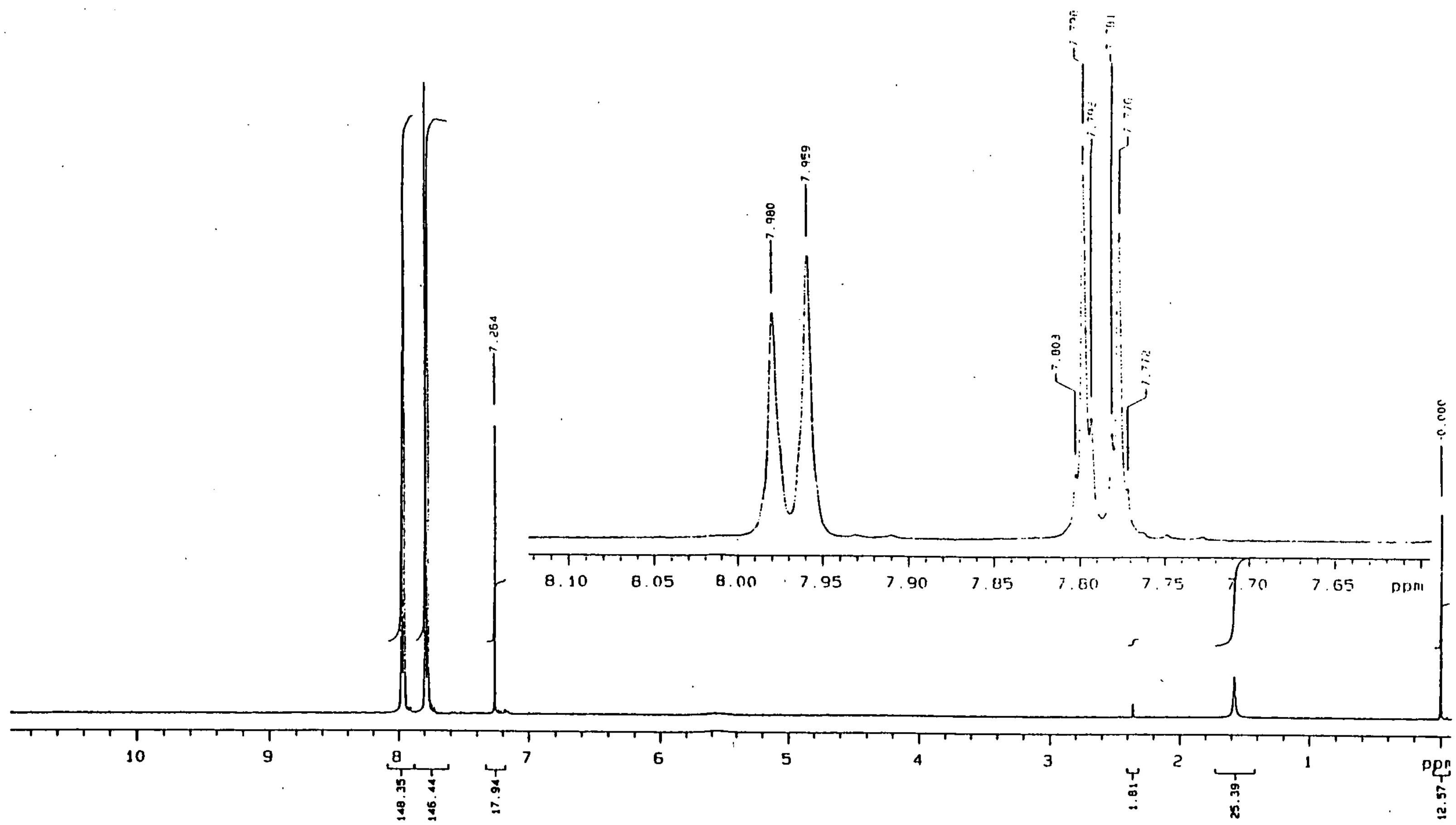
Appendix 1.2.3 ^{1}H Nmr spectrum of 1,3-dimesitoylbenzene.



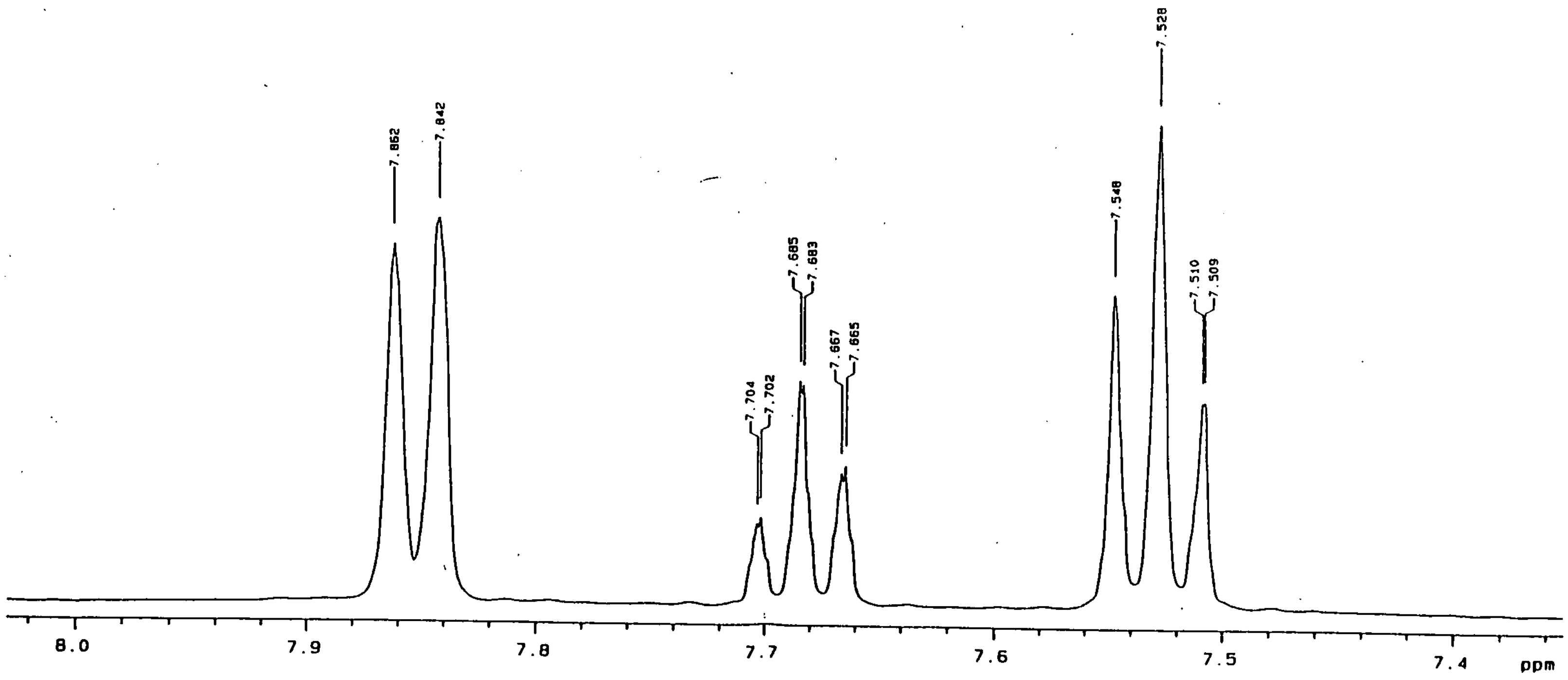
Appendix 1.2.4 ^{1}H Nmr spectrum of 4-nitrobenzoylbiphenyl.



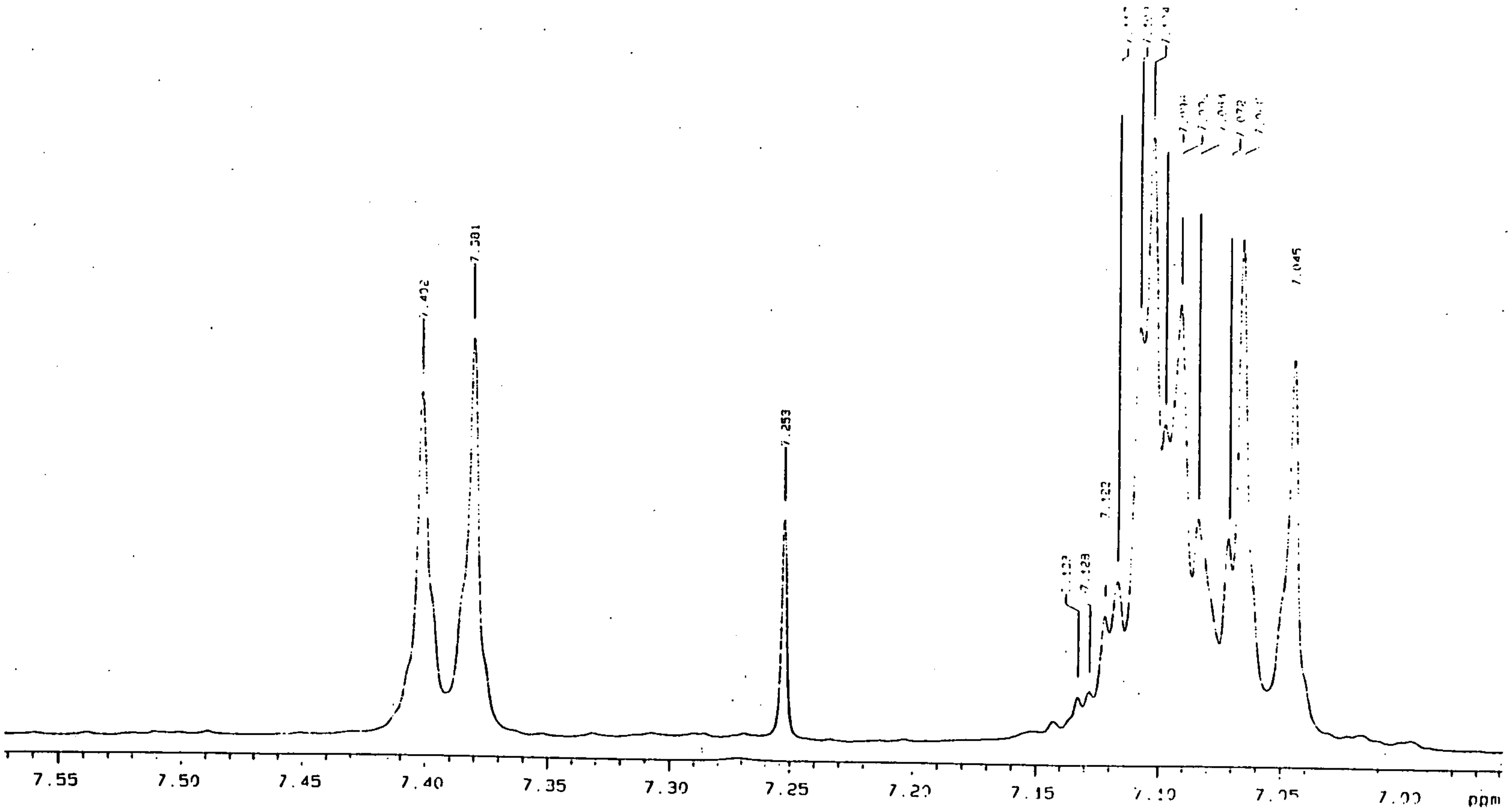
Appendix 1.2.5 ^{1}H Nmr spectrum of 4,4'-di(4-nitrobenzoyl)biphenyl.



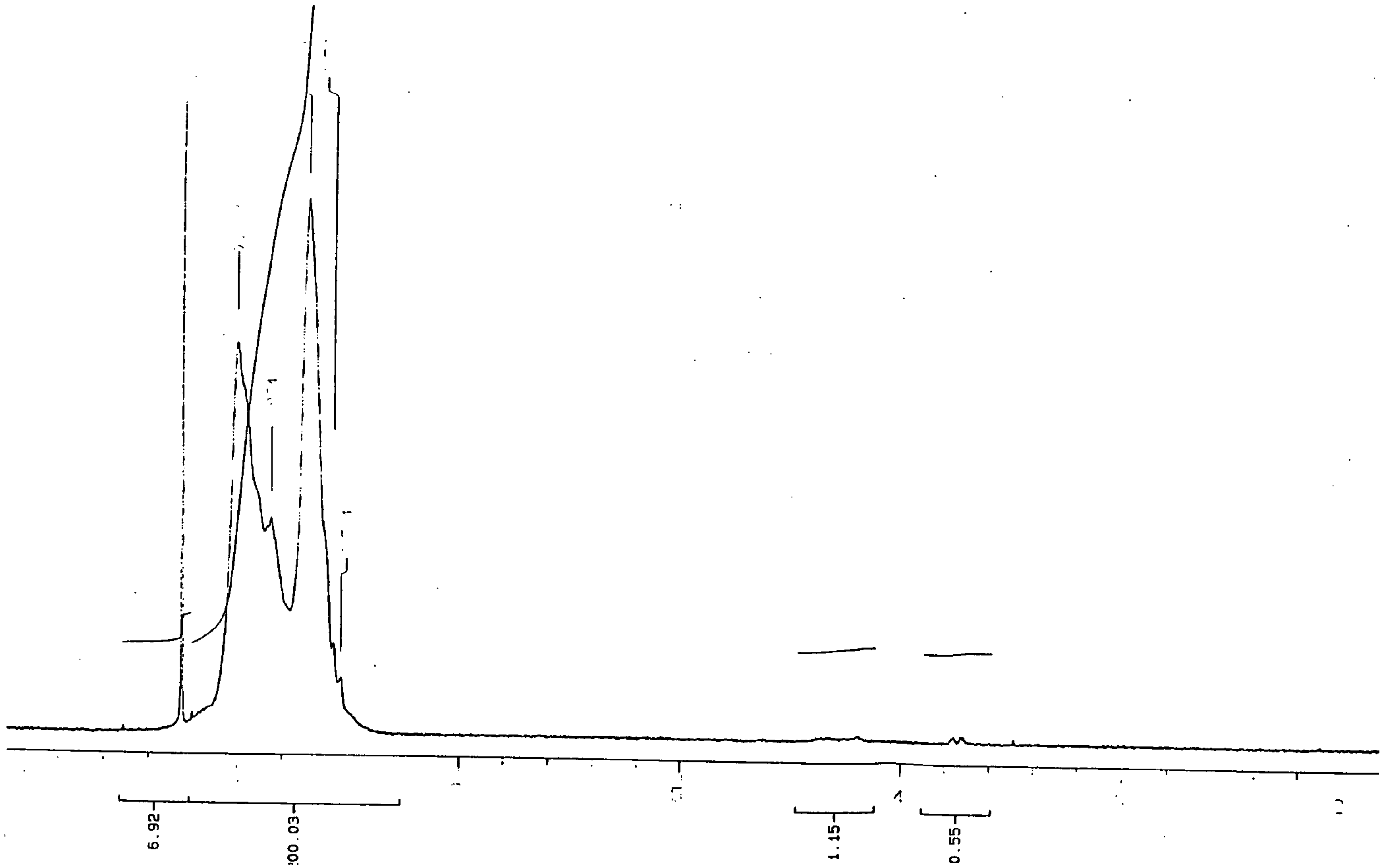
Appendix 1.2.6 ^{1}H Nmr spectrum of 4,4'-bis(pentafluorobenzoyl)biphenyl.



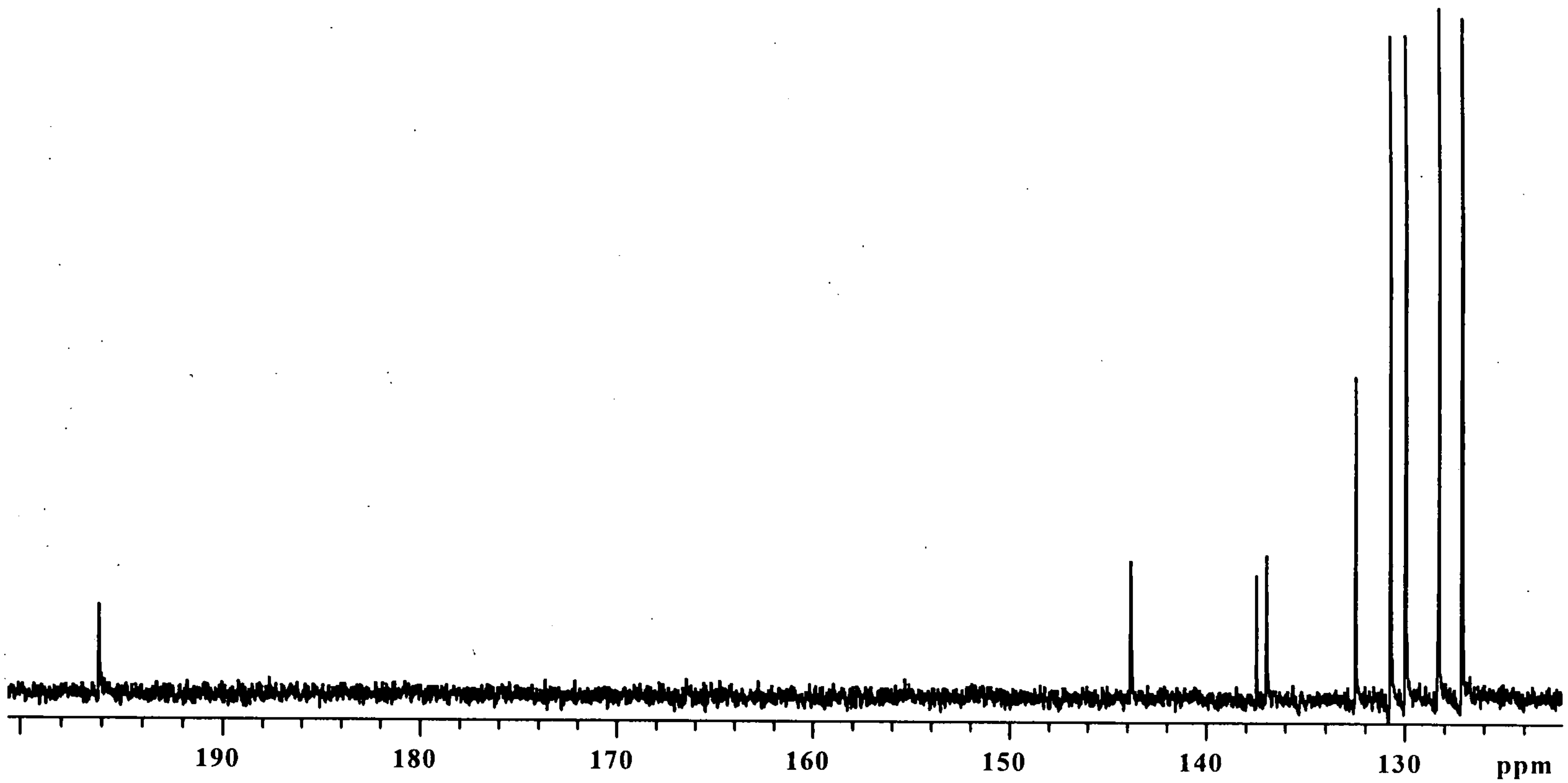
Appendix 1.2.7 ^{1}H Nmr spectrum of pentafluorobenzoylbenzene.



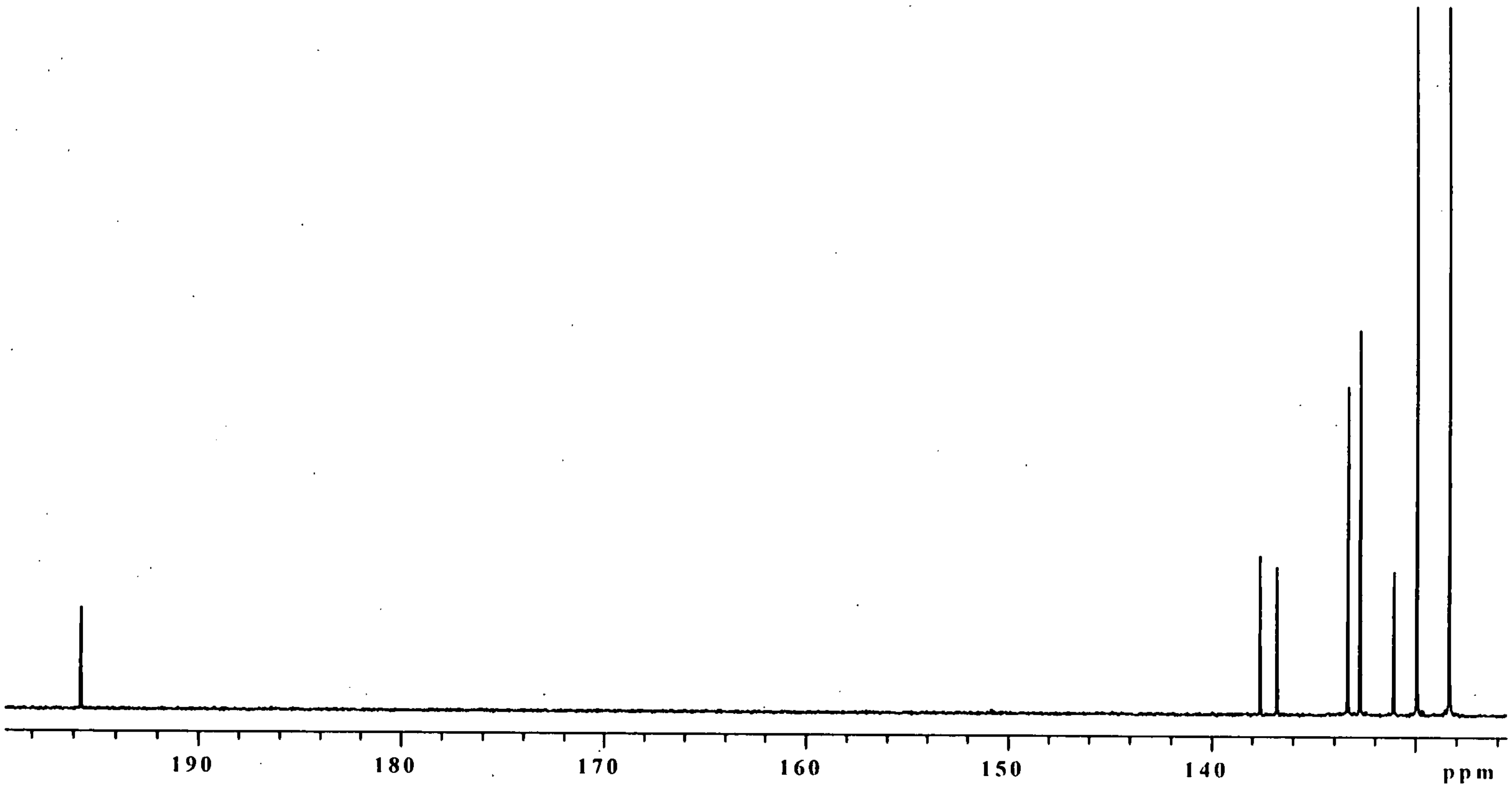
Appendix 1.2.8 ^{1}H Nmr spectrum of the cyclic trimer.



Appendix 1.2.9 ^{1}H Nmr spectrum of m-PPV-DP.



Appendix 1.3.1 ^{13}C Nmr spectrum of 4,4'-dibenzoylbiphenyl.



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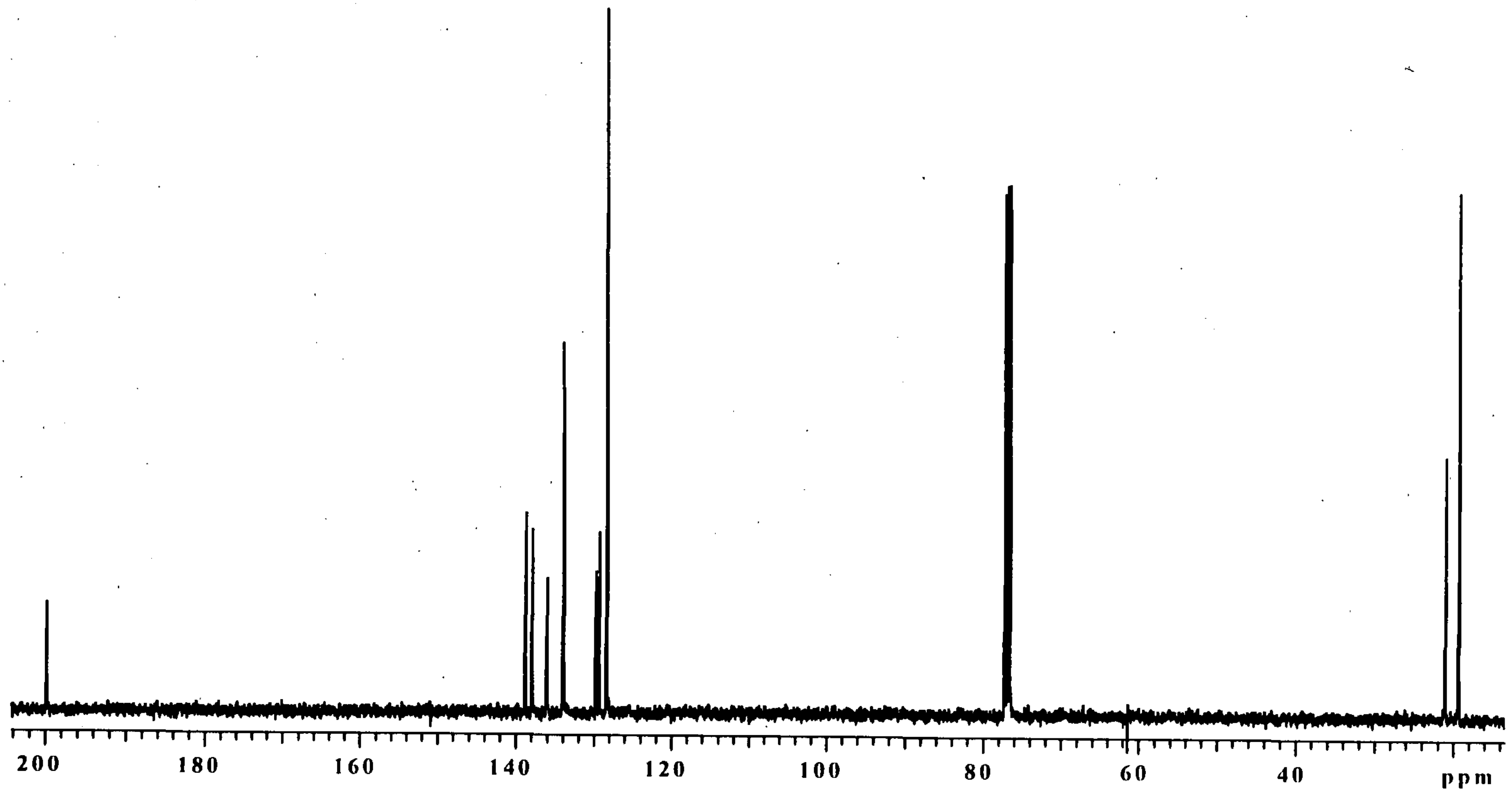
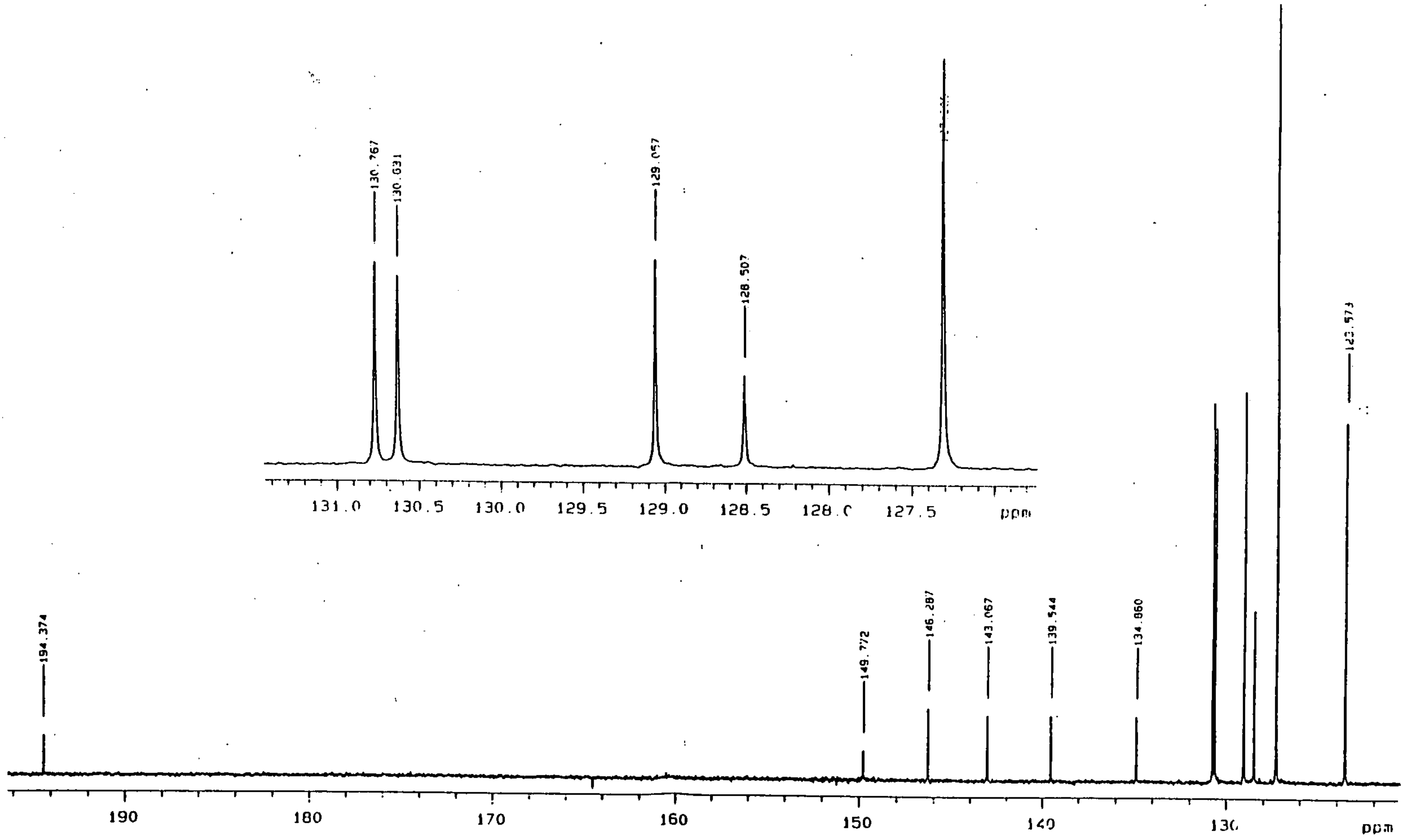
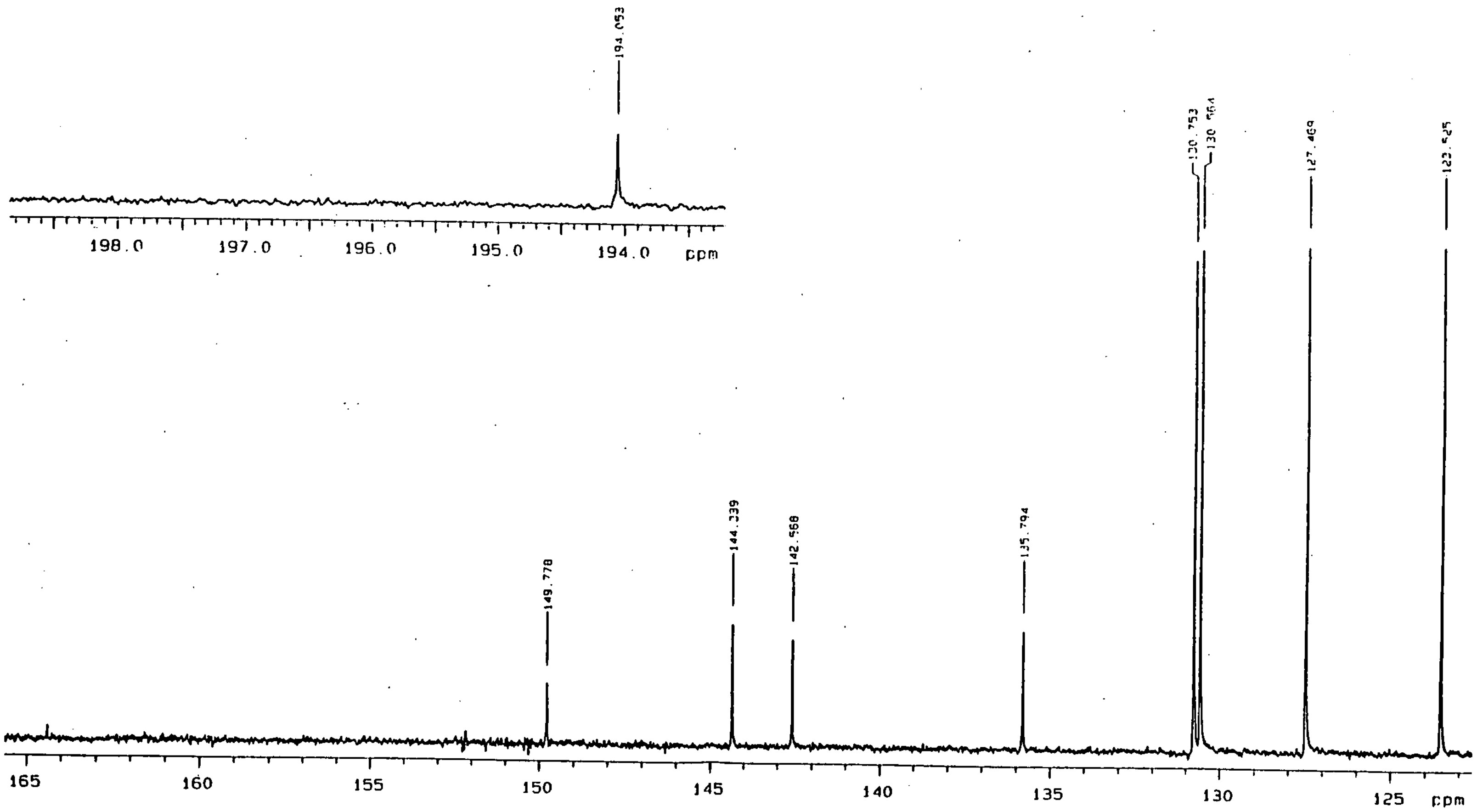


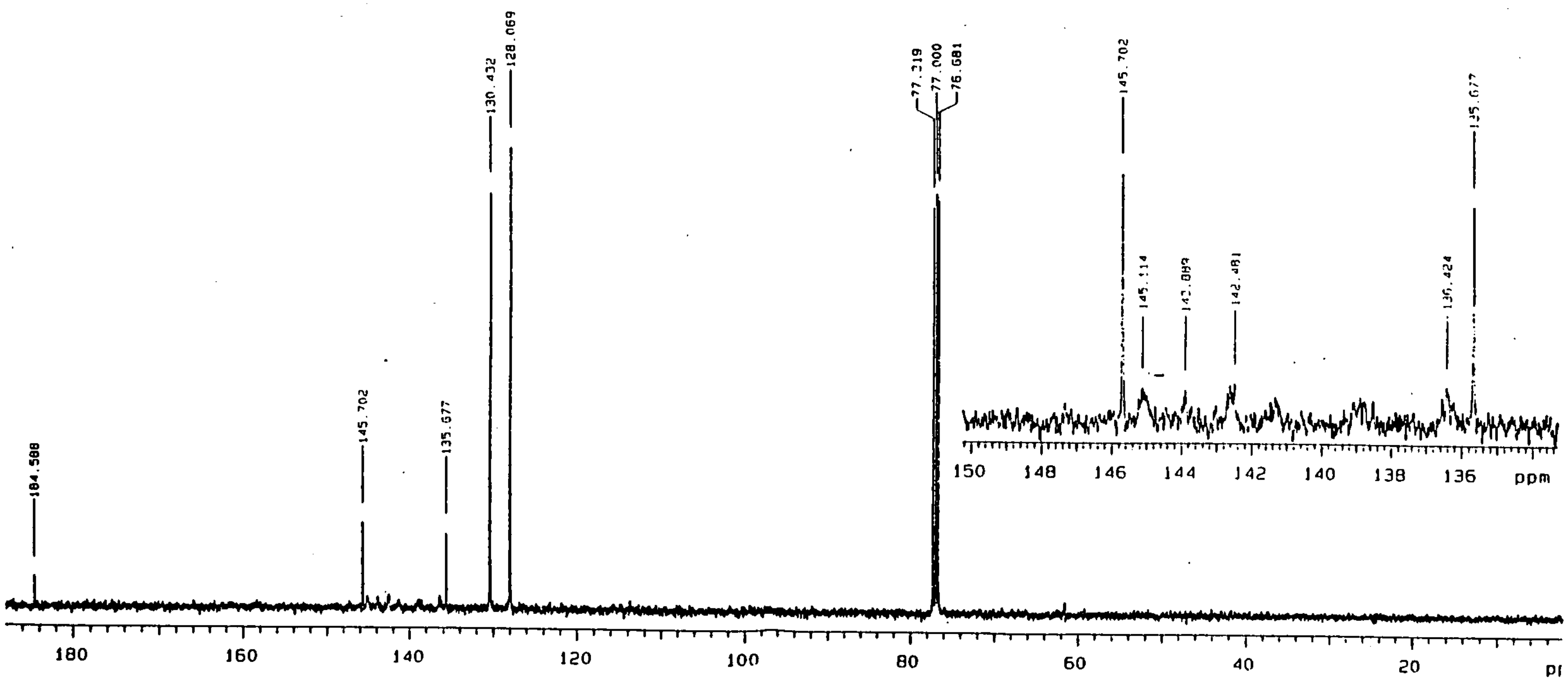
Appendix 1.3.3 ^{13}C Nmr spectrum of 1,3-dimesitoylbenzene.



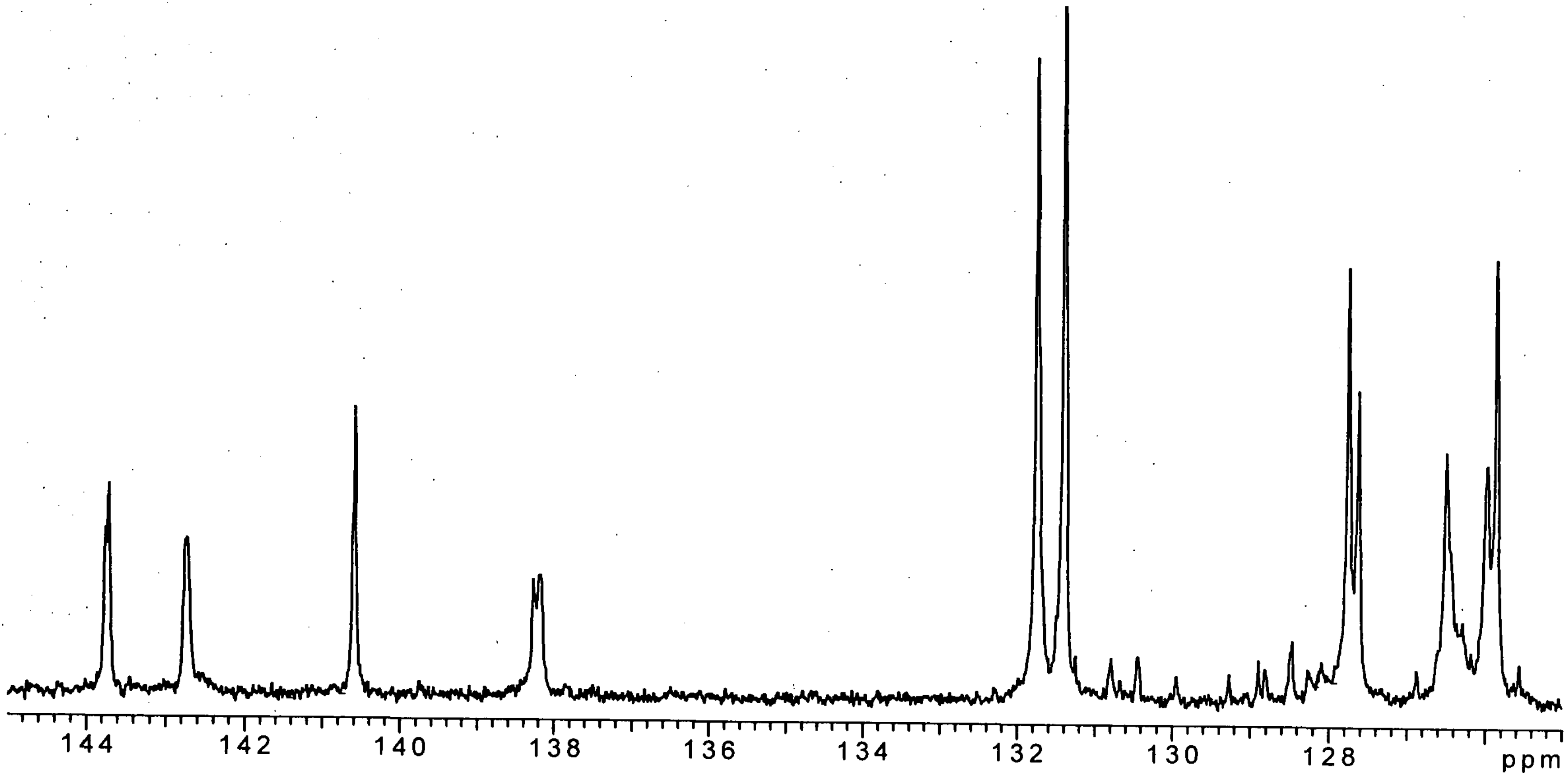
Appendix 1.3.4 ^{13}C Nmr spectrum of 4-nitrobenzoylbiphenyl.



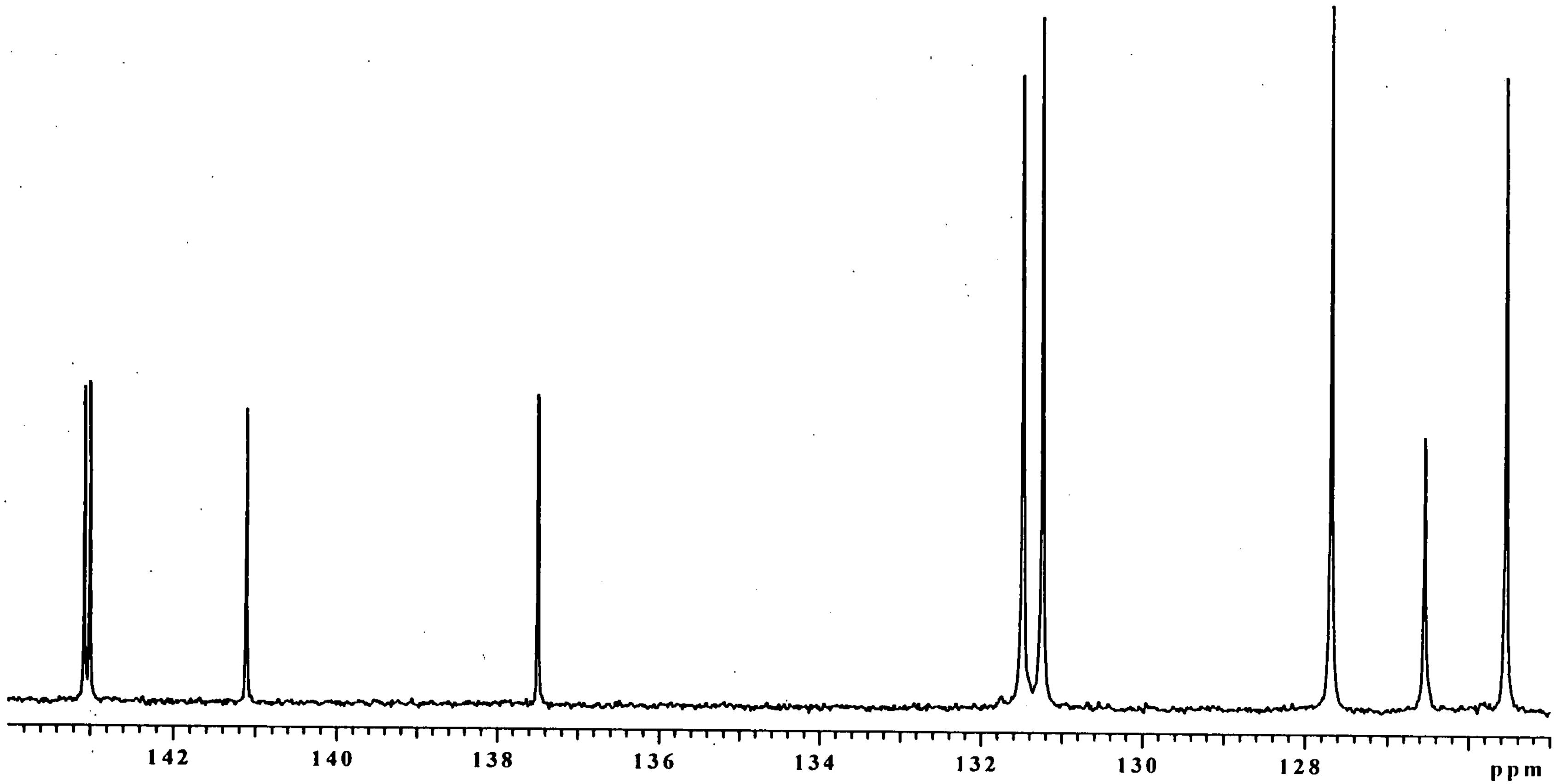
Appendix 1.3.5 ^{13}C Nmr spectrum of 4,4'-di(4-nitrobenzoyl)biphenyl.



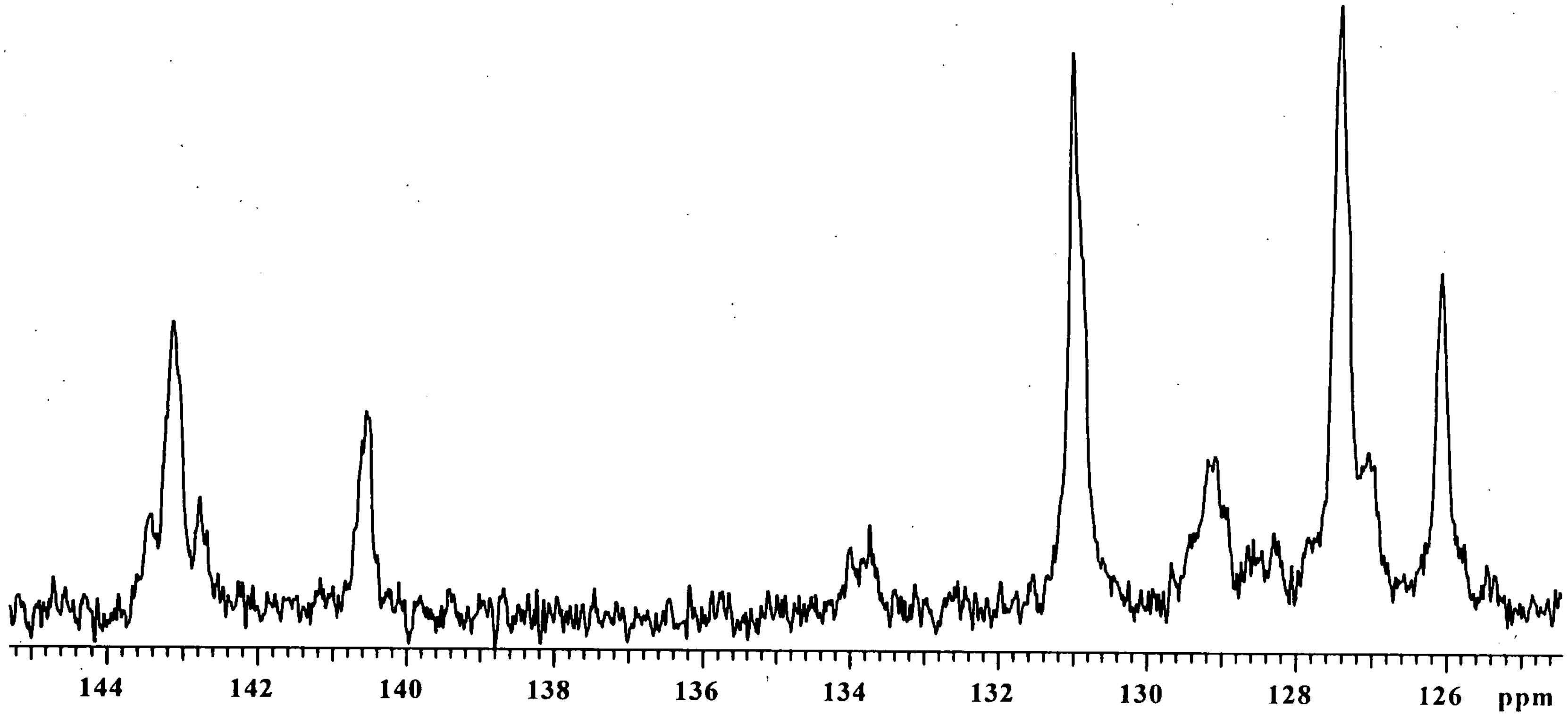
Appendix 1.3.6 ^{13}C Nmr spectrum of 4,4'-bis(pentafluorobenzoyl)biphenyl.



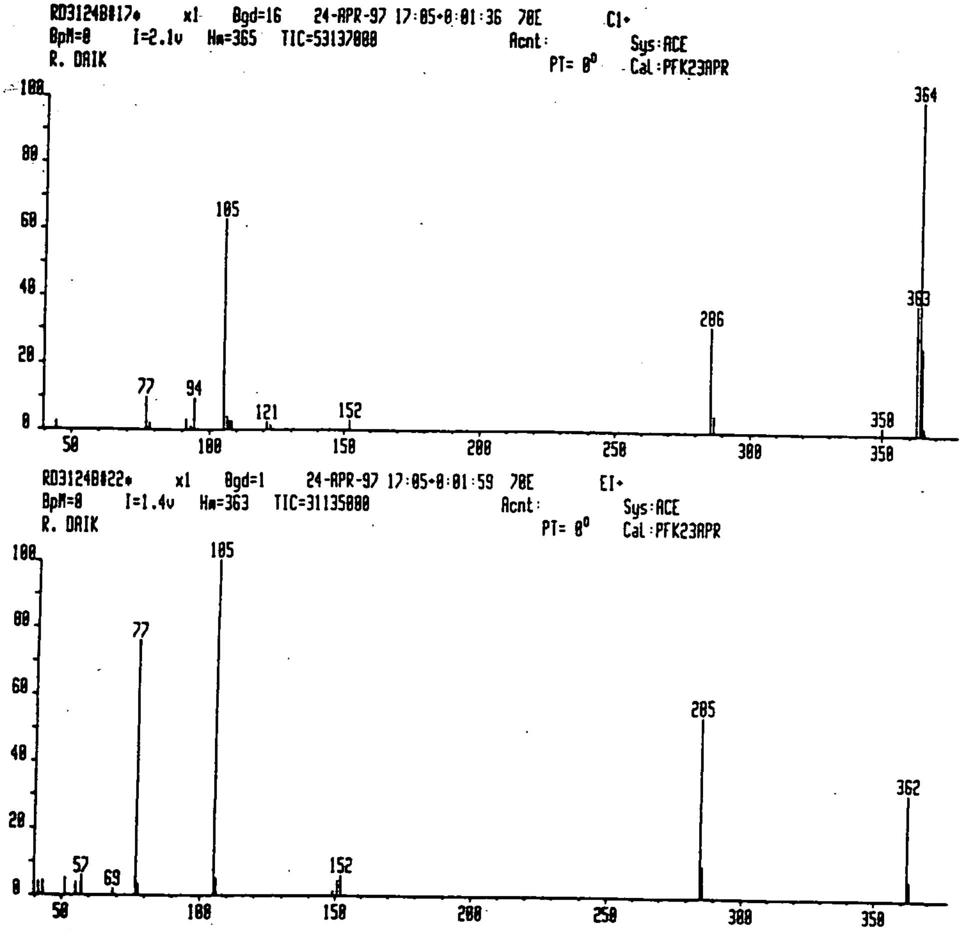
Appendix 1.3.7 ^{13}C Nmr spectrum of PDPV prepared in the preliminary experiment.



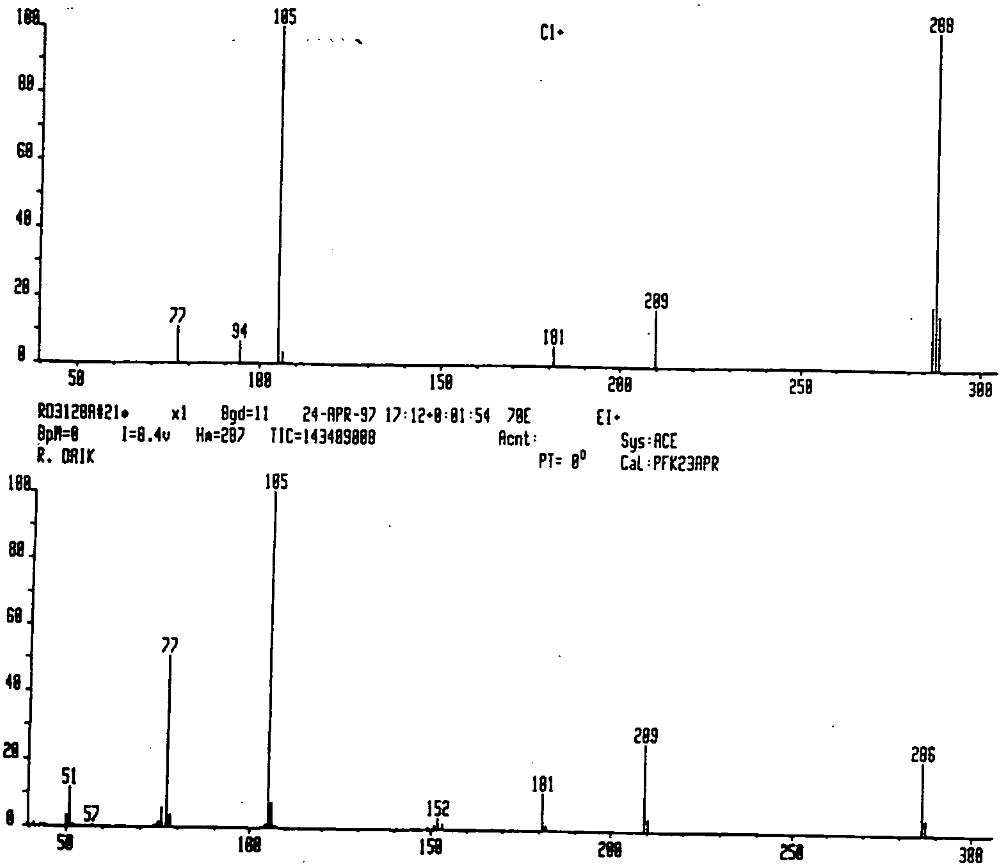
Appendix 1.3.8 ^{13}C Nmr spectrum of the cyclic trimer.



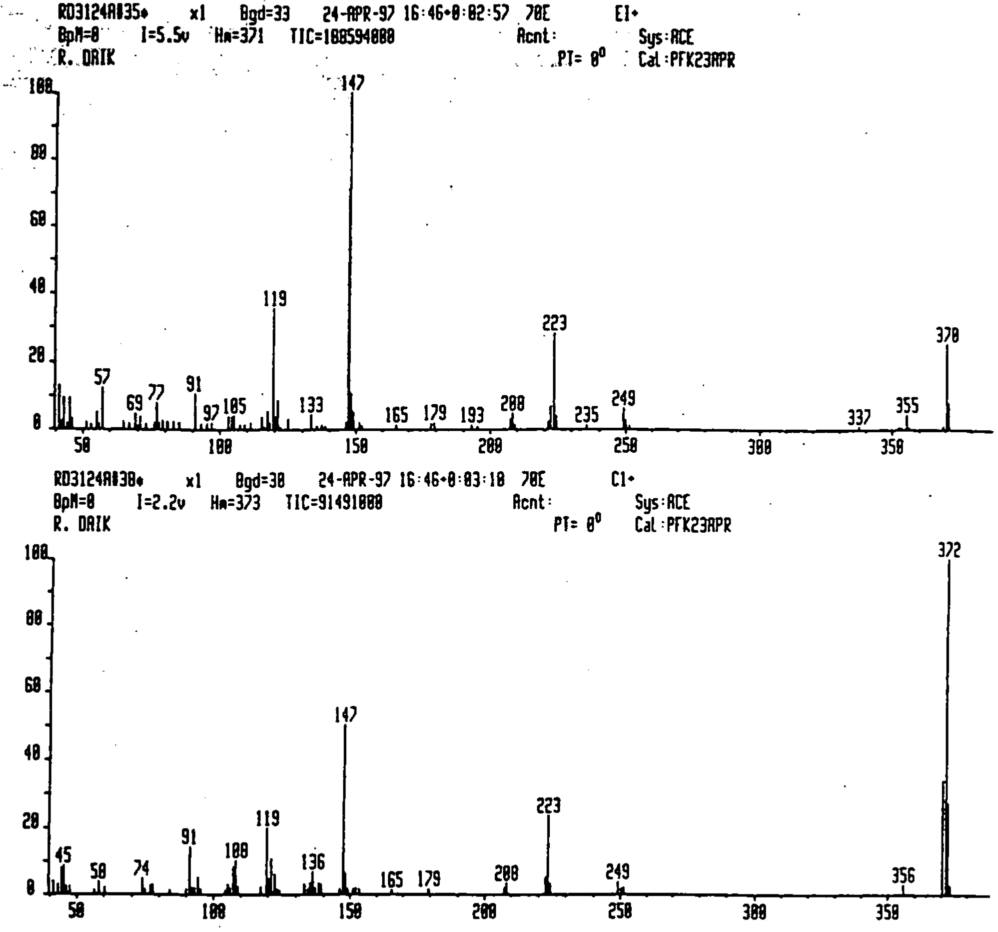
Appendix 1.3.9 ^{13}C Nmr spectrum of m-PPV-DP



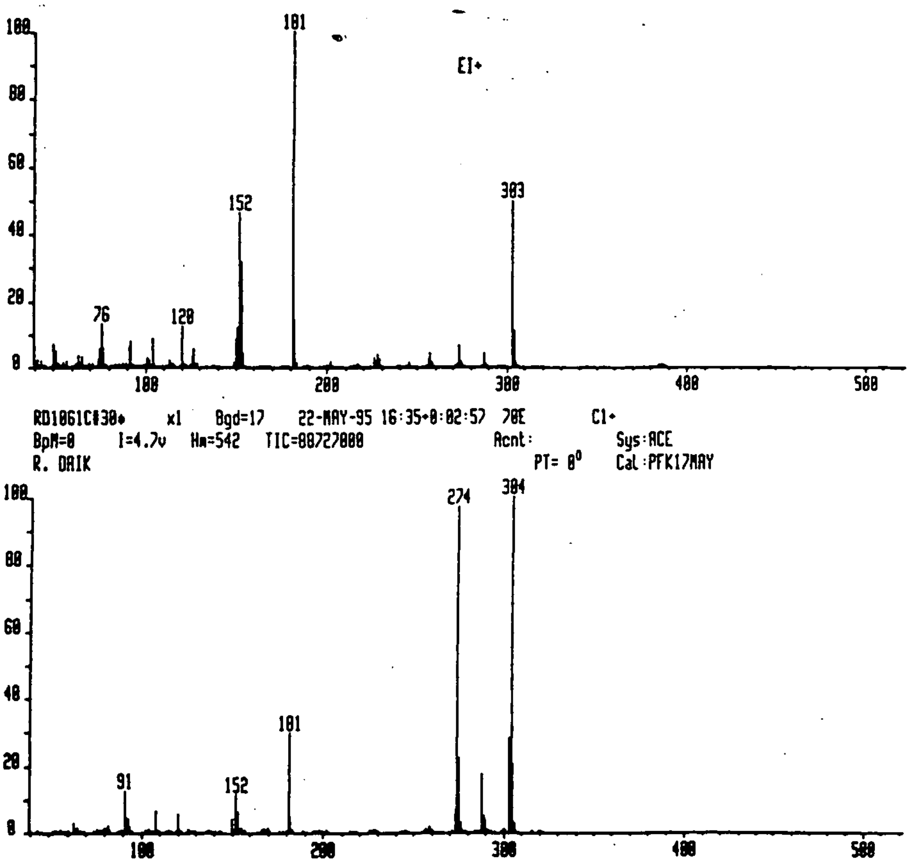
Appendix 1.4.1 Mass spectrum of 4,4'-dibenzoylbiphenyl.



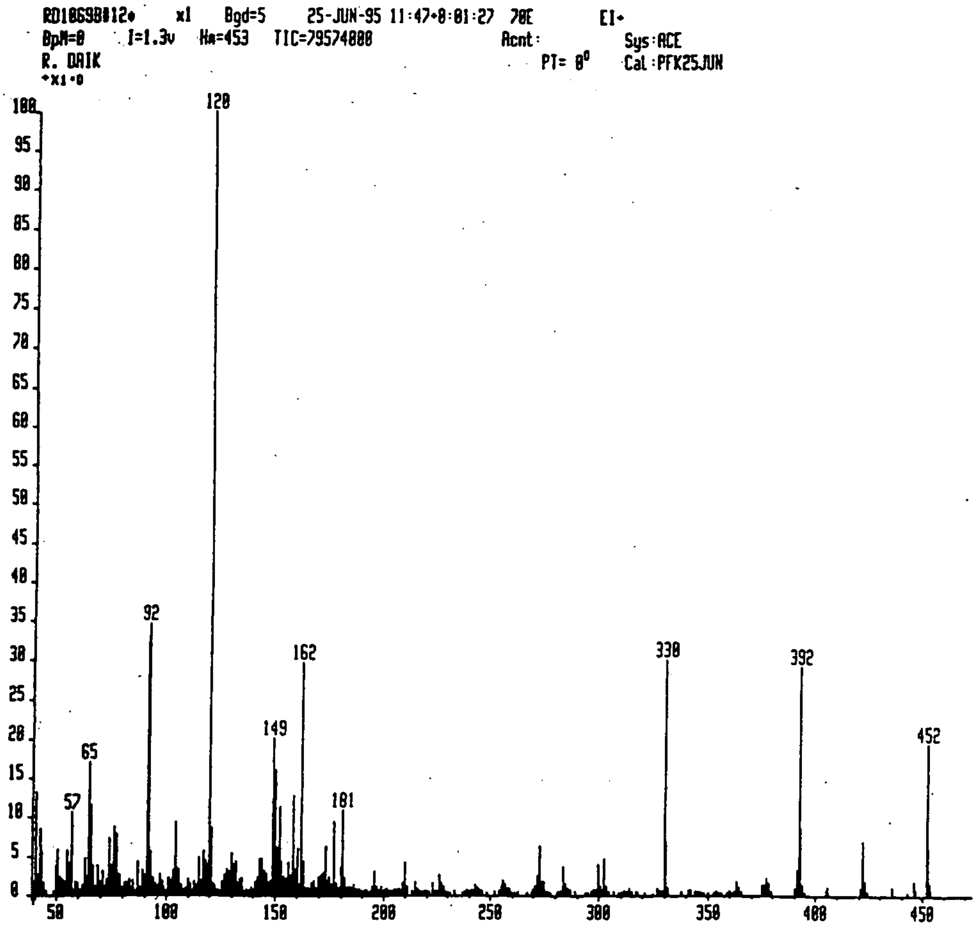
Appendix 1.4.2 Mass spectrum of 1,3-dibenzoylbenzene.



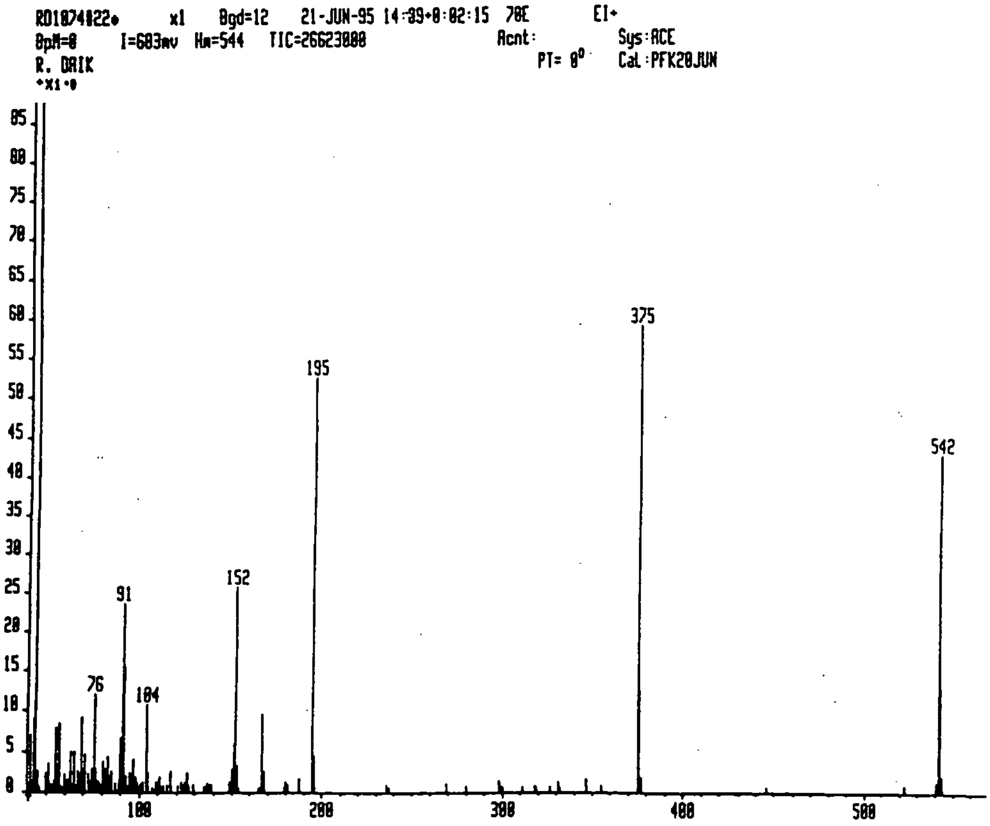
Appendix 1.4.3 Mass spectrum of 1,3-dimesitoylbenzene.



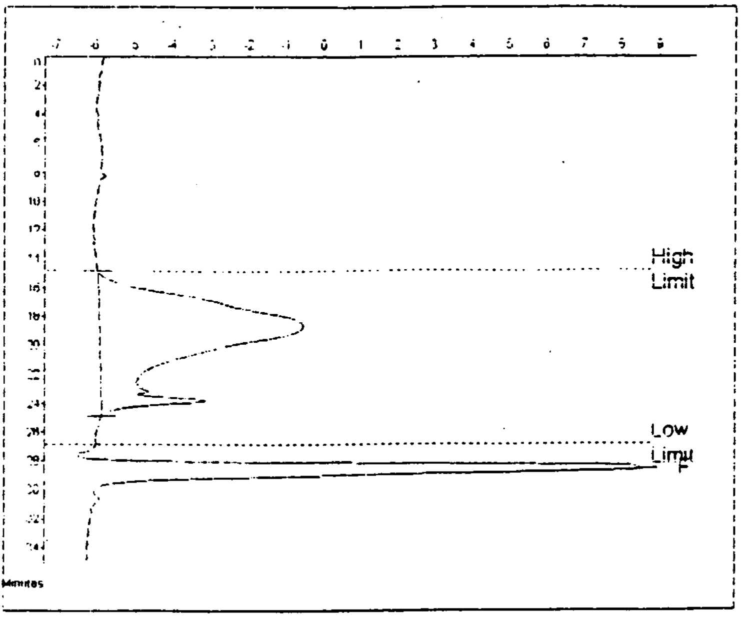
Appendix 1.4.4 Mass spectrum of 4-nitrobenzoylbiphenyl.



Appendix 1.4.5 Mass spectrum of 4,4’-di(4-nitrobenzoyl)biphenyl.



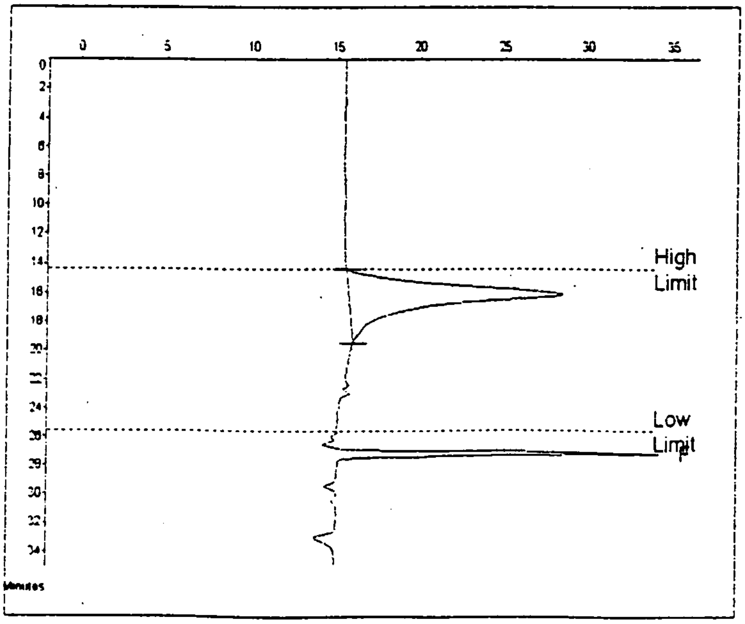
Appendix 1.4.6 Mass spectrum of 4,4’-bis(pentafluorobenzoyl)biphenyl..



Molecular Weight Averages

Mp = [illegible]
Mn = [illegible]
Mw = 41791
Polydispersity = [illegible]
Mz = [illegible]
Mz+1 = [illegible]
Mv = [illegible]
Peak Area = [illegible]

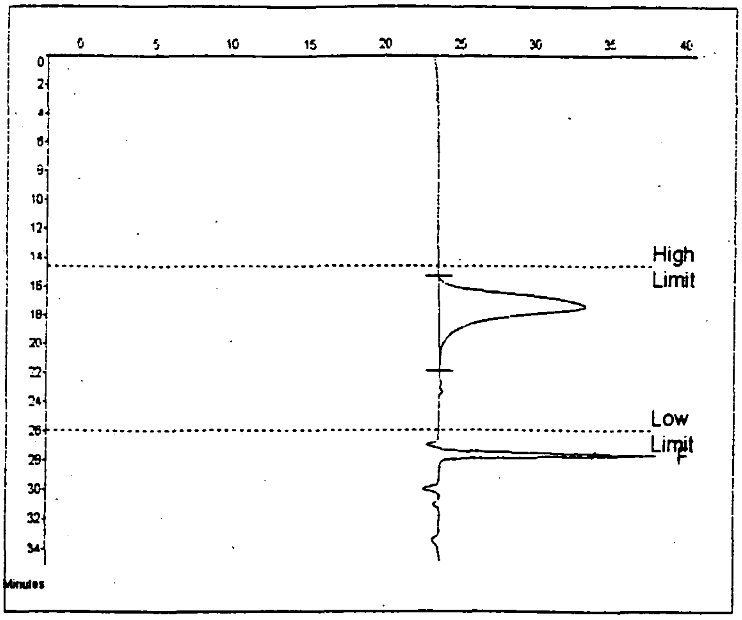
Appendix 1.5.1 A representative GPC trace of the as made PDPV.



Molecular Weight Averages

Mp = 155069
Mn = 88060
Mw = 166889
Polydispersity = 1.896
Mz = 254803
Mz+1 = 350568
Mv = 155165
Peak Area = 241367

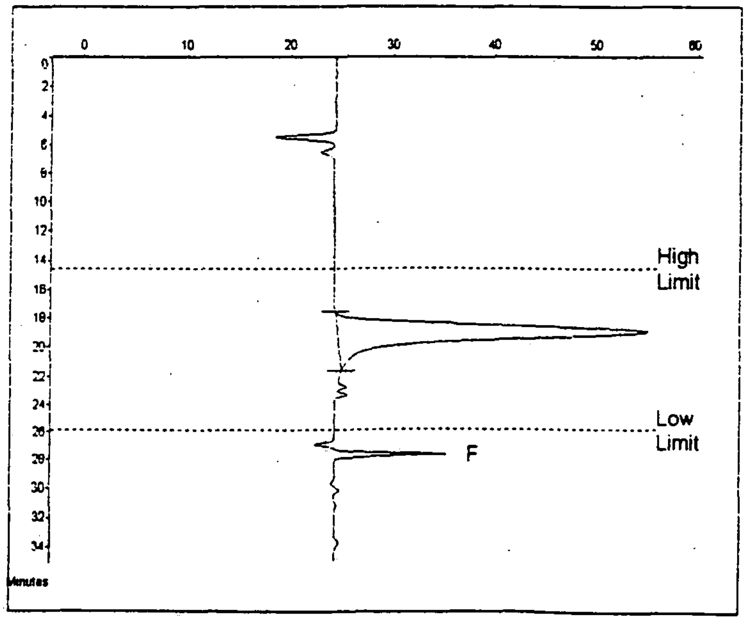
Appendix 1.5.2 GPC trace of the fractionated PDPV (fraction 1).



Molecular Weight Averages

Mp =	70832	Mz =	113095
Mn =	42917	Mz+1 =	151562
Mw =	78129	Mv =	73338
Polydispersity =	1.820	Peak Area =	213752

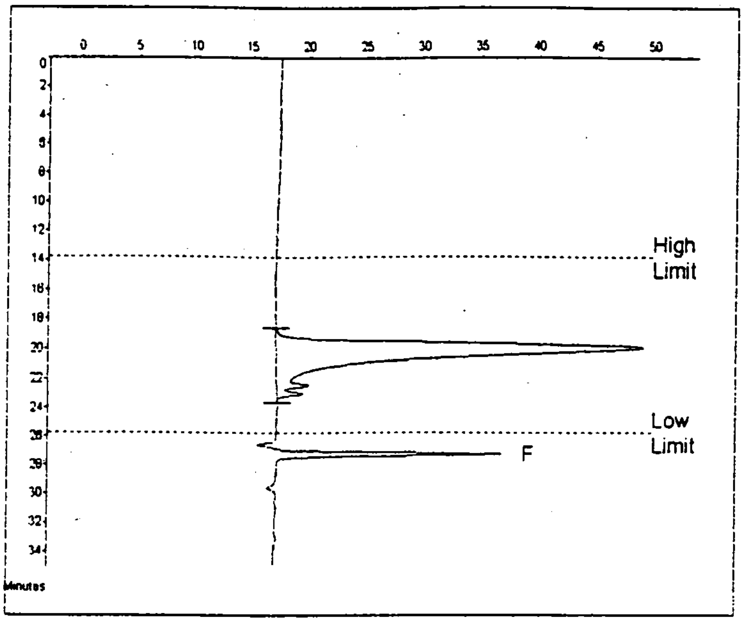
Appendix 1.5.3 GPC trace of the fractionated PDPV (fraction 3).



Molecular Weight Averages

Mp =	17442	Mz =	19269
Mn =	13625	Mz+1 =	21621
Mw =	16601	Mv =	16197
Polydispersity =	1.218	Peak Area =	435494

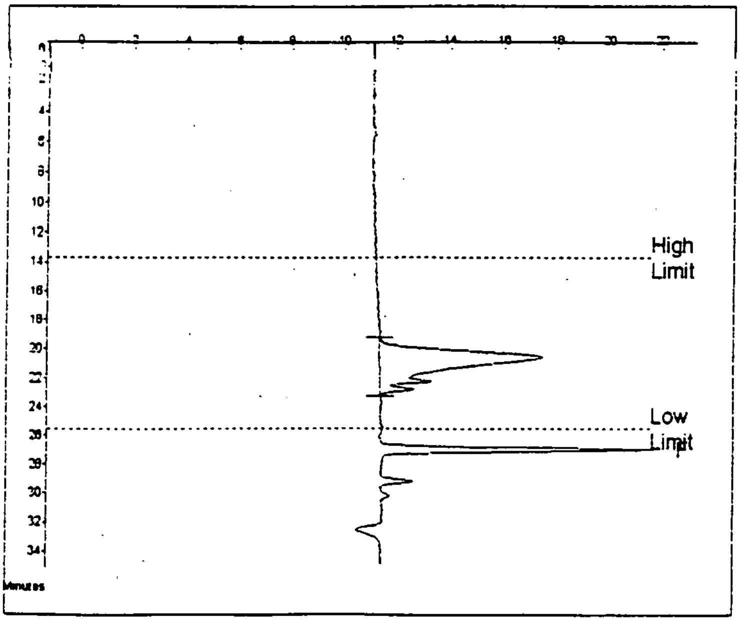
Appendix 1.5.4 GPC trace of the fractionated PDPV (fraction 6).



Molecular Weight Averages

Mp =	7324	[illegible]	Mz =	7028
Mn =	4155	4160	Mz+1 =	7852
Mw =	5911		Mv =	5718
Polydispersity =	1.422		Peak Area =	462140

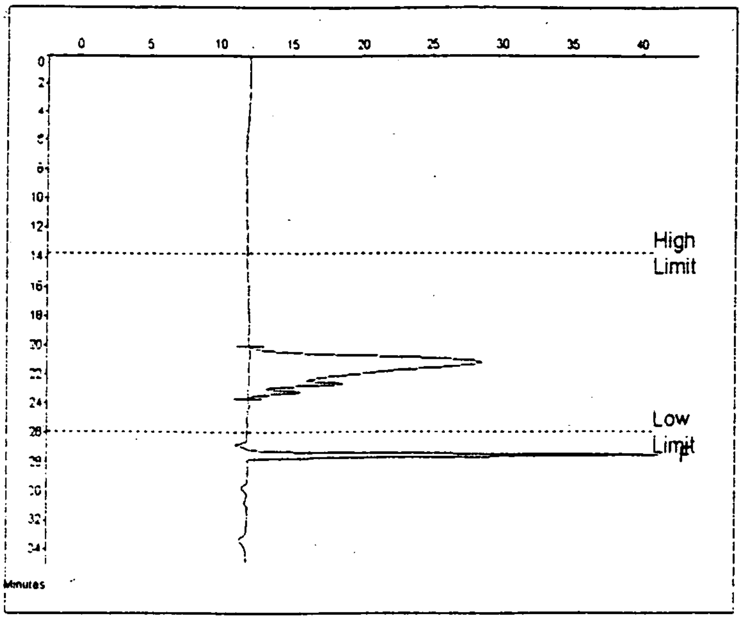
Appendix 1.5.5 GPC trace of the fractionated PDPV (fraction 10).



Molecular Weight Averages

Mp =	3883		Mz =	3927
Mn =	2471	2470	Mz+1 =	4473
Mw =	3255		Mv =	3148
Polydispersity =	1.317	1.2	Peak Area =	108852

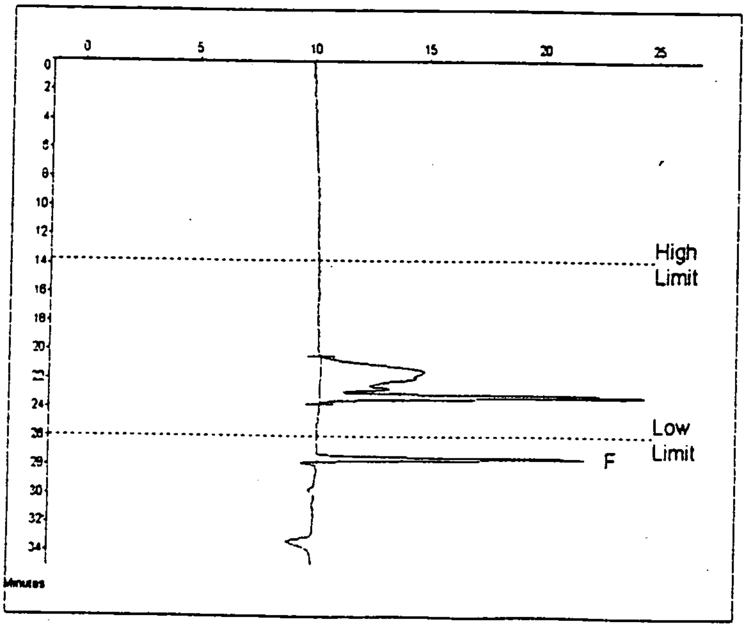
Appendix 1.5.6 GPC trace of the fractionated PDPV (fraction 14).



Molecular Weight Averages

Mp =	3030 (4)	Mz =	3001
Mn =	1972 (6)	Mz+1 =	3399
Mw =	2515	Mv =	2438
Polydispersity =	1.275	Peak Area =	296202

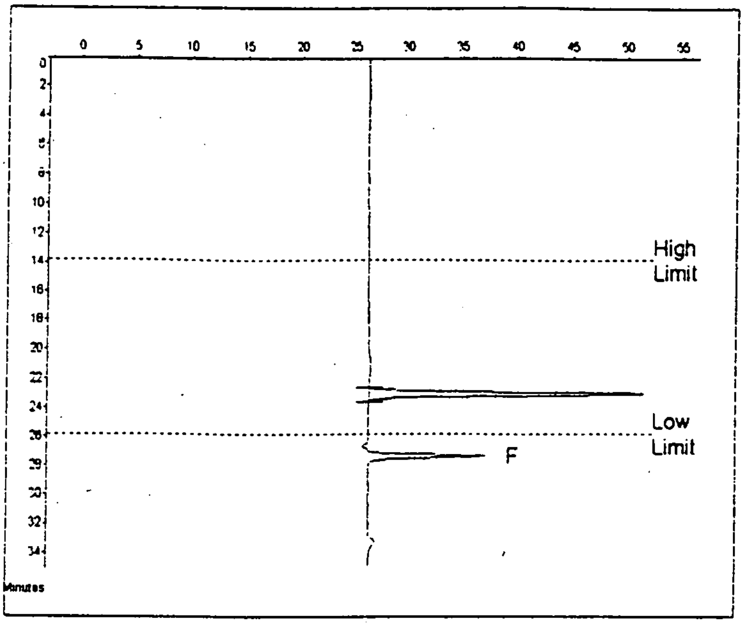
Appendix 1.5.7 GPC trace of the fractionated PDPV (fraction 15).



Molecular Weight Averages

Mp =	759	Mz =	2103
Mn =	1150 (3)	Mz+1 =	2598
Mw =	1561	Mv =	1487
Polydispersity =	1.358	Peak Area =	136041

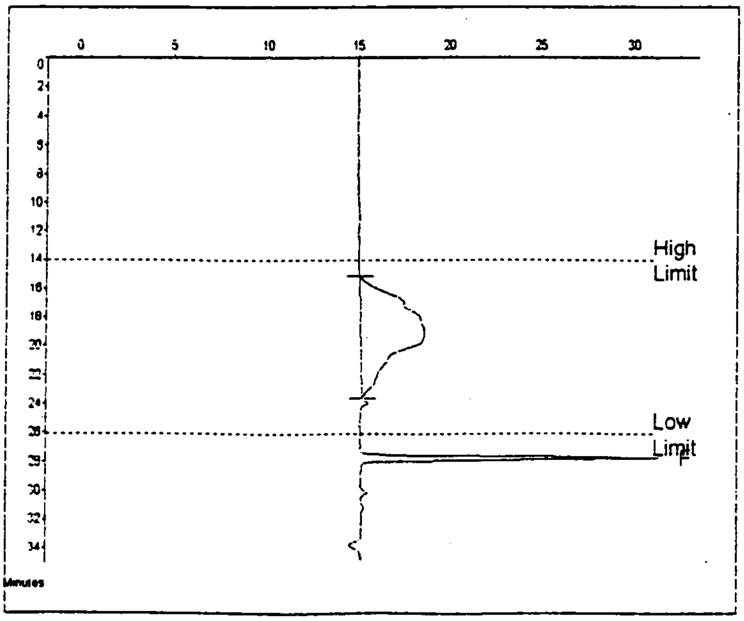
Appendix 1.5.8 GPC trace of the fractionated PDPV (fraction 17).



Molecular Weight Averages

Mp =	807 4	Mz =	803
Mn =	793	Mz+1 =	809
Mw =	798	Mv =	797
Polydispersity =	1.007	Peak Area =	97065

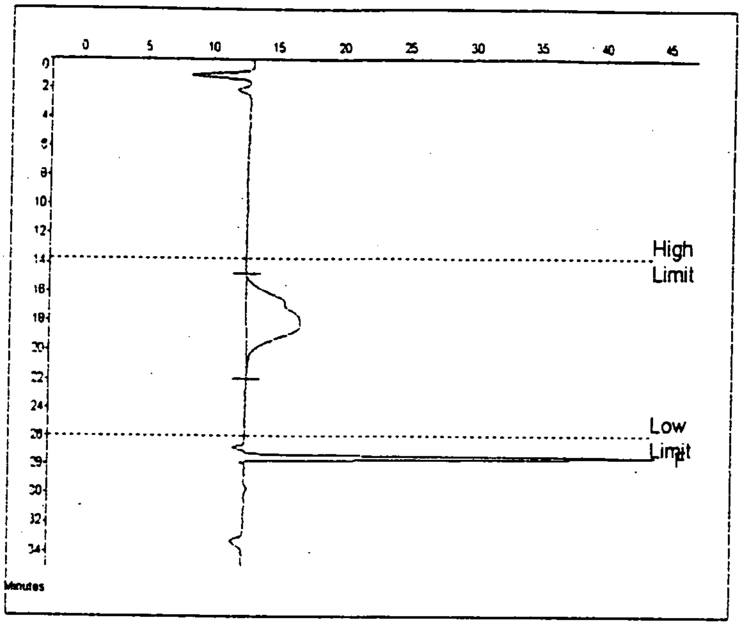
Appendix 1.5.9 GPC trace of the fractionated PDPV (fraction 18, cyclic trimer).



Molecular Weight Averages

Mp =	16628	Mz =	150383
Mn =	7488	Mz+1 =	255909
Mw =	45794	Mv =	38054
Polydispersity =	6.114	Peak Area =	191675

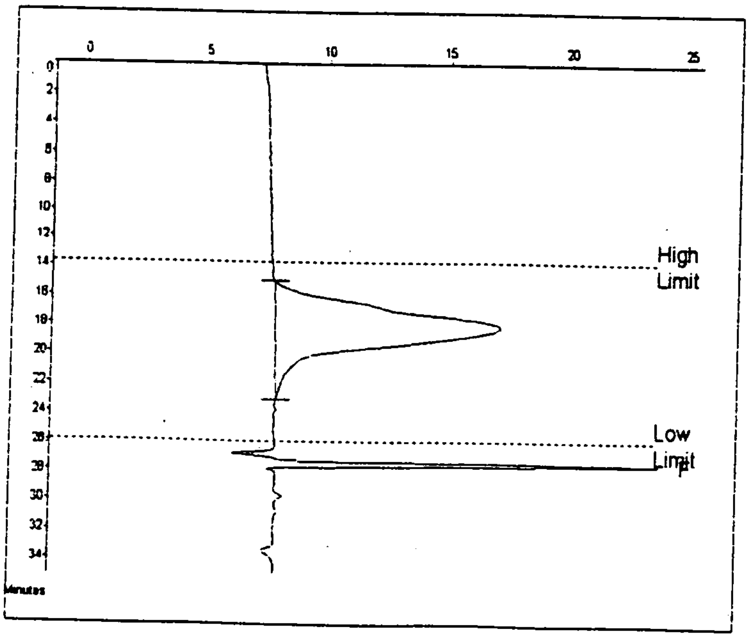
Appendix 1.5.10 GPC trace of the as made m-PPV-DP.



Molecular Weight Averages

Mp = 32647
Mz = 162537
Mn = 27273
Mz+1 = 272711
Mw = 70825
Mv = 61374
Polydispersity = 2.597
Peak Area = 152867

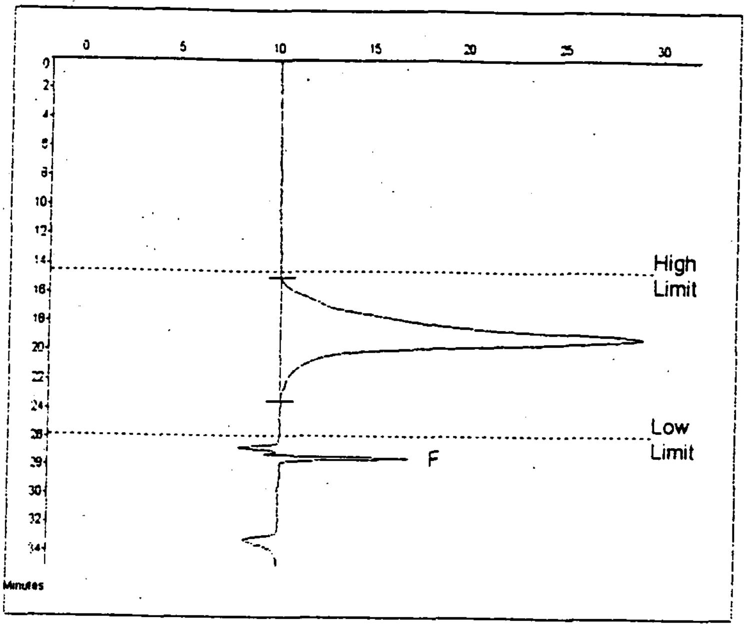
Appendix 1.5.11 GPC trace of the fractionated m-PPV-DP (fraction 1).



Molecular Weight Averages

Mp = 32797
Mz = 116458
Mn = 17436
Mz+1 = 203894
Mw = 49863
Mv = 43258
Polydispersity = 2.860
Peak Area = 317347

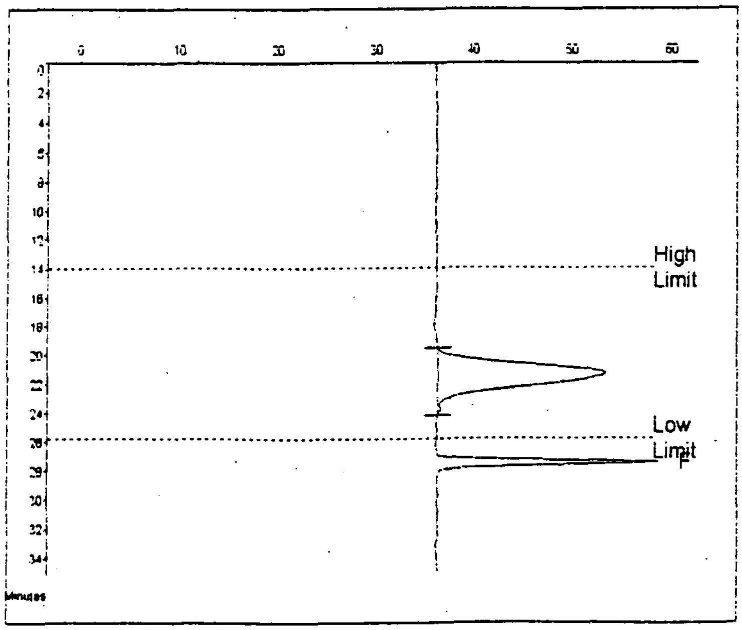
Appendix 1.5.12 GPC trace of the fractionated m-PPV-DP (fraction 3).



Molecular Weight Averages

Mp =	15060	Mz =	87983
Mn =	12674	Mz+1 =	208425
Mw =	29252	Mv =	25140
Polydispersity =	2.308	Peak Area =	429815

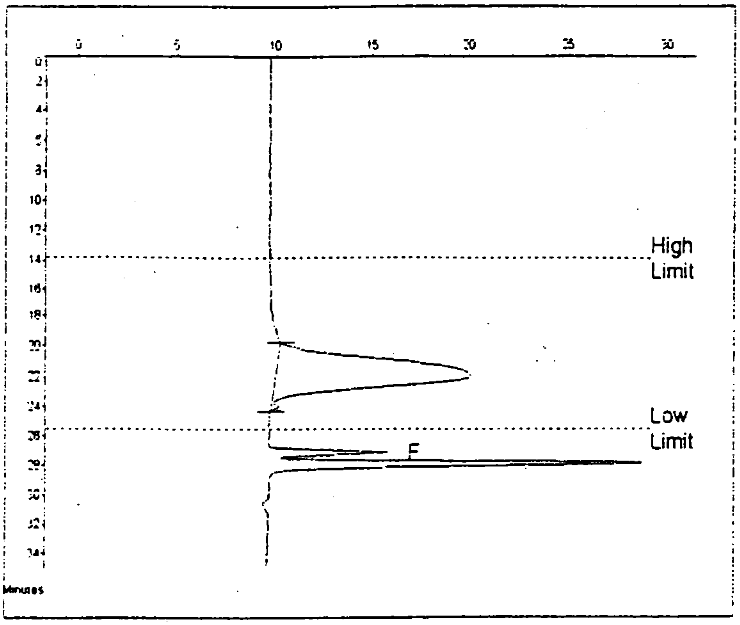
Appendix 1.5.13 GPC trace of the fractionated m-PPV-DP (fraction 5).



Molecular Weight Averages

Mp =	2817	Mz =	3179
Mn =	2061	Mz+1 =	3832
Mw =	2583	Mv =	2501
Polydispersity =	1.253	Peak Area =	347285

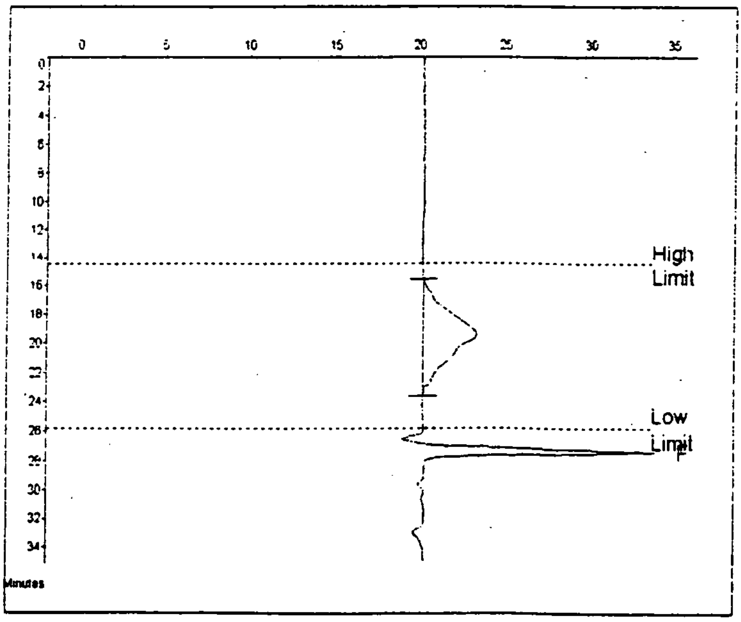
Appendix 1.5.14 GPC trace of the fractionated m-PPV-DP (fraction 9).



Molecular Weight Averages

Mp =	1475	Mz =	2340
Mn =	1398	Mz+1 =	2938
Mw =	1812	Mv =	1742
Polydispersity =	1.298	Peak Area =	245721

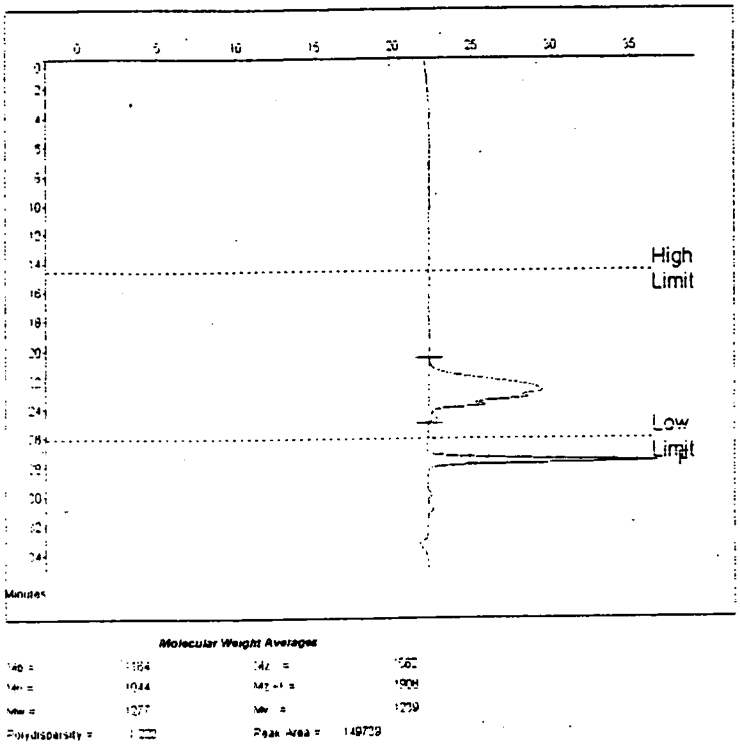
Appendix 1.5.15 GPC trace of the fractionated m-PPV-DP (fraction 11).



Molecular Weight Averages

Mp =	11828	Mz =	67669
Mn =	5569	Mz+1 =	136942
Mw =	20417	Mv =	16654
Polydispersity =	3.666	Peak Area =	130369

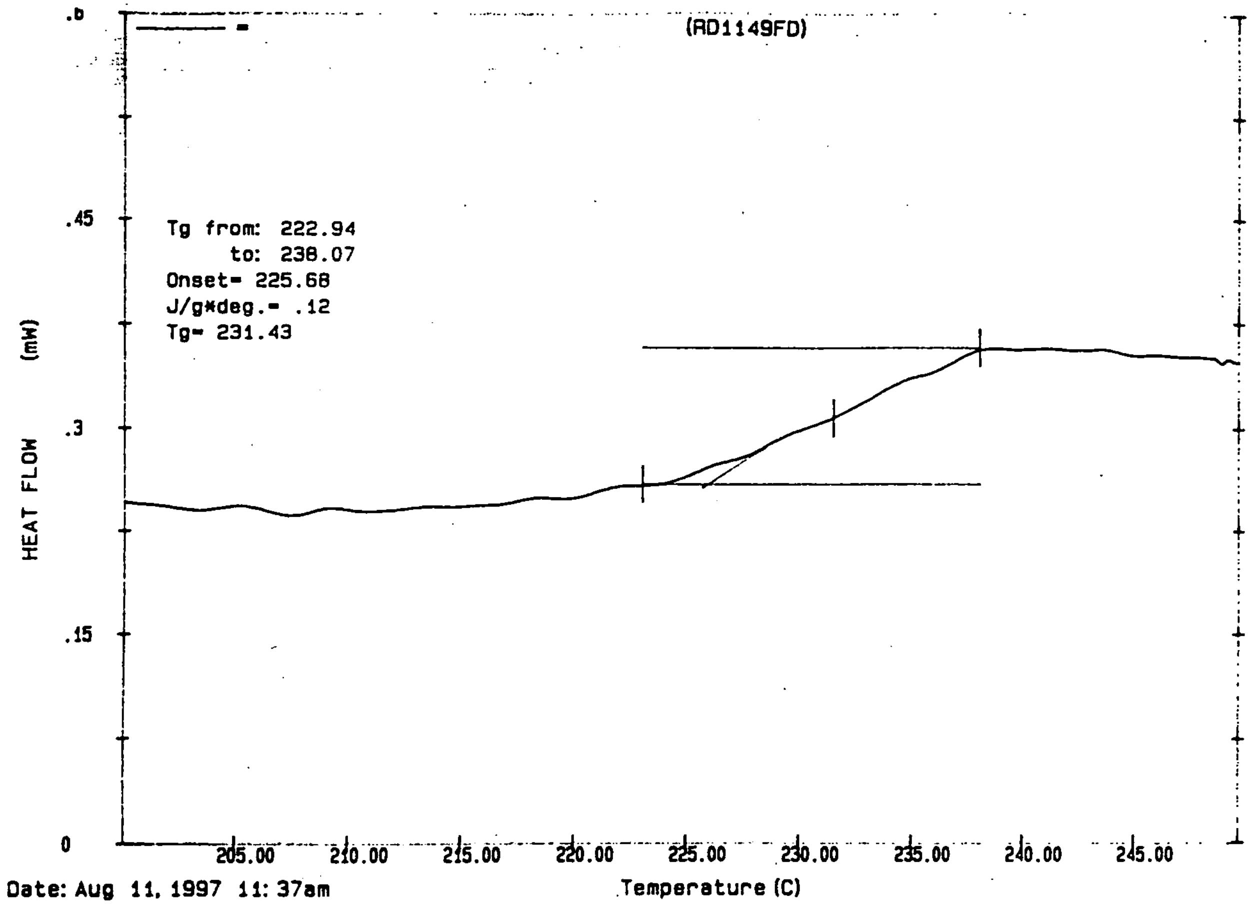
Appendix 1.5.16 A representative GPC trace of the as made PDPV-DF.



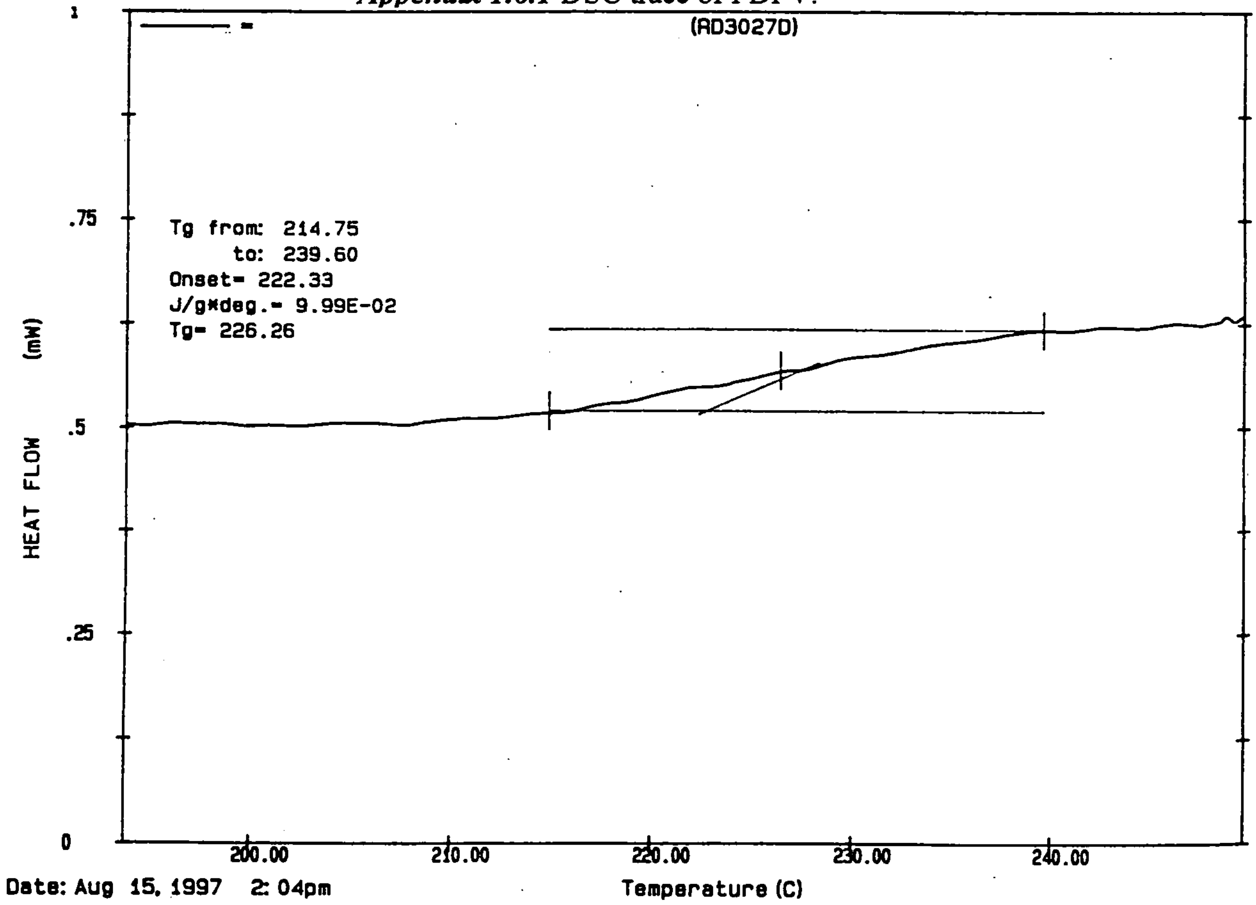
Molecular Weight Averages

Mp =	1164	Mz =	[illegible]
Mn =	1044	Mz+1 =	1908
Mw =	1277	Mv =	1279
Polydispersity =	[illegible]	Peak Area =	149739

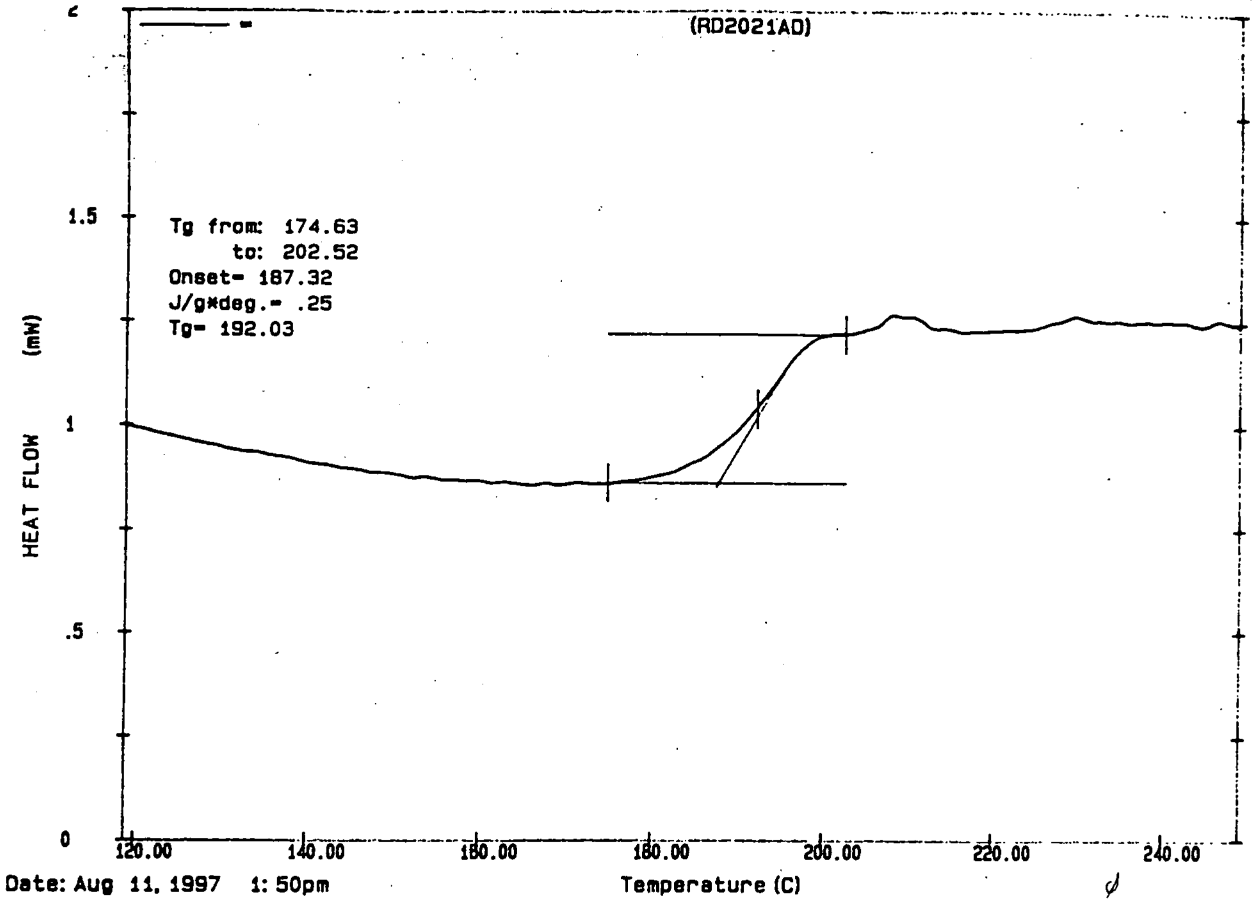
Appendix 1.5.17 A representative GPC trace of the as made m-PPV-DM.



Appendix 1.6.1 DSC trace of PDPV.



Appendix 1.6.2 DSC trace of PDPV-DF.



Appendix 1.6.3 DSC trace of m-PPV-DP.

Appendix 2 Analytical data for Chapter 3

Appendix 2.1 FTIR spectra

Appendix 2.2 ^{1}H Nmr spectra

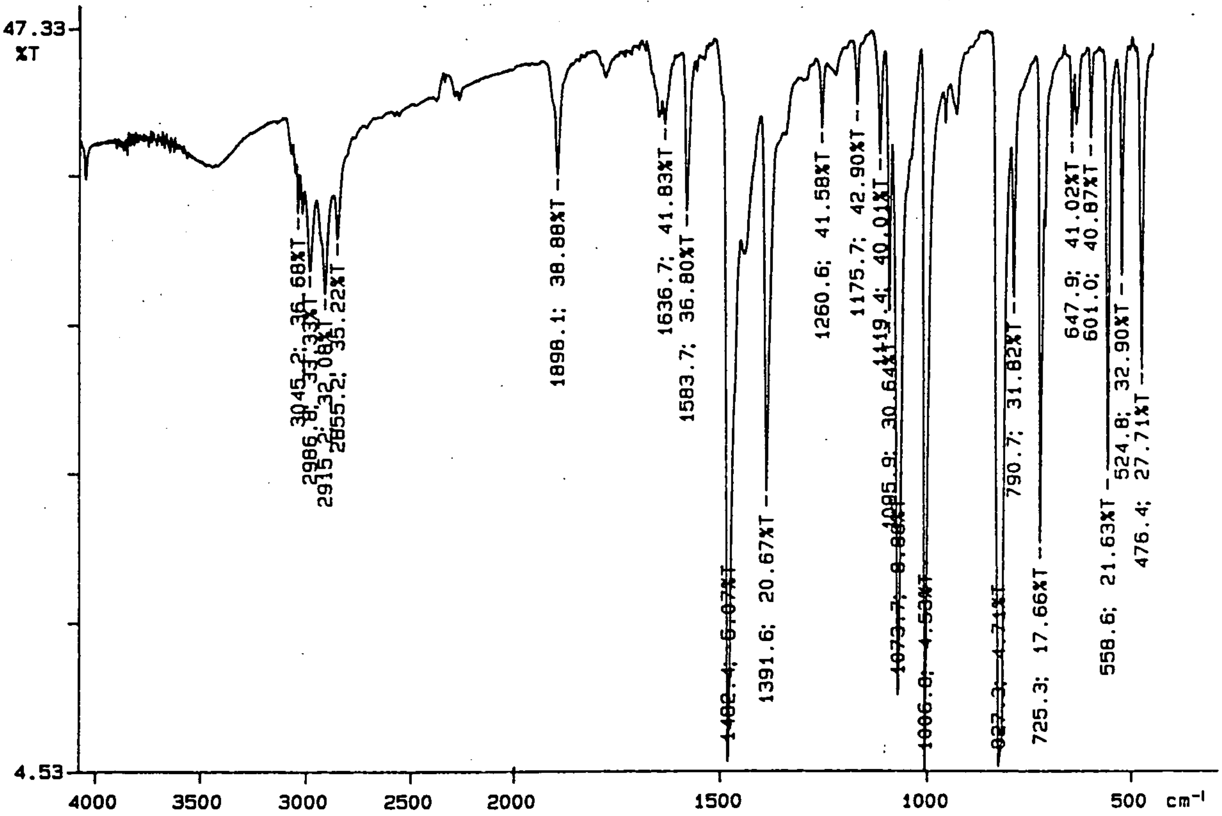
Appendix 2.3 ^{13}C Nmr spectra

Appendix 2.4 Mass spectra

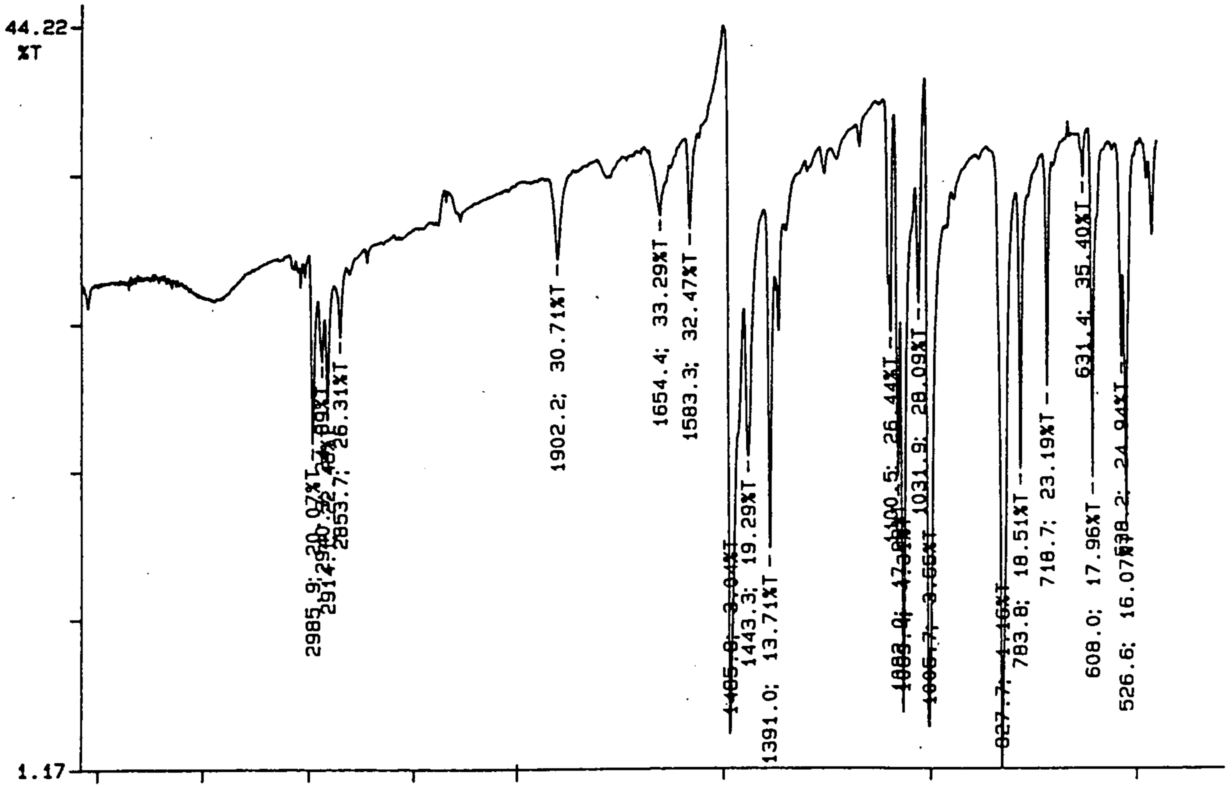
Appendix 2.5 GPC traces

Appendix 2.6 DSC traces

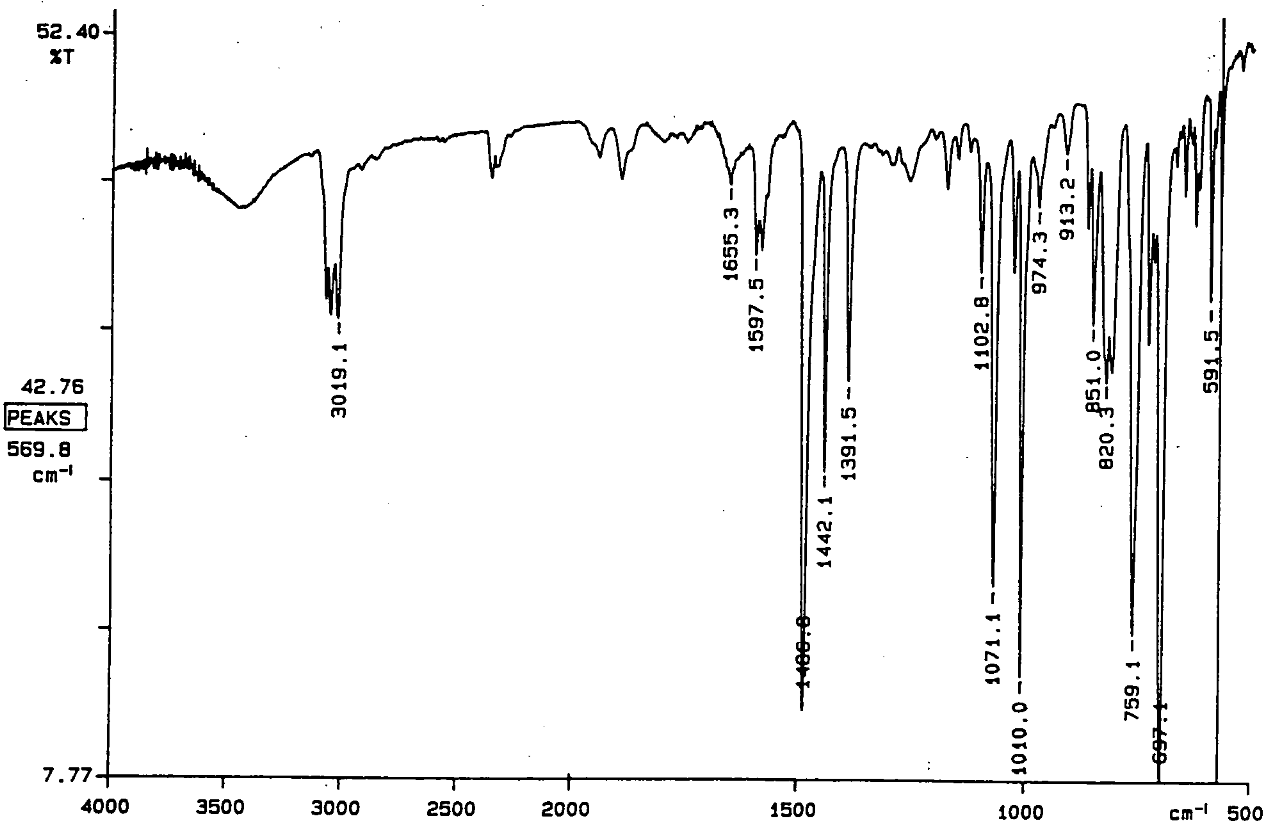
Appendix 2.7 Crystal structures



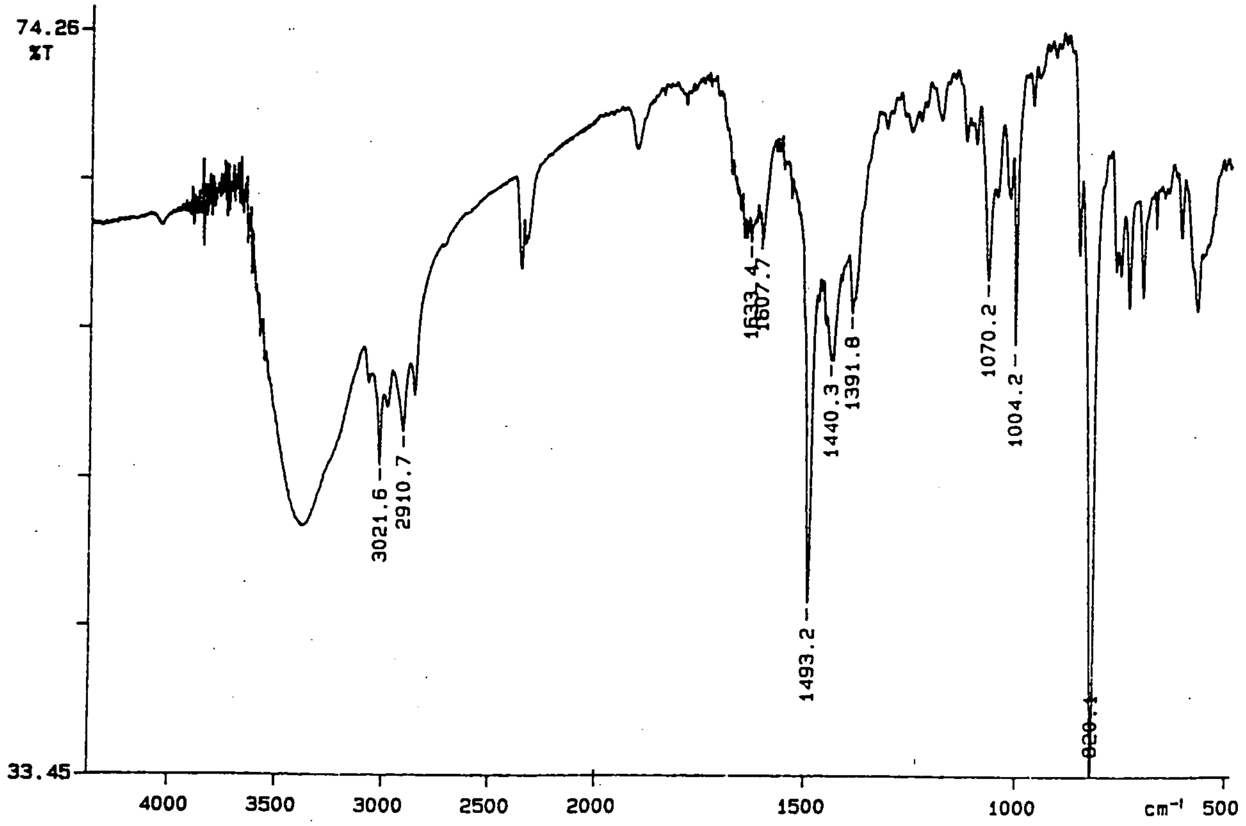
Appendix 2.1.1 FTIR spectrum of *cis*-2,3-di(4-bromophenyl)-2-butene.



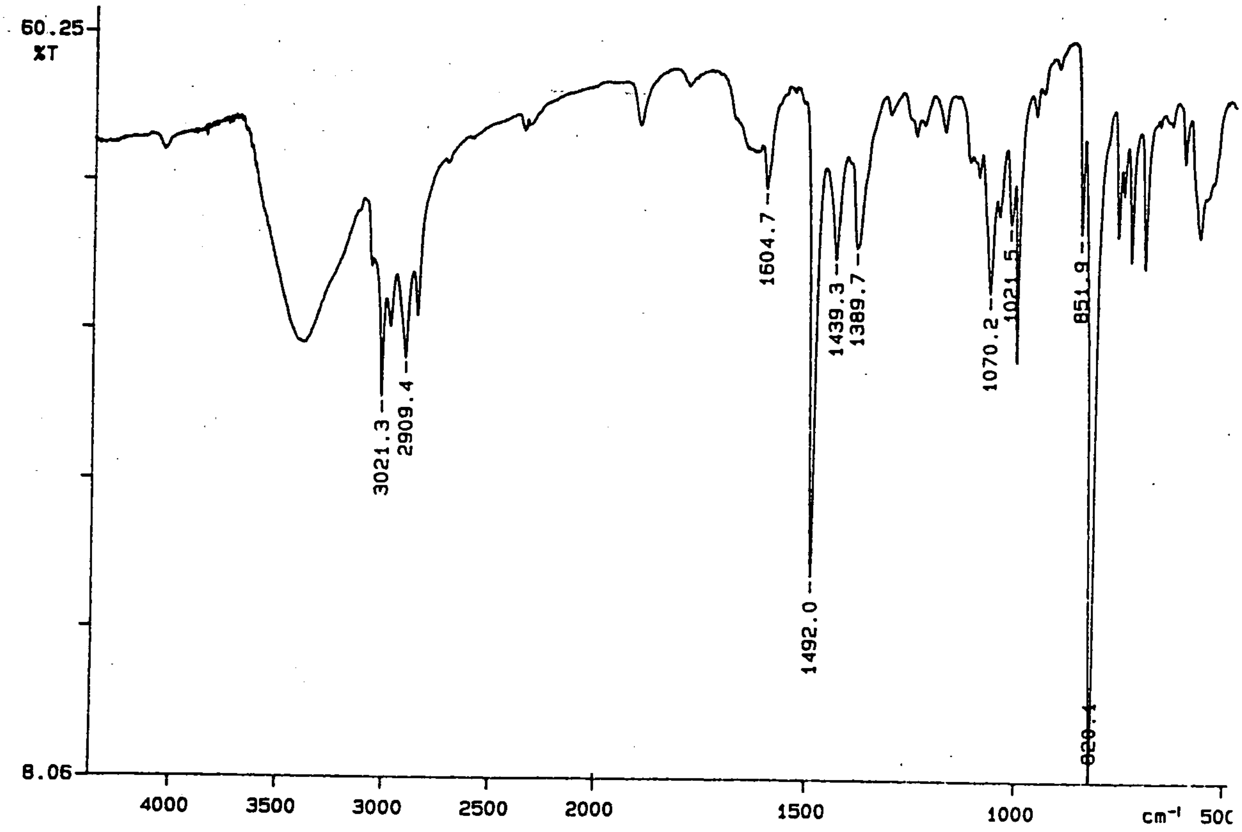
Appendix 2.1.2 FTIR spectrum of *trans*-2,3-di(4-bromophenyl)-2-butene.



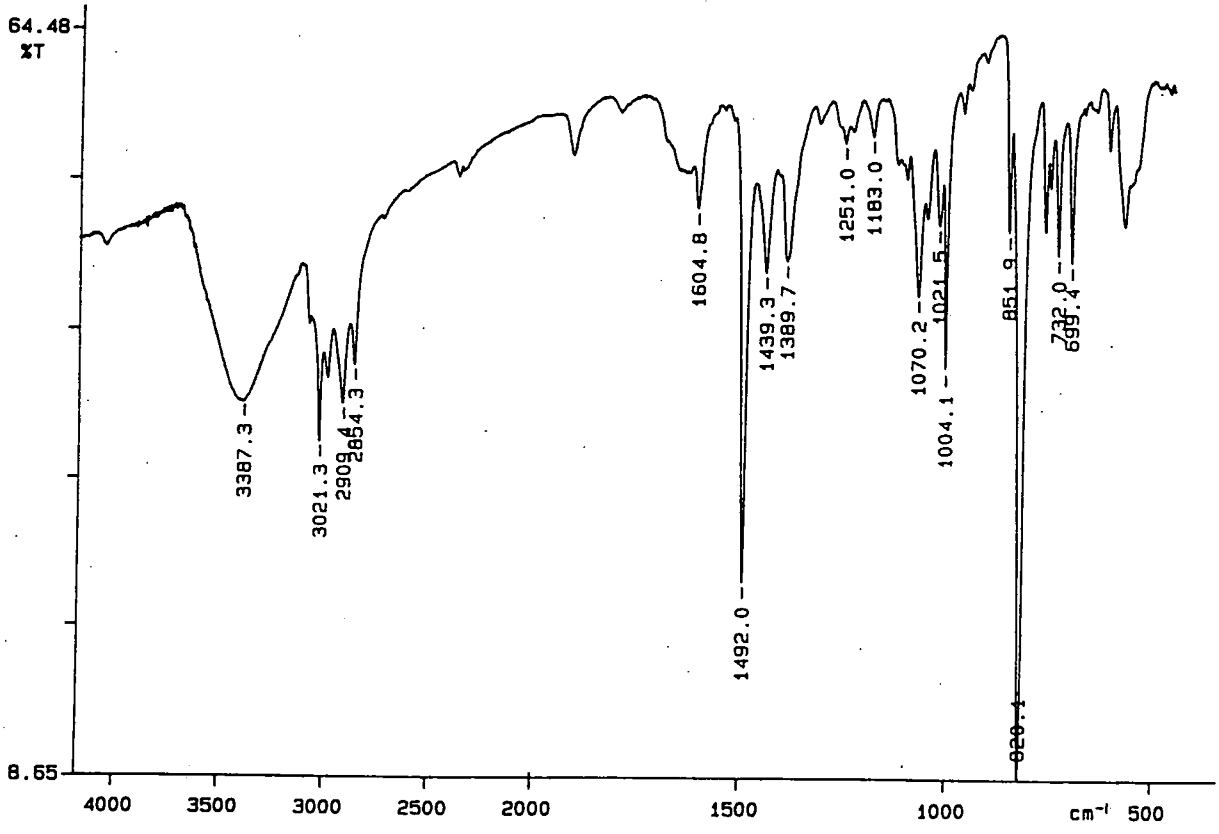
Appendix 2.1.3 FTIR spectrum of 1,2-di(4-bromophenyl)-1,2-diphenylethene.



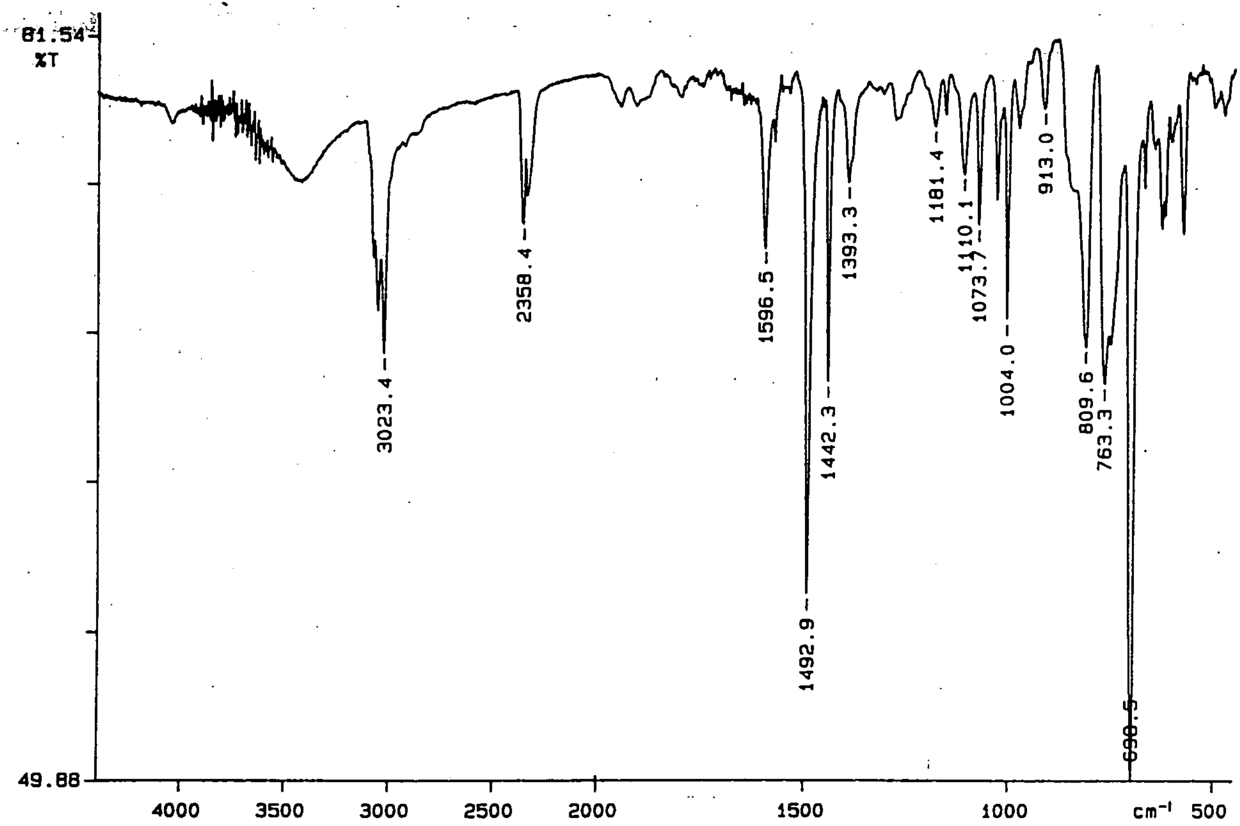
Appendix 2.1.4 FTIR spectrum of poly(4,4'-diphenylene dimethylvinylene) (100% *cis*).



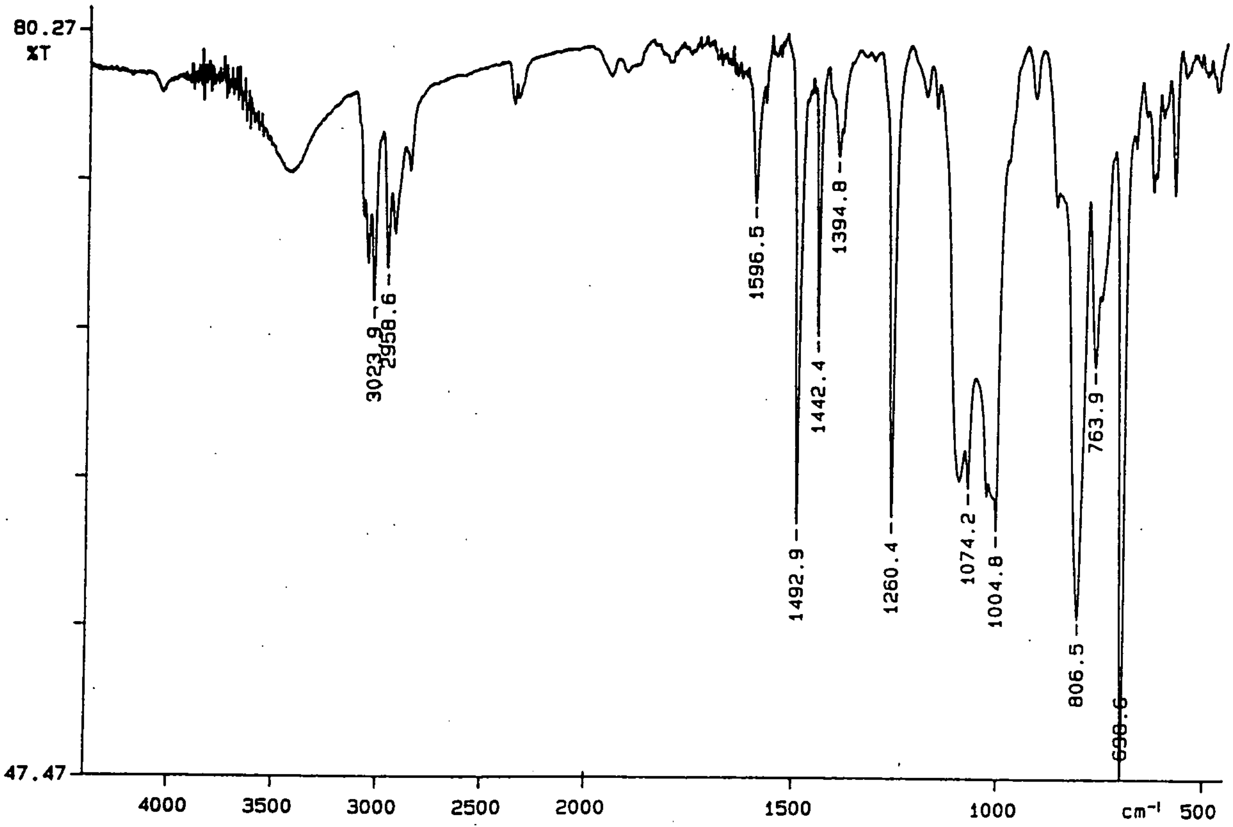
Appendix 2.1.5 FTIR spectrum of poly(4,4'-diphenylene dimethylvinylene) (90% *cis*).



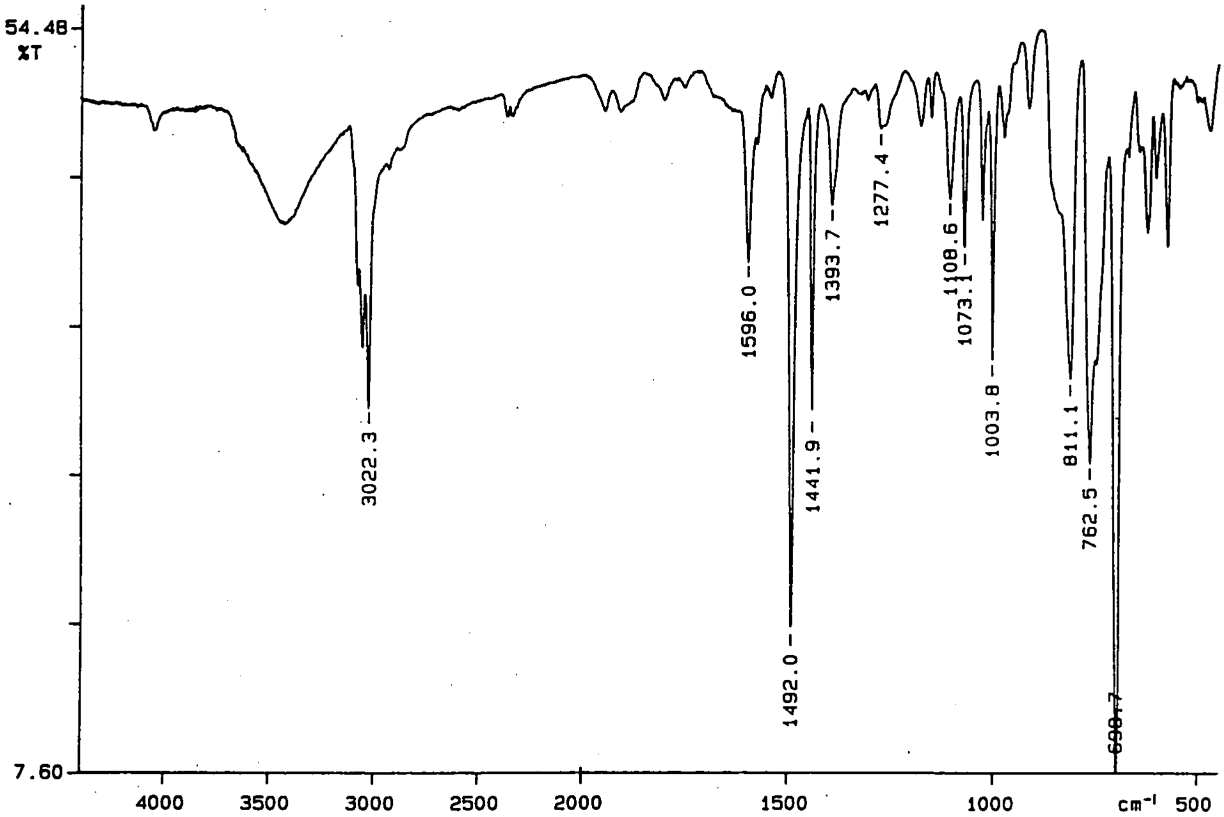
Appendix 2.1.6 FTIR spectrum of poly(4,4'-diphenylene dimethylvinylene) (80% *cis*).



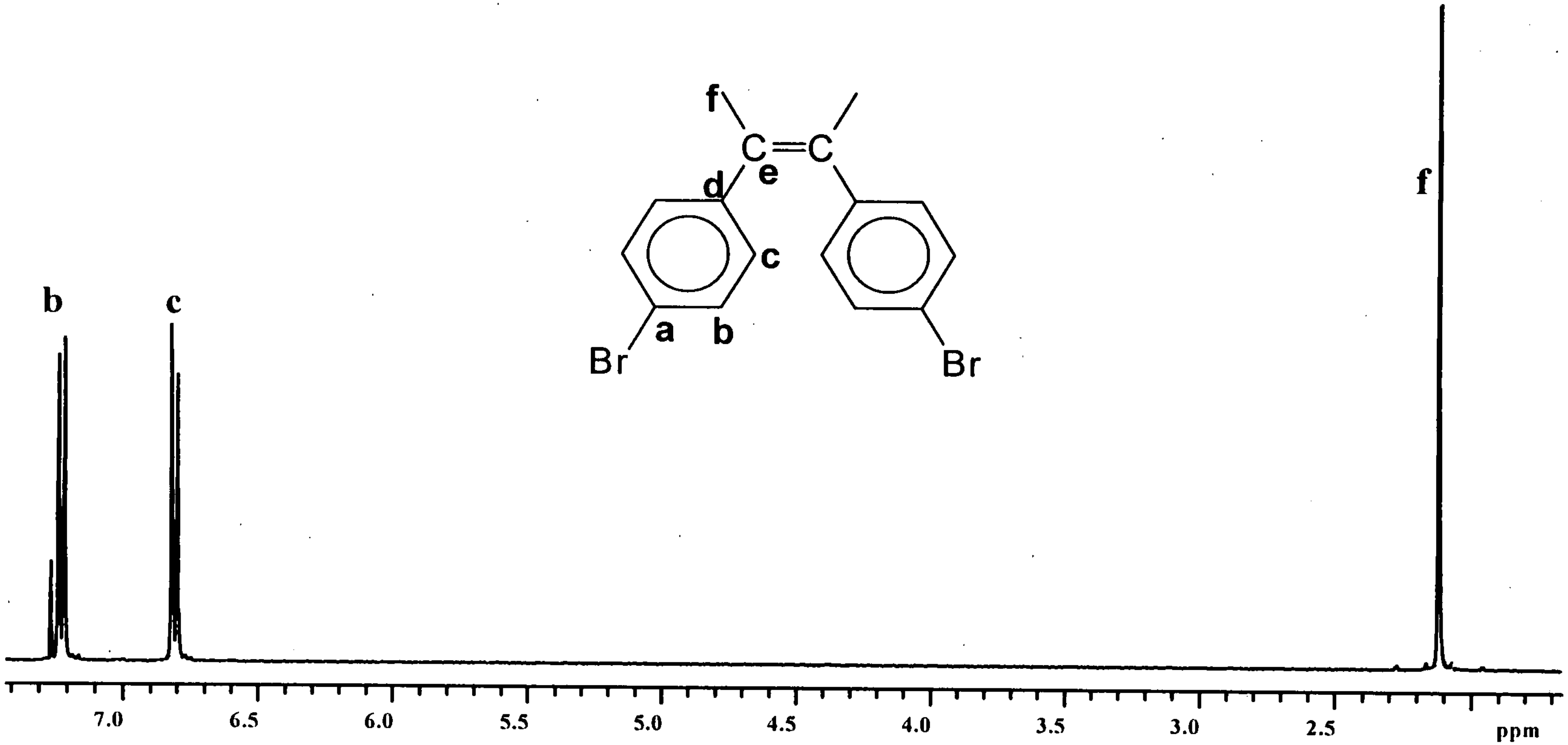
Appendix 2.1.7 FTIR spectrum of poly(4,4'-diphenylene diphenylvinylene) (59% *cis*).



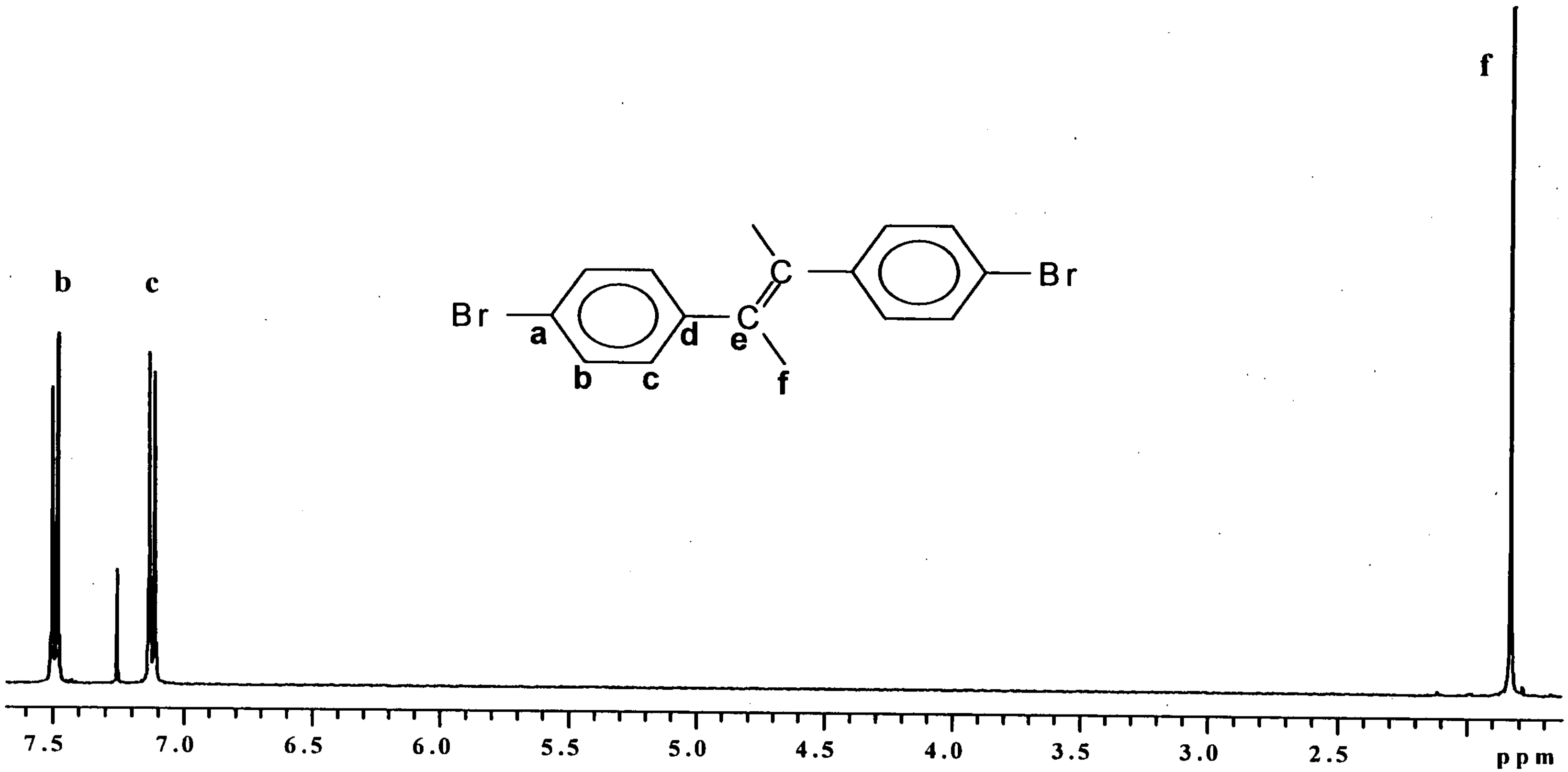
Appendix 2.1.8 FTIR spectrum of poly(4,4'-diphenylene diphenylvinylene) (48% *cis*)



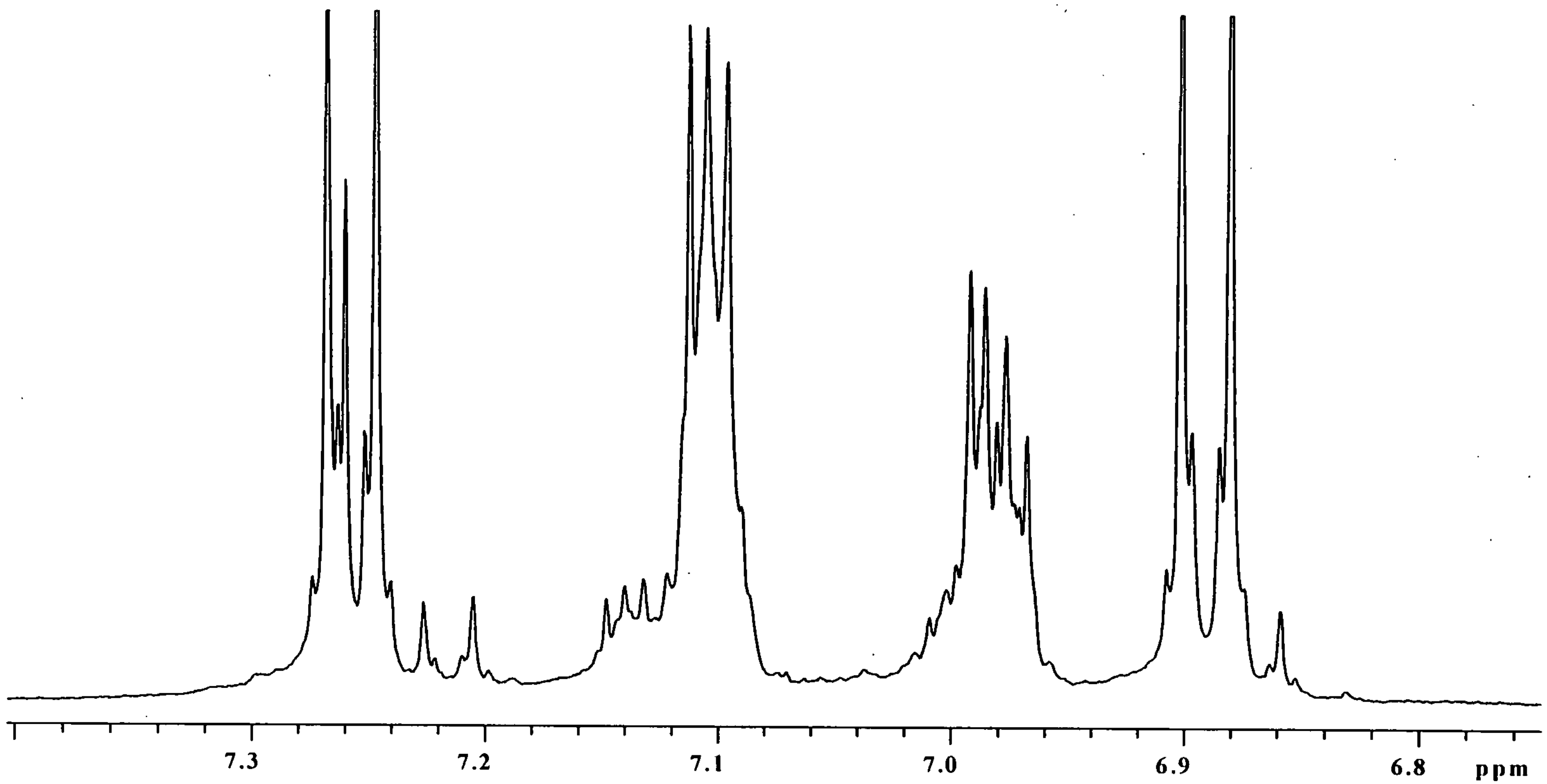
Appendix 2.1.9 FTIR spectrum of poly(4,4'-diphenylene diphenylvinylene) (37% *cis*).



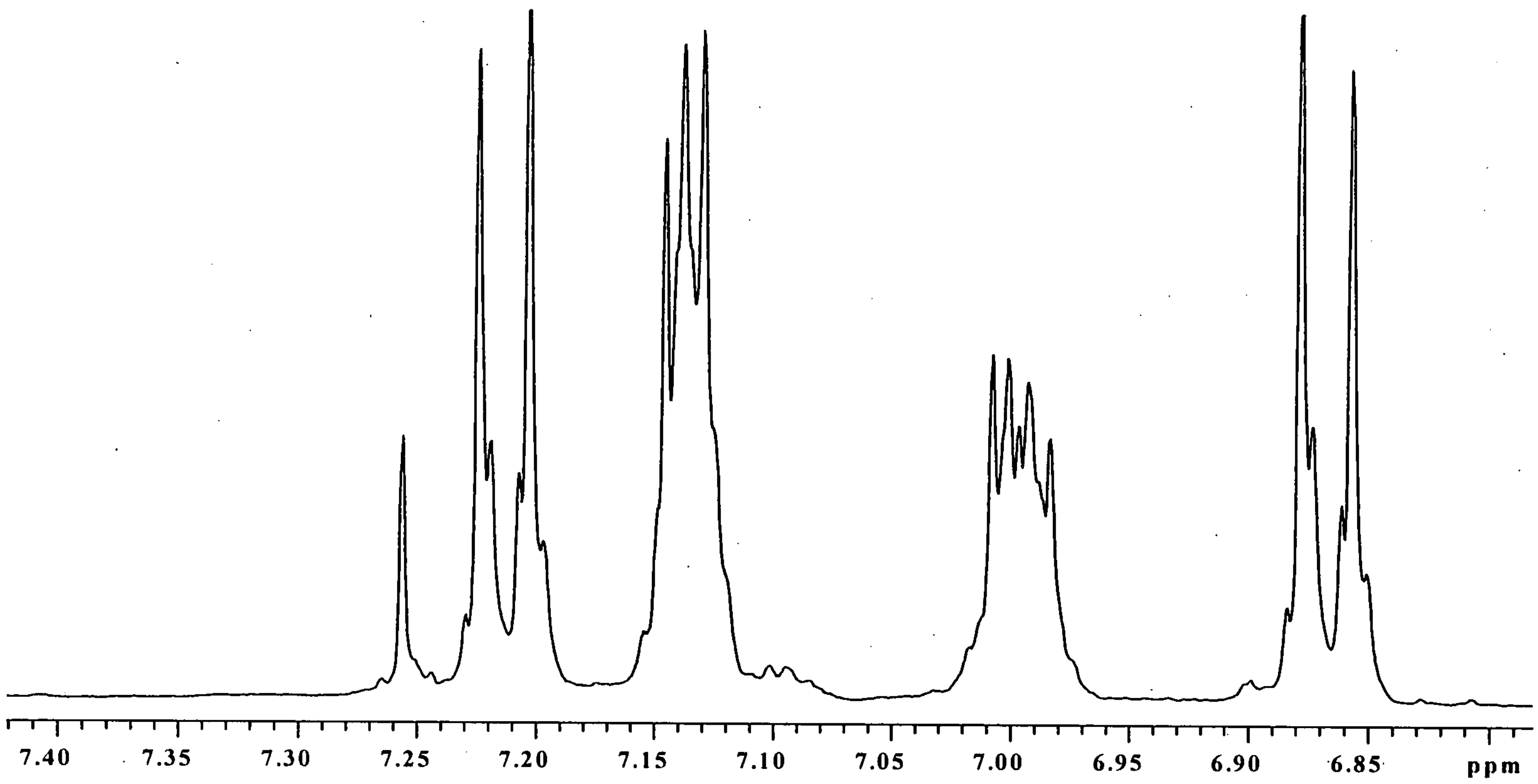
Appendix 2.2.1 ^{1}H Nmr spectrum of *cis*-2,3-di(4-bromophenyl)-2-butene.



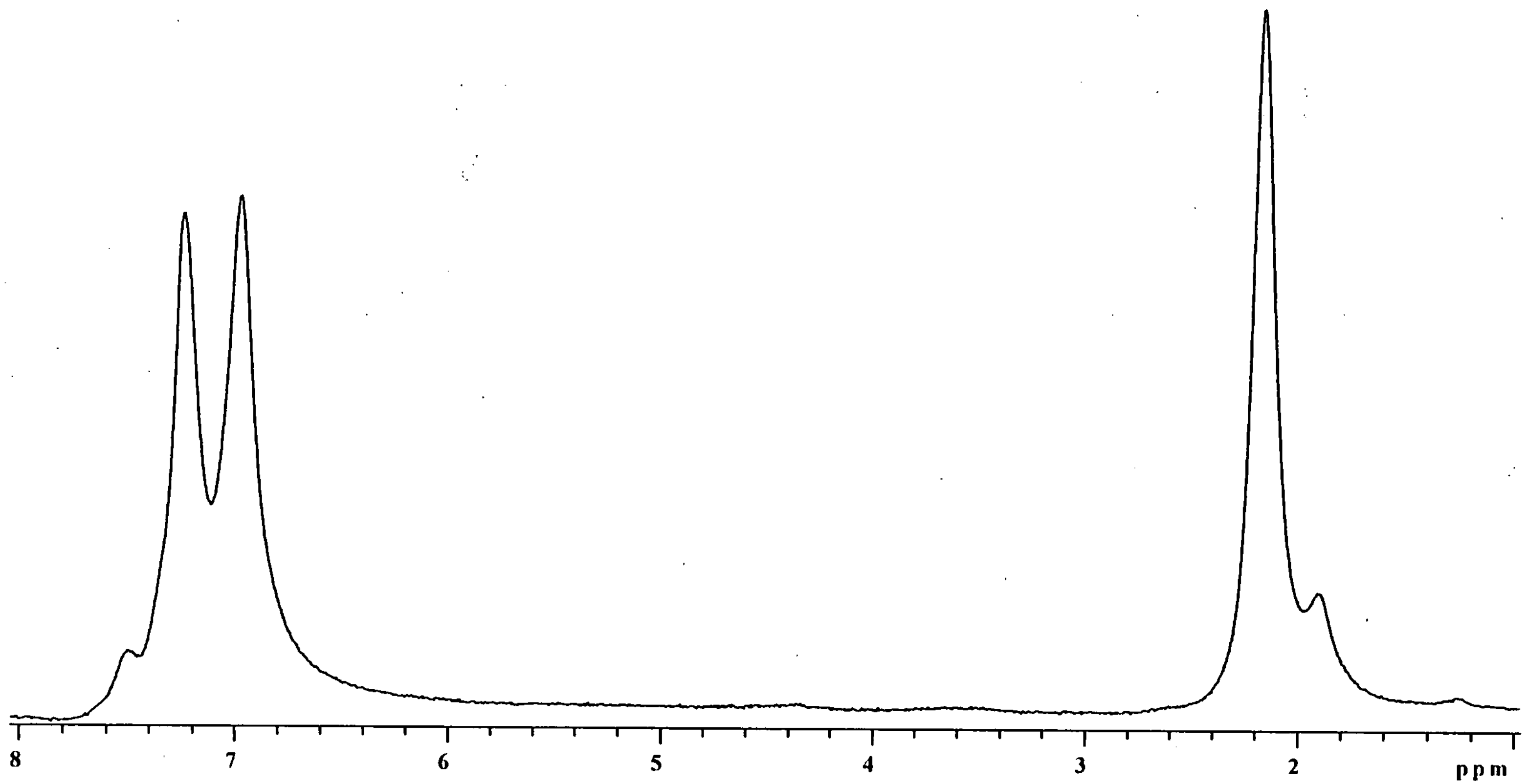
Appendix 2.2.2 ^{1}H Nmr spectrum of *trans*-2,3-di(4-bromophenyl)-2-butene.



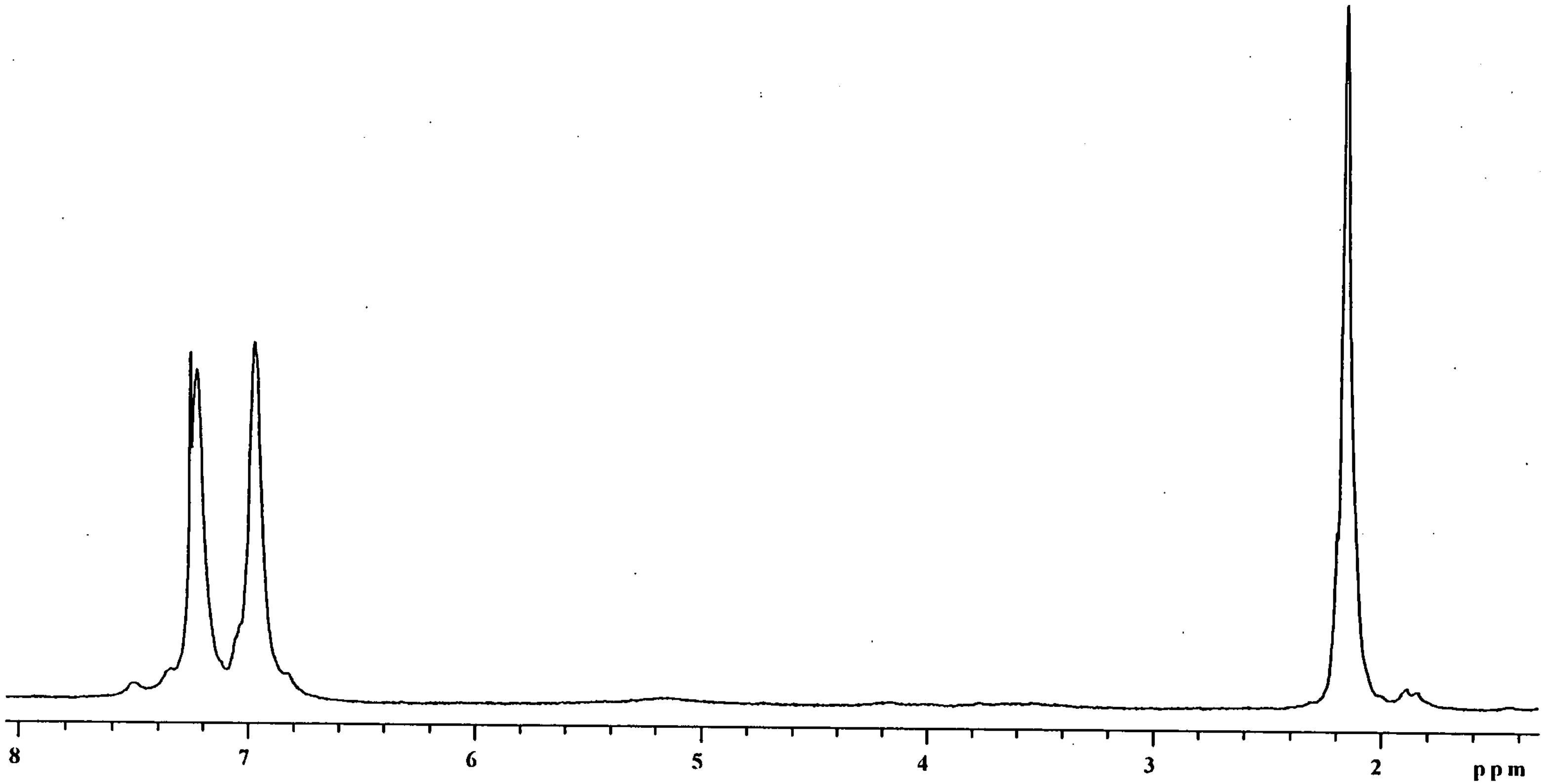
Appendix 2.2.3. ^{1}H Nmr spectrum of *cis*-1,2-di(4-bromophenyl)-1,2-diphenylethene.



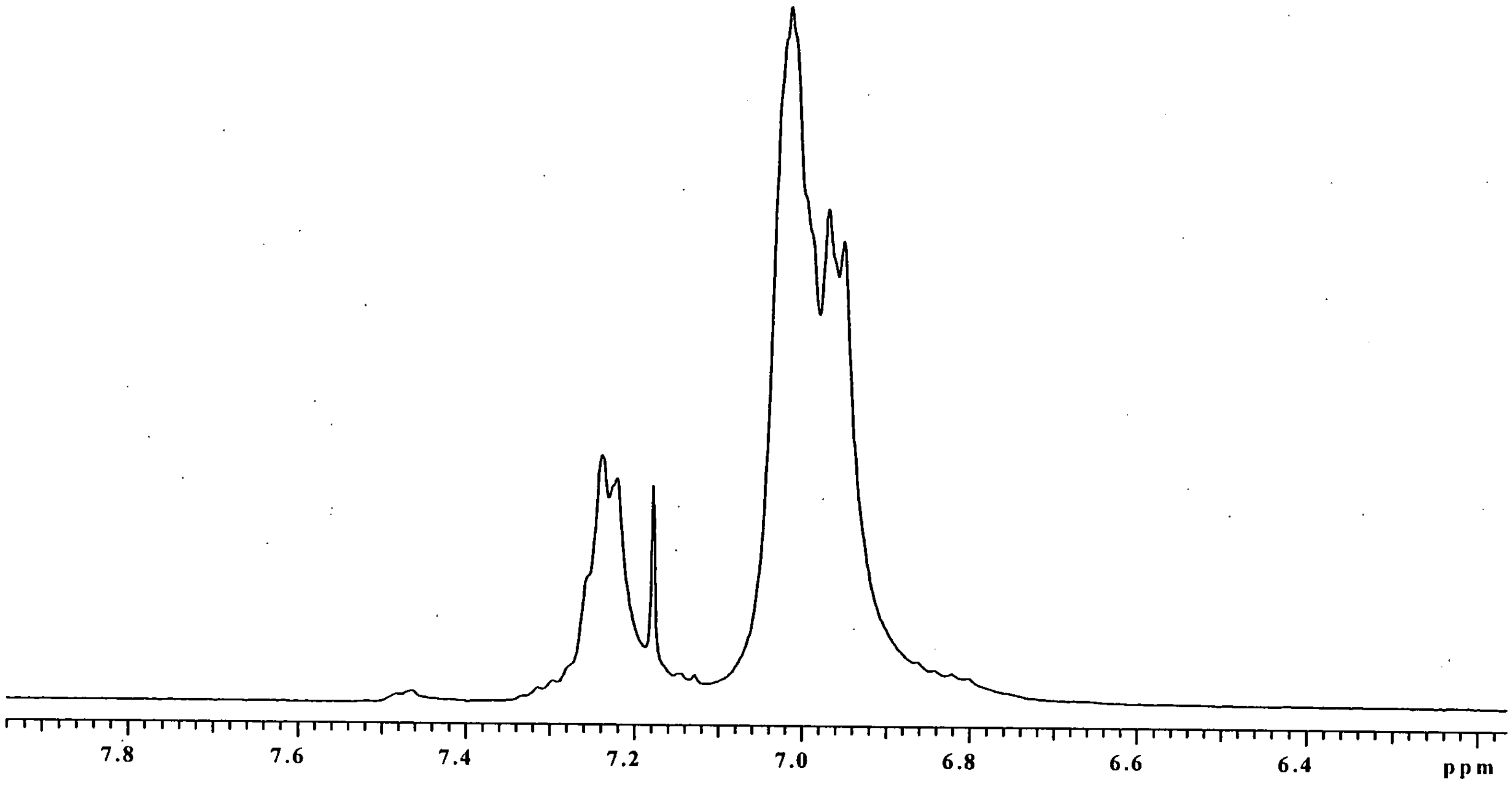
Appendix 2.2.4. ^{1}H Nmr spectrum of *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene.



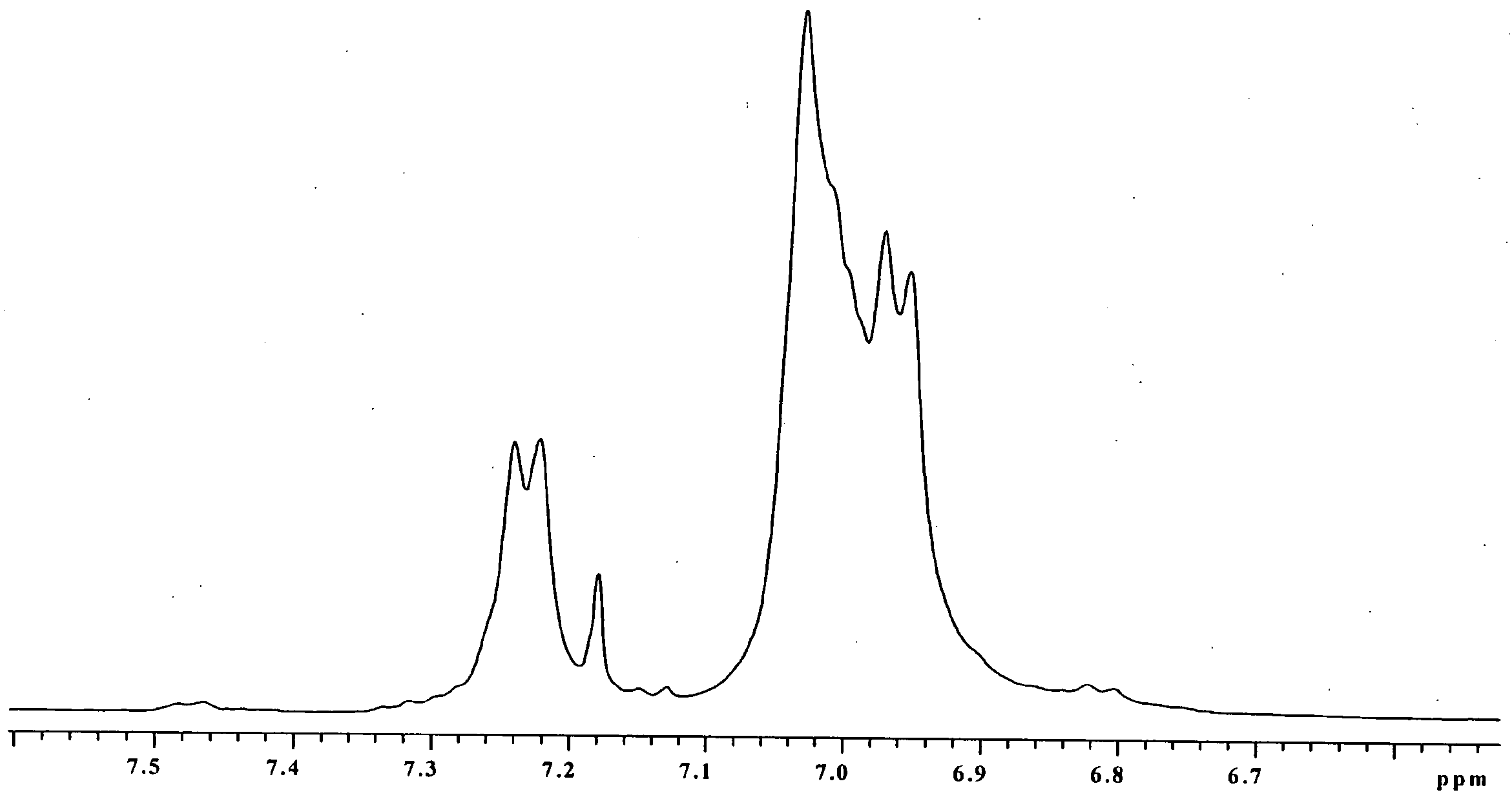
Appendix 2.2.5. ^{1}H Nmr spectrum of poly(4,4'-diphenylene dimethylvinylene) (90% *cis*).



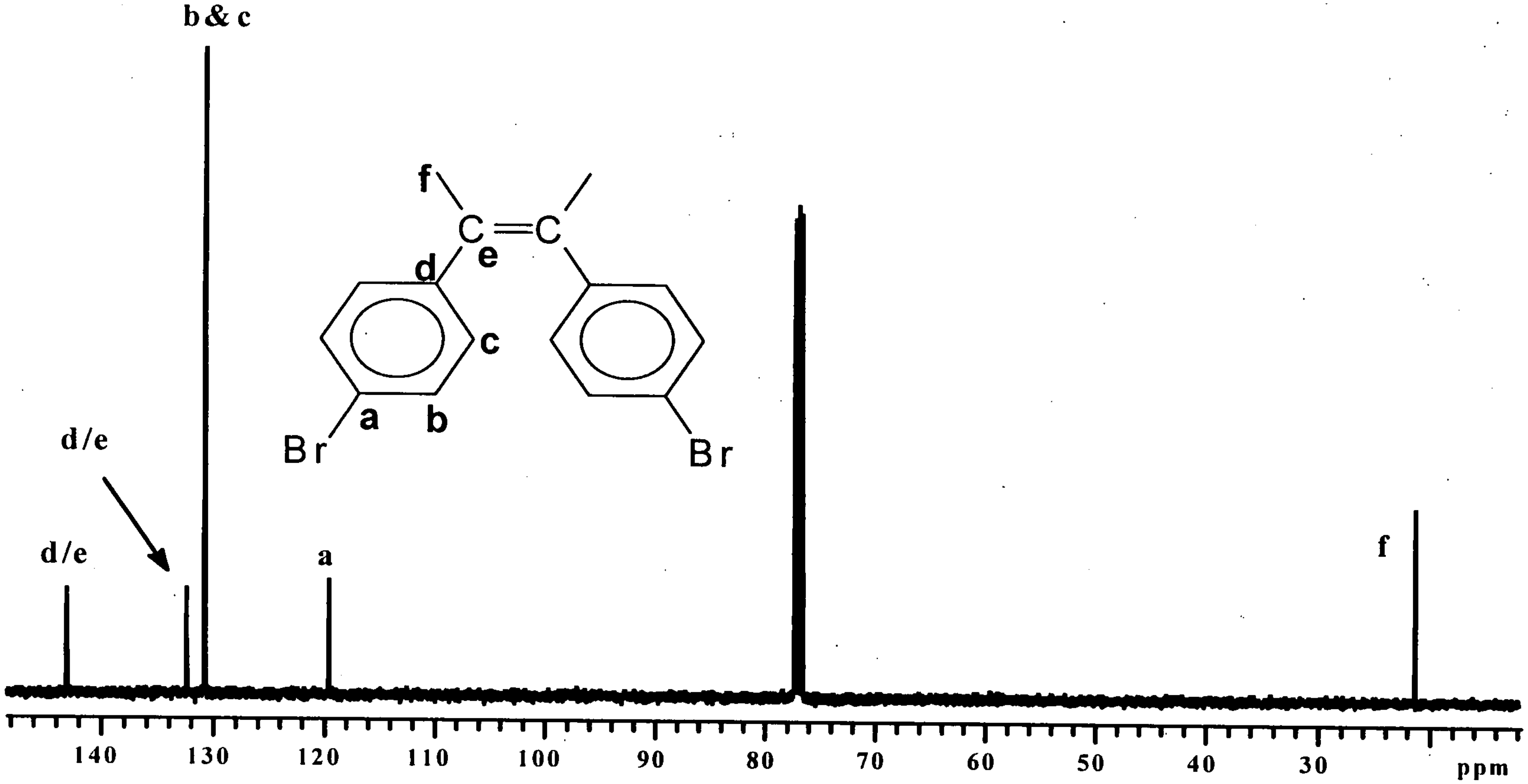
Appendix 2.2.6. ^{1}H Nmr spectrum of poly(4,4'-diphenylene dimethylvinylene) (100% *cis*).



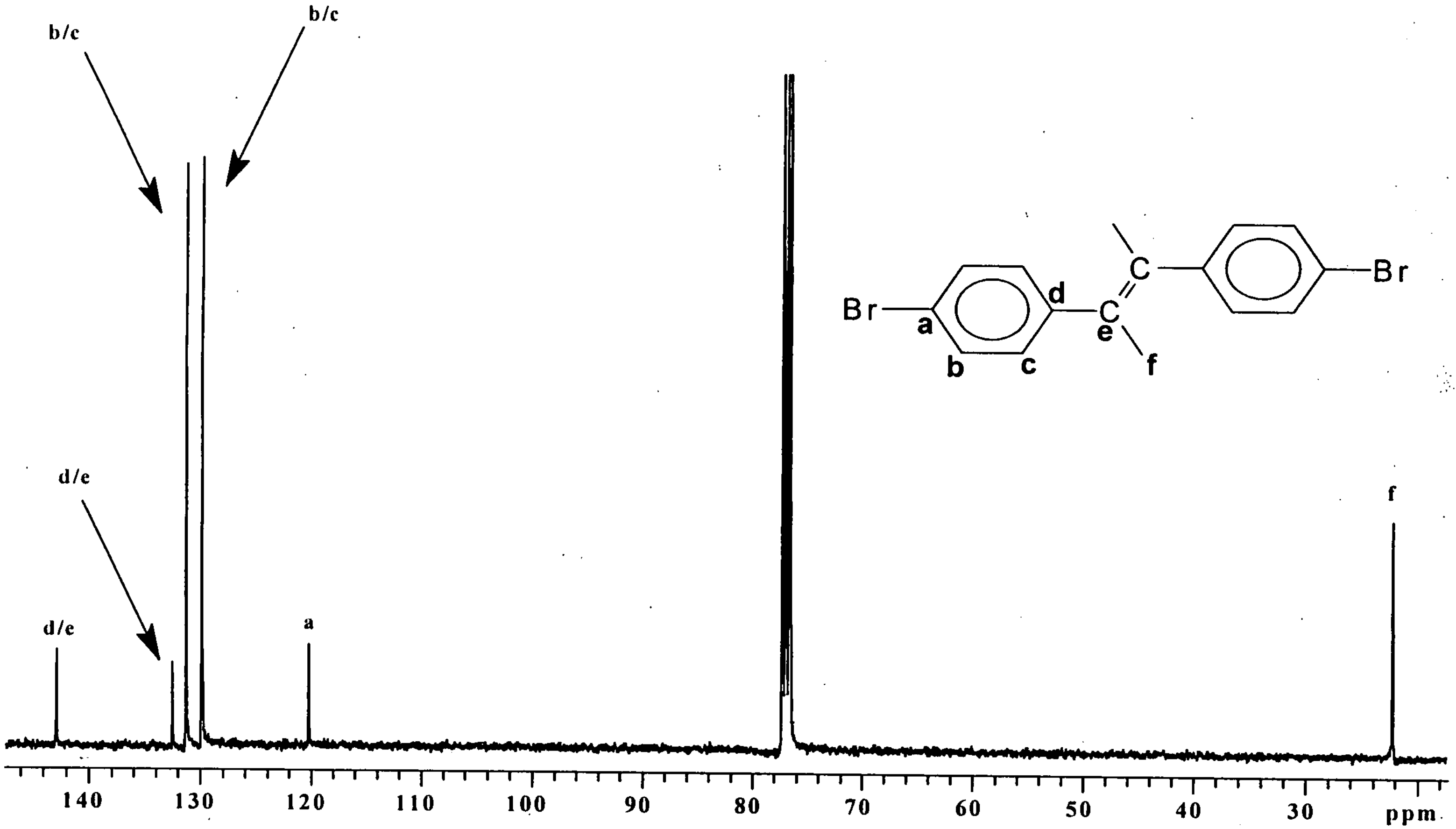
Appendix 2.2.7. ^{1}H Nmr spectrum of poly(4,4'-diphenylene diphenylvinylene) (59% *cis*).



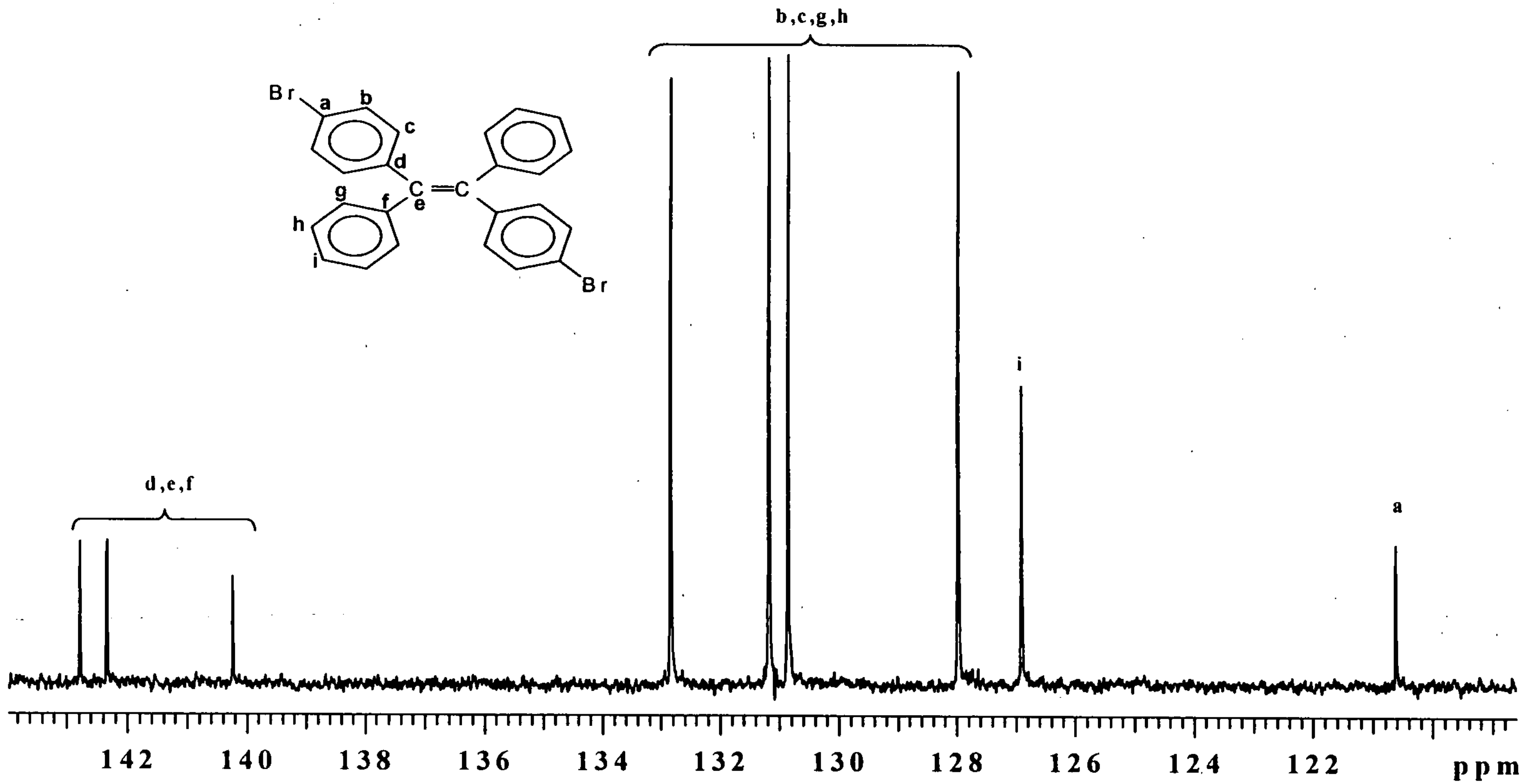
Appendix 2.2.8. ^{1}H Nmr spectrum of poly(4,4'-diphenylene diphenylvinylene) (37% *cis*).



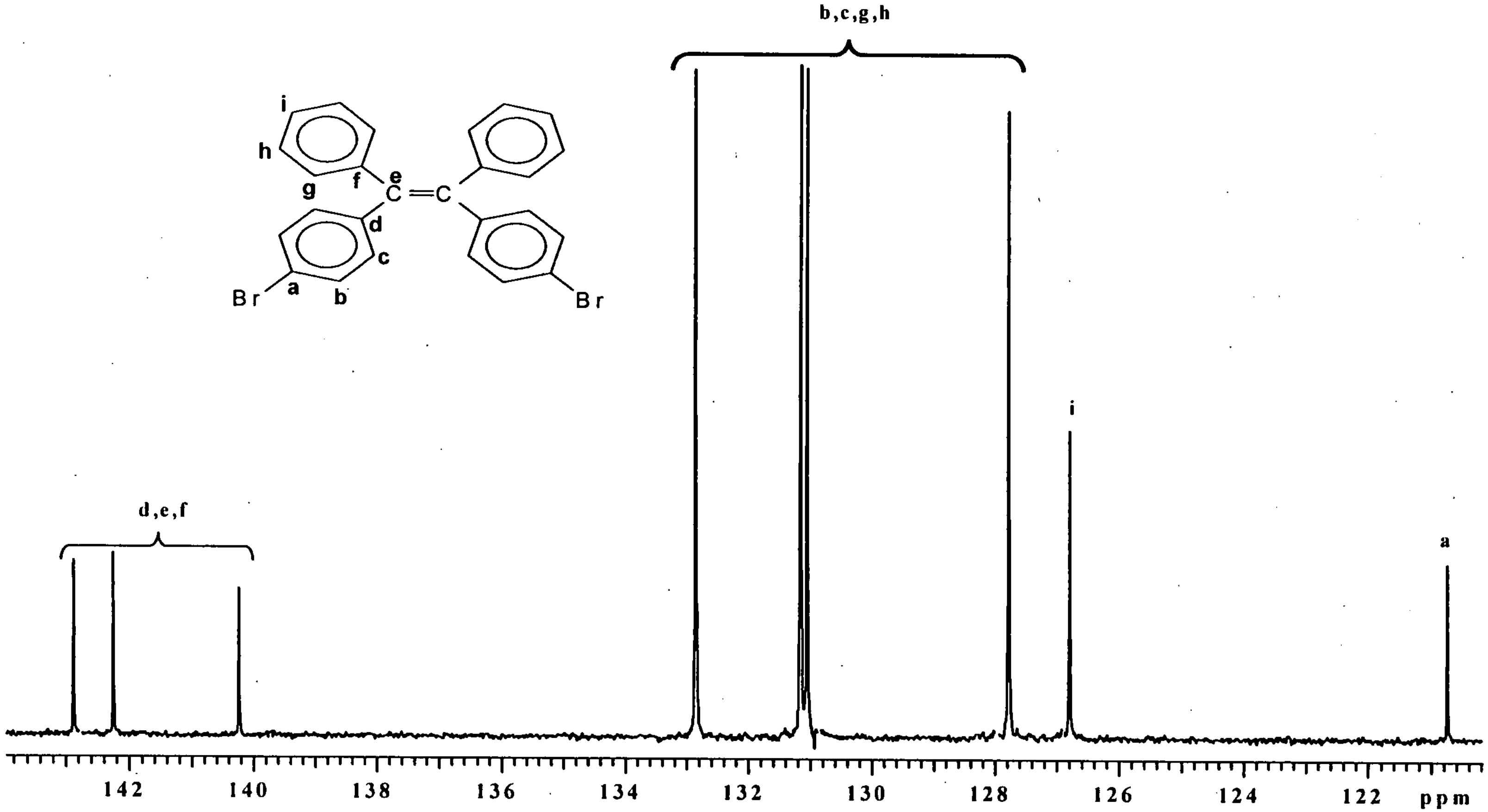
Appendix 2.3.1. ^{13}C Nmr spectrum of *cis*-2,3-di(4-bromophenyl)-2-butene.



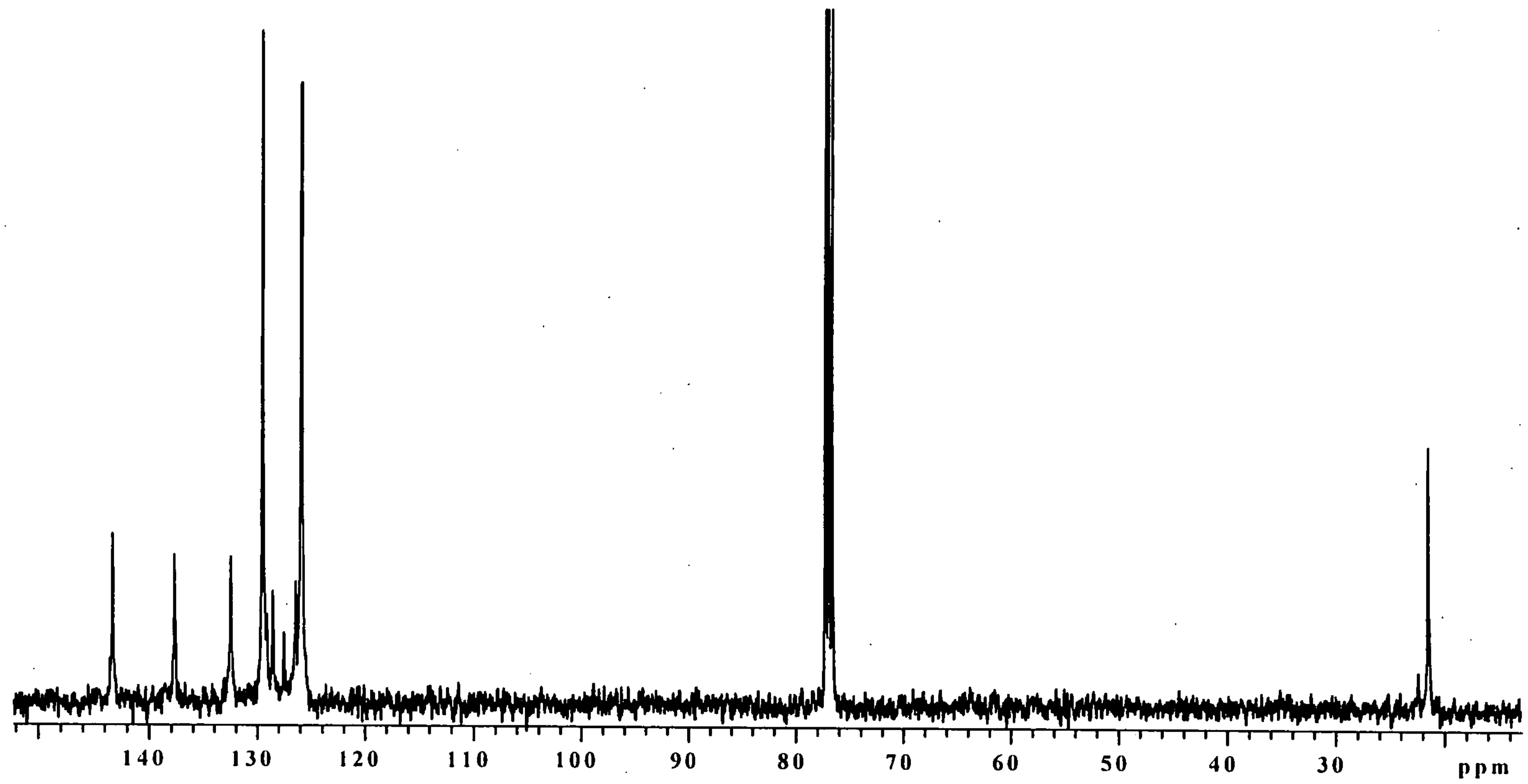
Appendix 2.3.2. ^{13}C Nmr spectrum of *trans*-2,3-di(4-bromophenyl)-2-butene



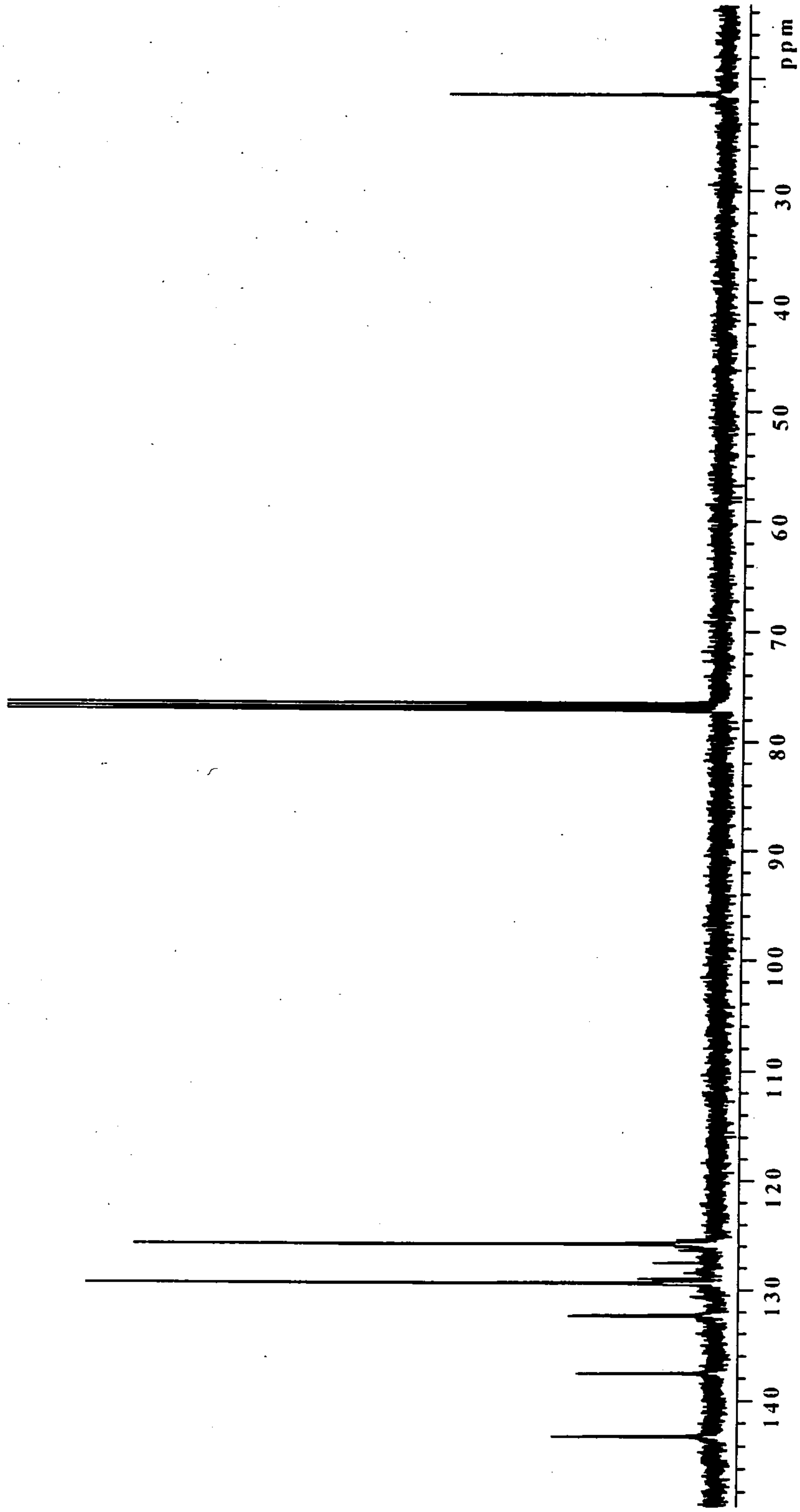
Appendix 2.3.3. ^{13}C Nmr spectrum of *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene.



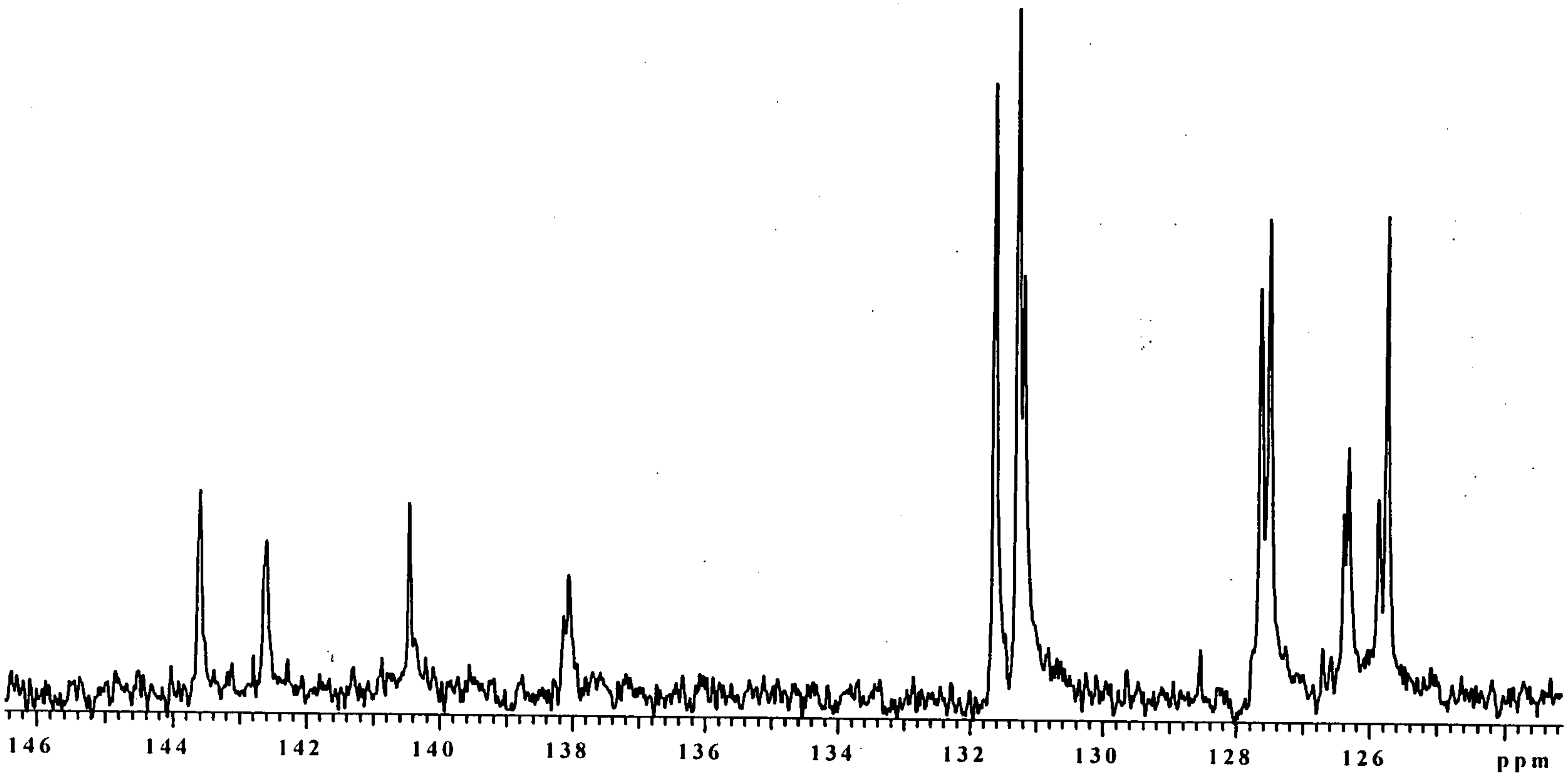
Appendix 2.3.4. ^{13}C Nmr spectrum of *cis*-1,2-di(4-bromophenyl)-1,2-diphenylethene.



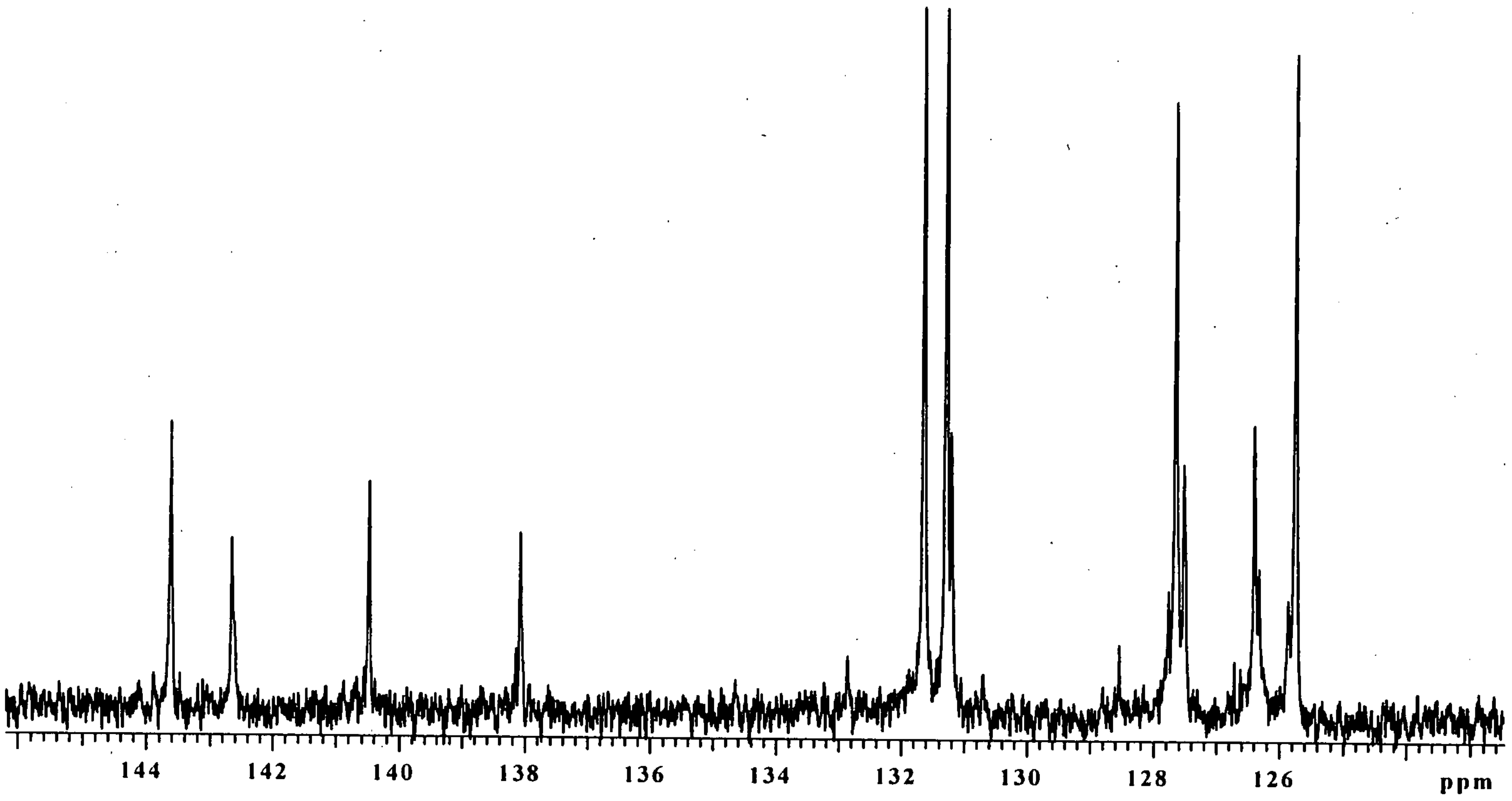
Appendix 2.3.5. ^{13}C Nmr spectrum of poly(4,4'di-phenylene dimethylvinylene) (90% *cis*).



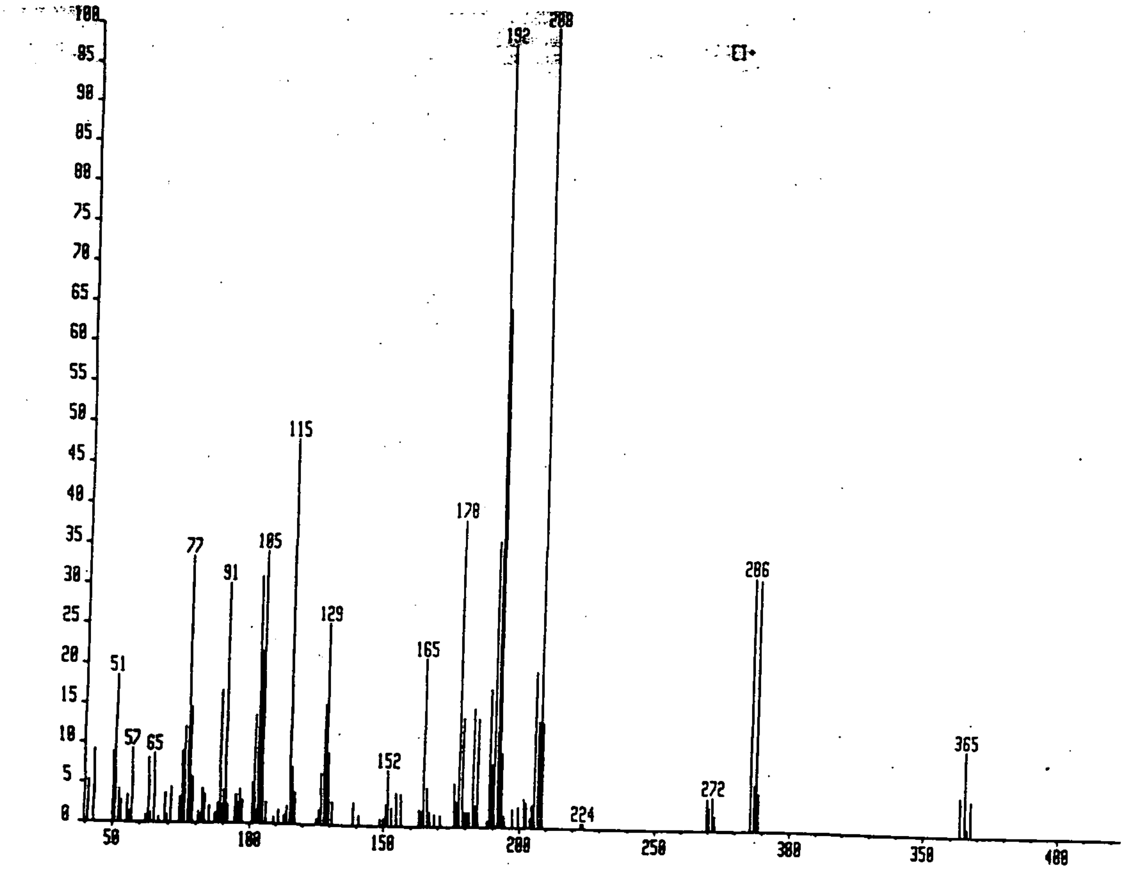
Appendix 2.3.6. ^{13}C Nmr spectrum of poly(4,4'di-phenylene dimethylvinylene) (100% *cis*).



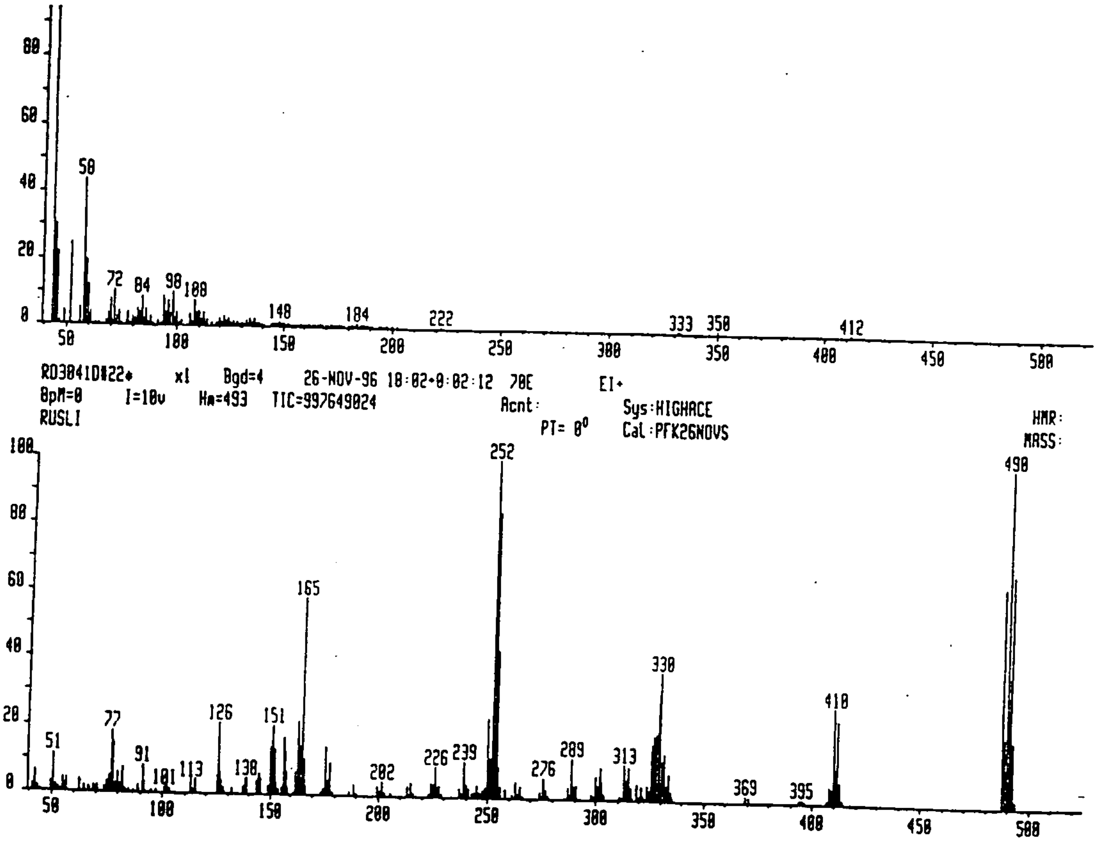
Appendix 2.3.7. ^{13}C Nmr spectrum of poly(4,4'di-phenylene diphenylvinylene) (59% *cis*).



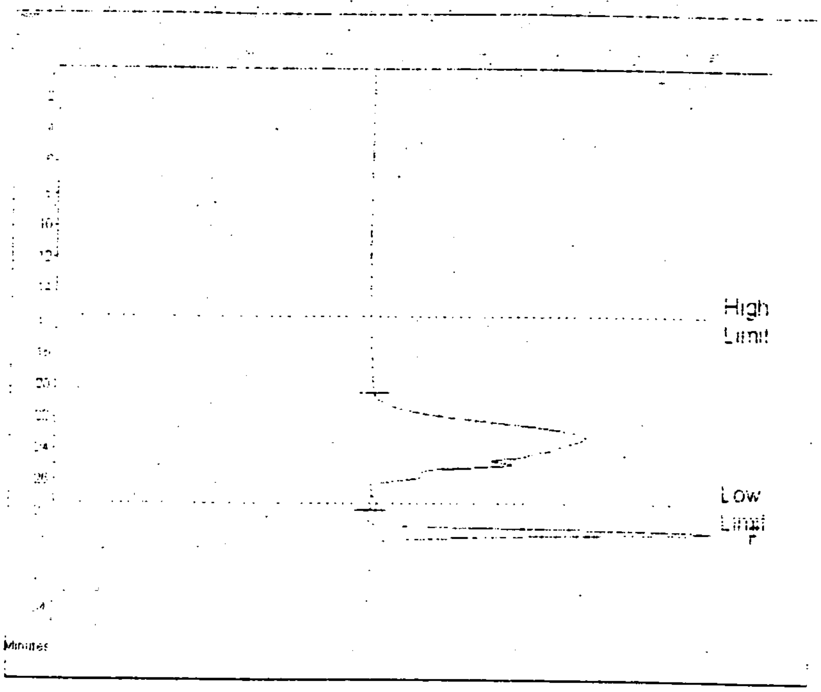
Appendix 2.3.8. ^{13}C Nmr spectrum of poly(4,4’di-phenylene diphenylvinylene) (37% *cis*).



Appendix 2.4.1 Mass spectrum of *trans*-2,3-di(4-bromophenyl)-2-butene.



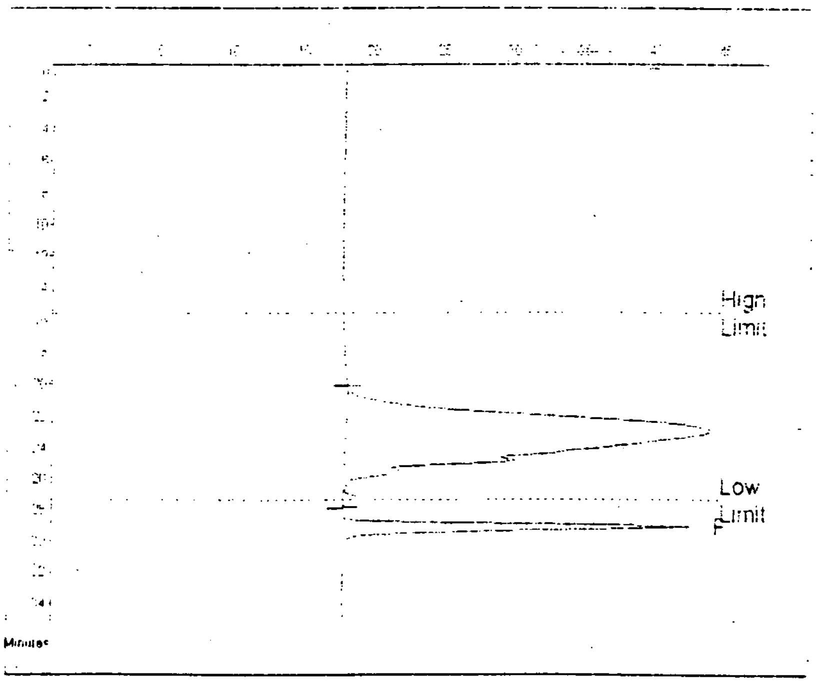
Appendix 2.4.2 Mass spectrum of *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene.



Molecular Weight Averages

Mp =	1826	Mz =	2819
Mn =	1076	Mz+1 =	4102
Mw =	1796	Mv =	1671
Polydispersity =	1.669	Peak Area =	483151

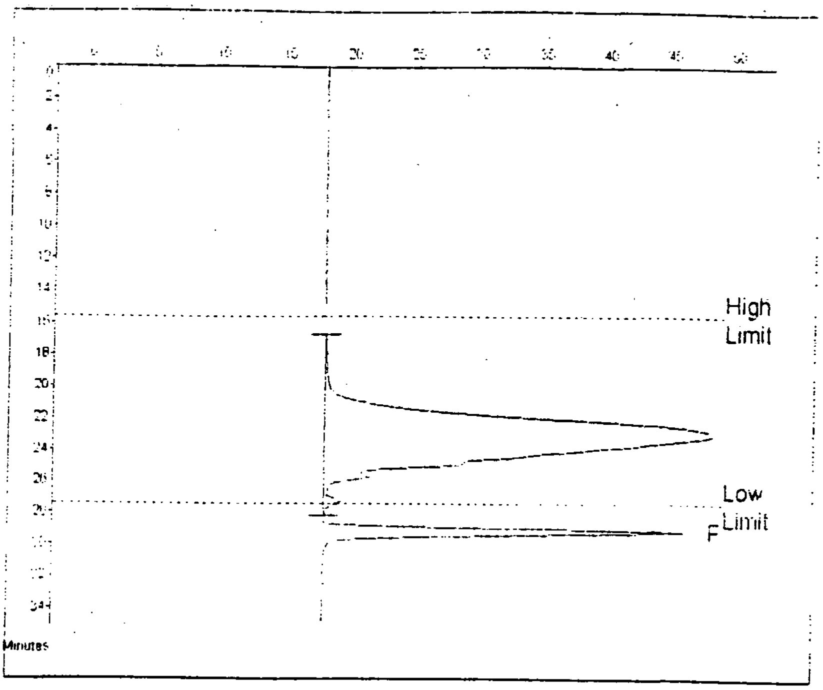
Appendix 2.5.1 GPC trace of PDMeV (100% *cis*, cat. B, 2 days).



Molecular Weight Averages

Mp =	2149	Mz =	3305
Mn =	1366	Mz+1 =	4532
Mw =	2109	Mv =	1970
Polydispersity =	1.544	Peak Area =	858297

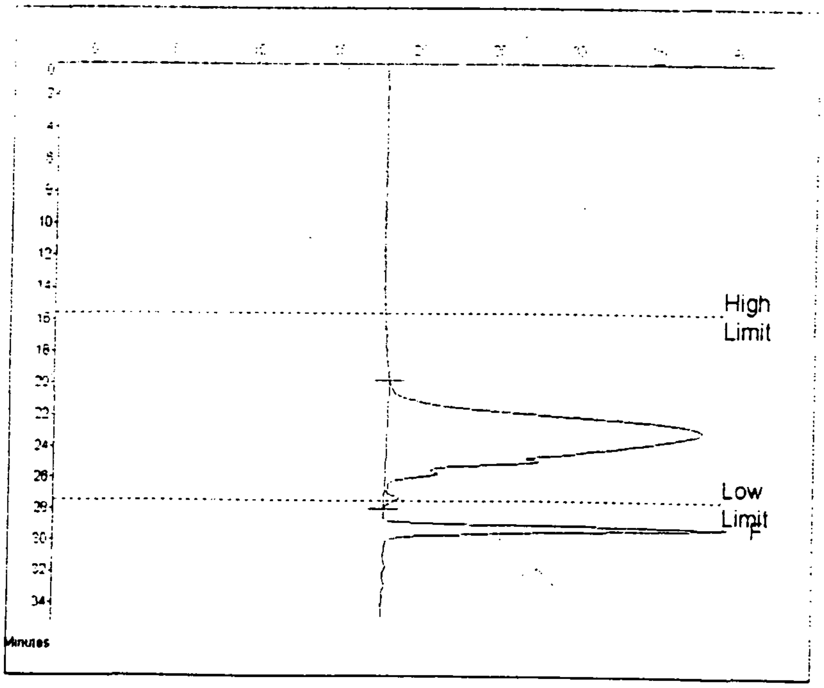
Appendix 2.5.2 GPC trace of PDMeV (90% *cis*, cat. B, 2 days).



Molecular Weight Averages

Mp =	2182	Mz =	10329
Mn =	1330	Mz+1 =	85368
Mw =	2479	Mv =	2217
Polydispersity =	1.864	Peak Area =	999026

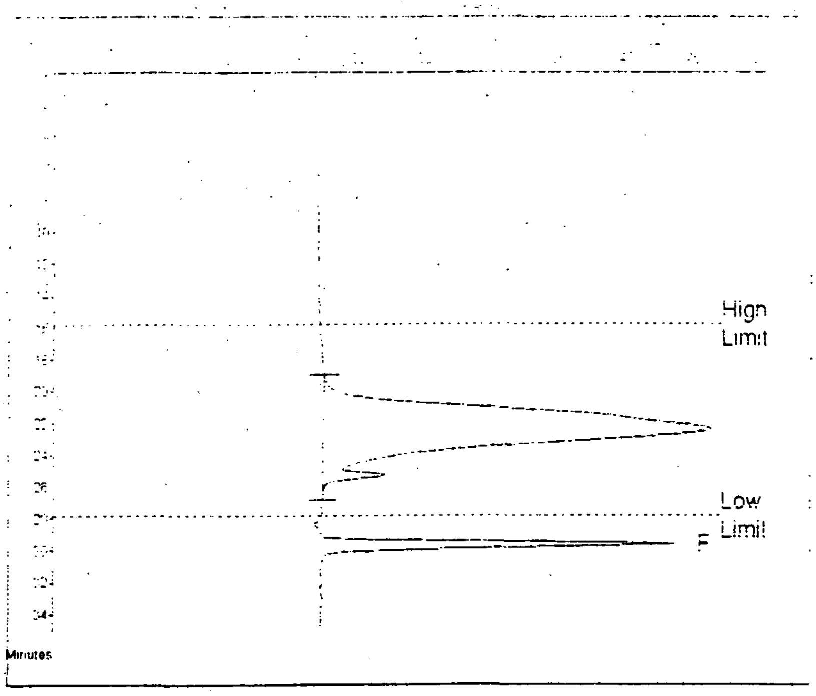
Appendix 2.5.3 GPC trace of PDMeV (80% *cis*, cat. B, 2 days).



Molecular Weight Averages

Mp =	2158	Mz =	3381
Mn =	1231	Mz+1 =	5197
Mw =	2114	Mv =	1963
Polydispersity =	1.717	Peak Area =	578856

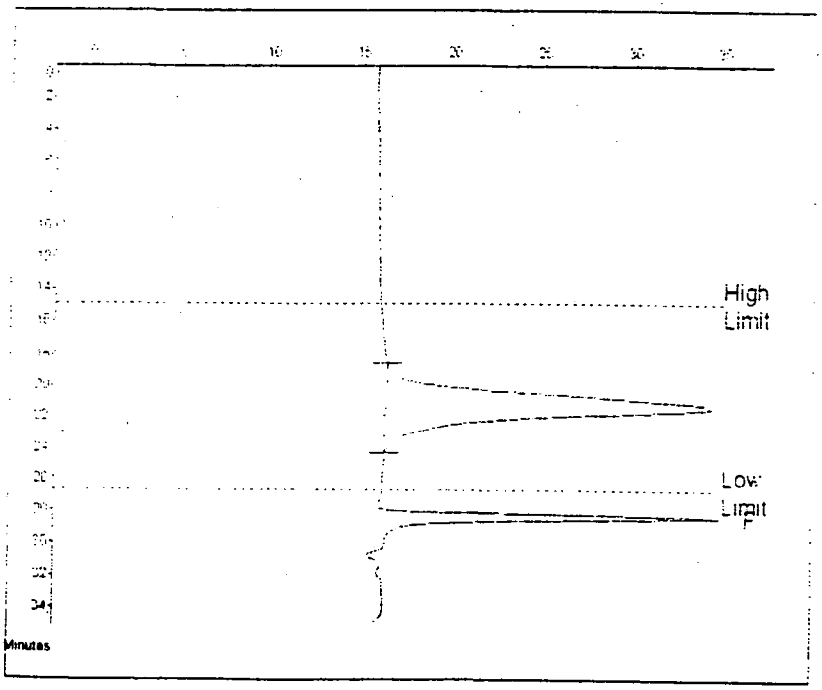
Appendix 2.5.4 GPC trace of PDMeV (80% *cis*, cat. B, 4 days).



Molecular Weight Averages

Mp =	4045	Mz =	7577
Mn =	2913	Mz+1 =	11367
Mw =	4967	Mv =	4633
Polydispersity =	1.705	Peak Area =	862559

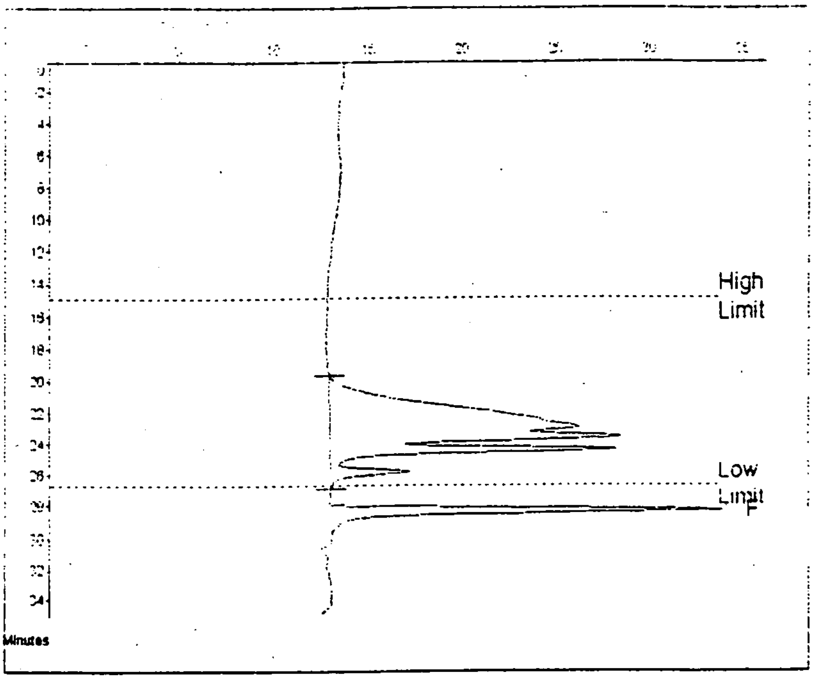
Appendix 2.5.7 GPC trace of PDMeV (80% *cis*, cat. D, 2 days).



Molecular Weight Averages

Mp =	4196	Mz =	5666
Mn =	3589	Mz+1 =	9360
Mw =	4875	Mv =	4857
Polydispersity =	1.358	Peak Area =	282002

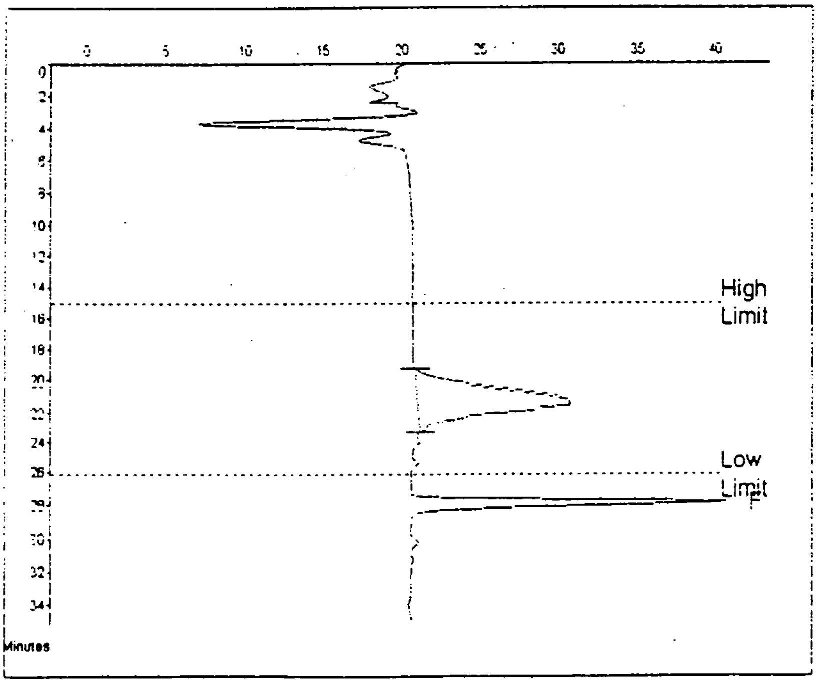
Appendix 2.5.8 GPC trace of PDPV (~50% *cis*, cat. B, 2 days).



Molecular Weight Averages

Mp = 352
Mz = 2904
Mn = 900
Mz+1 = 4585
Mw = 1640
Mv = 1498
Polydispersity = 1.822
Peak Area = 480976

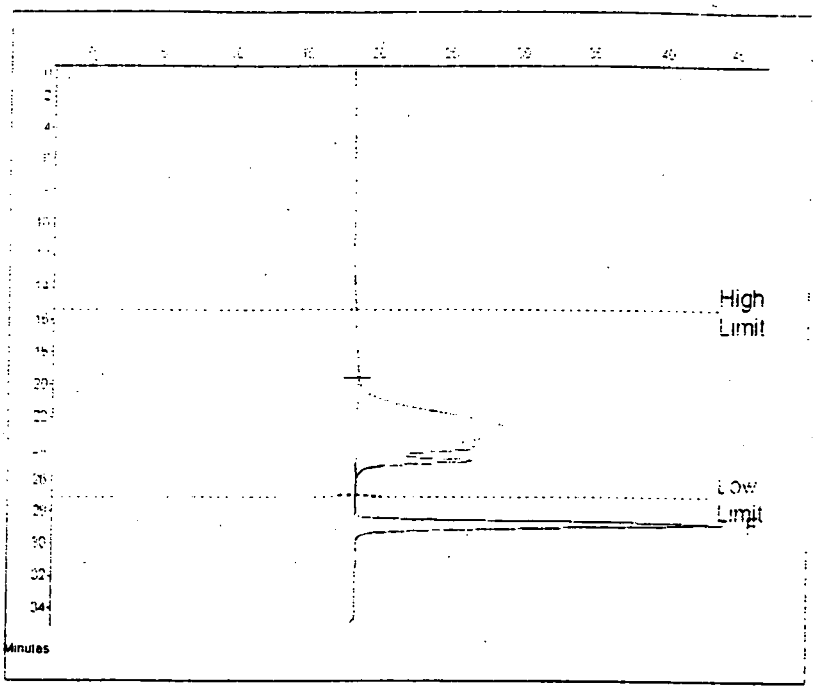
Appendix 2.5.9 GPC trace of PDPV (~50% *cis*, cat. C, 2 days).



Molecular Weight Averages

Mp = 2357
Mz = 4751
Mn = 2903
Mz+1 = 5981
Mw = 3708
Mv = 3572
Polydispersity = 1.277
Peak Area = 213153

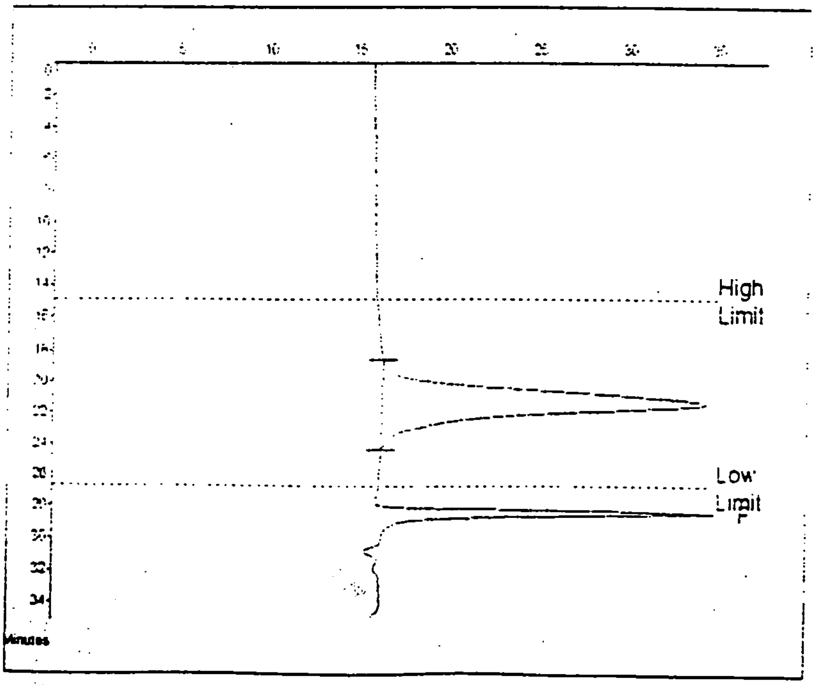
Appendix 2.5.10 GPC trace of PDPV (~50% *cis*, cat. D, 2 days).



Molecular Weight Averages

Mp =	2028	Mz =	3767
Mn =	1199	Mz+1 =	6014
Mw =	2175	Mv =	1994
Polydispersity =	1.814	Peak Area =	373328

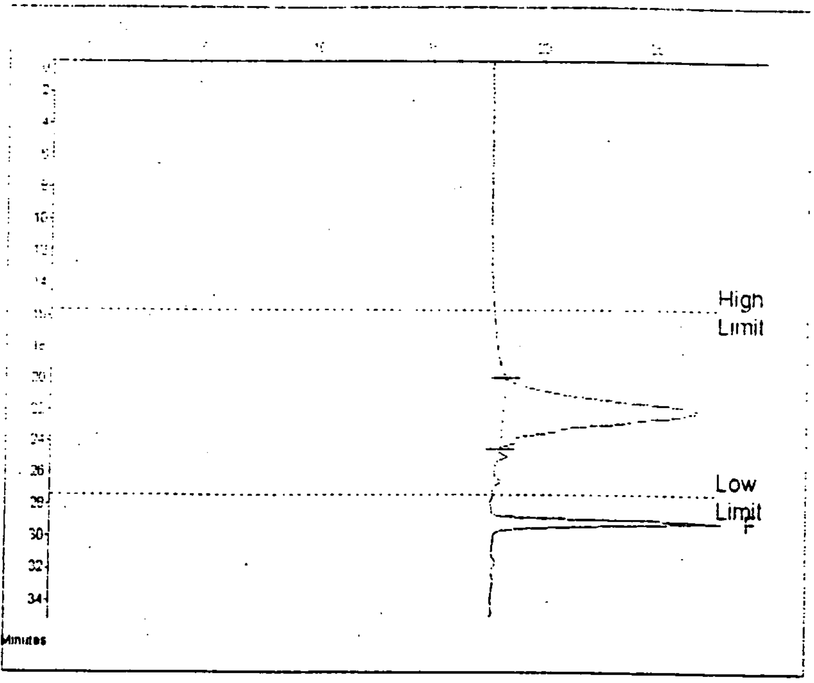
Appendix 2.5.11 GPC trace of PDPV (59% *cis*, cat. B, 2 days).



Molecular Weight Averages

Mp =	4136	Mz =	6666
Mn =	3588	Mz+1 =	9360
Mw =	4875	Mv =	4657
Polydispersity =	1.358	Peak Area =	282002

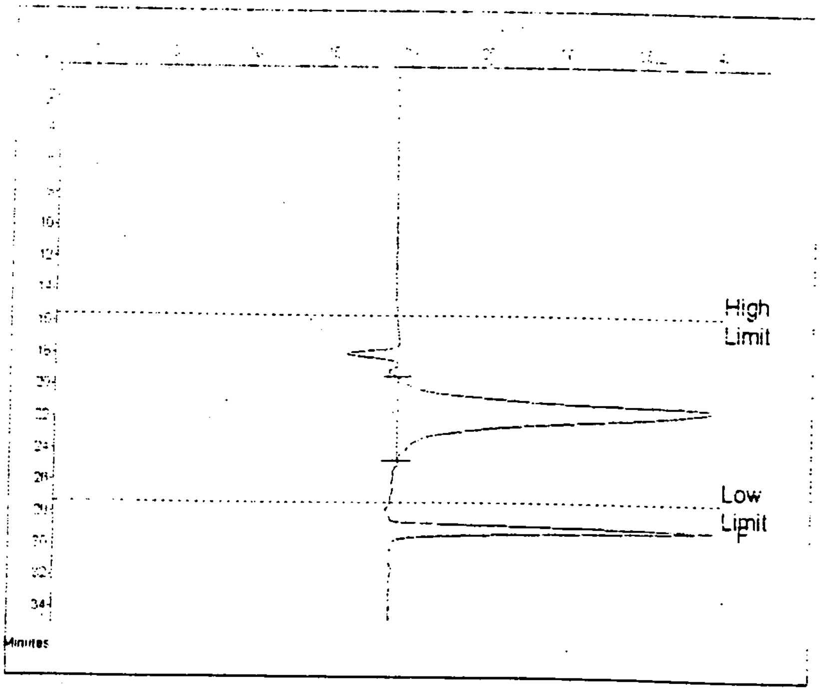
Appendix 2.5.12 GPC trace of PDPV (48% *cis*, cat. B, 2 days).



Molecular Weight Averages

Mp =	4129	Mz =	5909
Mn =	3308	Mz+1 =	7713
Mw =	4425	Mv =	4235
Polydispersity =	1.338	Peak Area =	197072

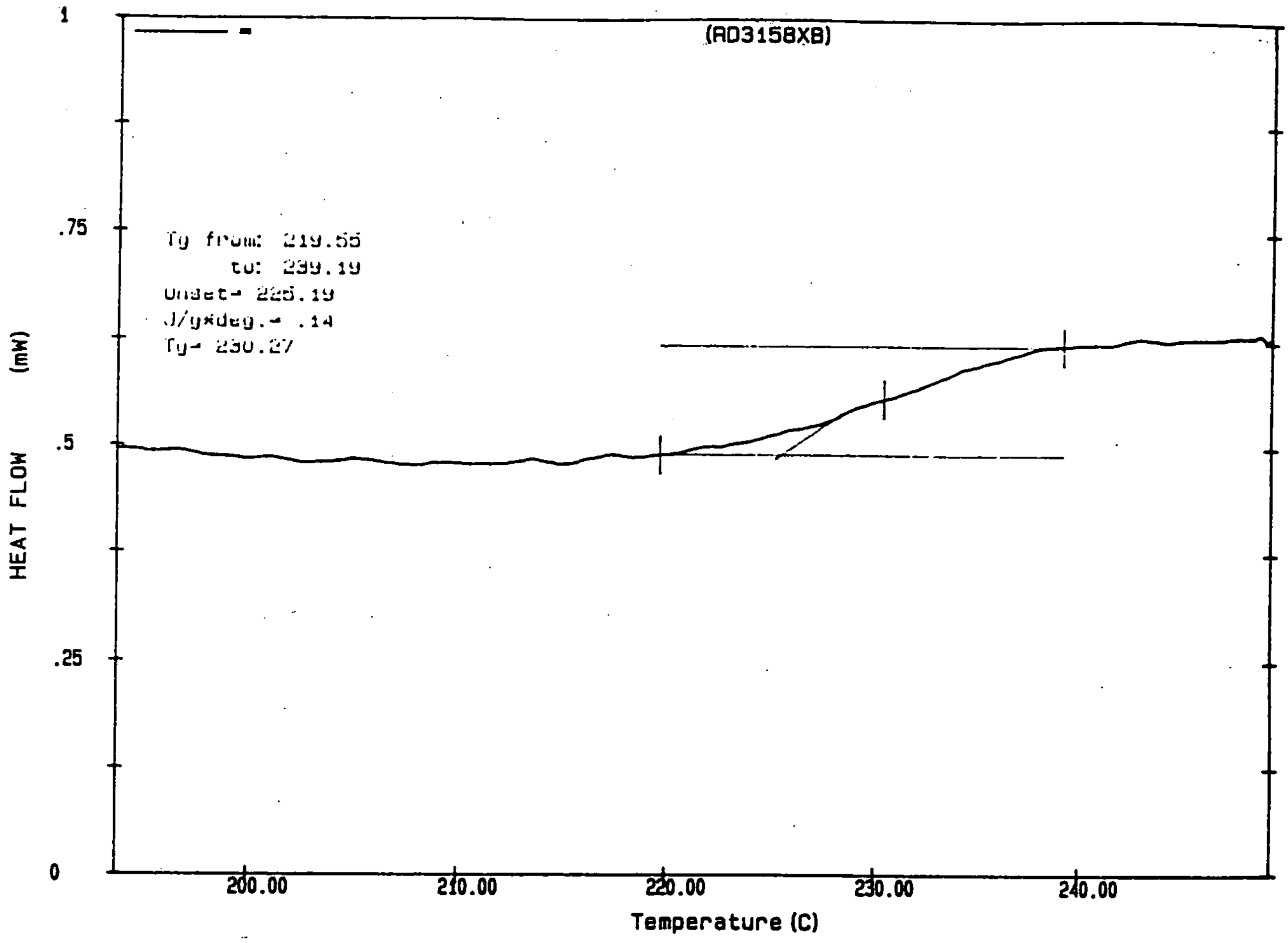
Appendix 2.5.13 GPC trace of PDPV (37% *cis*, cat. B, 2 days).



Molecular Weight Averages

Mp =	5906	Mz =	7189
Mn =	4301	Mz+1 =	8375
Mw =	5592	Mv =	5387
Polydispersity =	1.300	Peak Area =	386259

Appendix 2.5.14 GPC trace of PDPV (48% *cis*, cat. B, 4 days).



Appendix 2.6.1 DSC trace of poly(4,4'-diphenylene diphenylvinylene) (48% *cis* M_n=4300).

Appendix 2.7.2 The crystal structure of *trans*-1,2-di(4-bromophenyl)-1,2-diphenylethene.

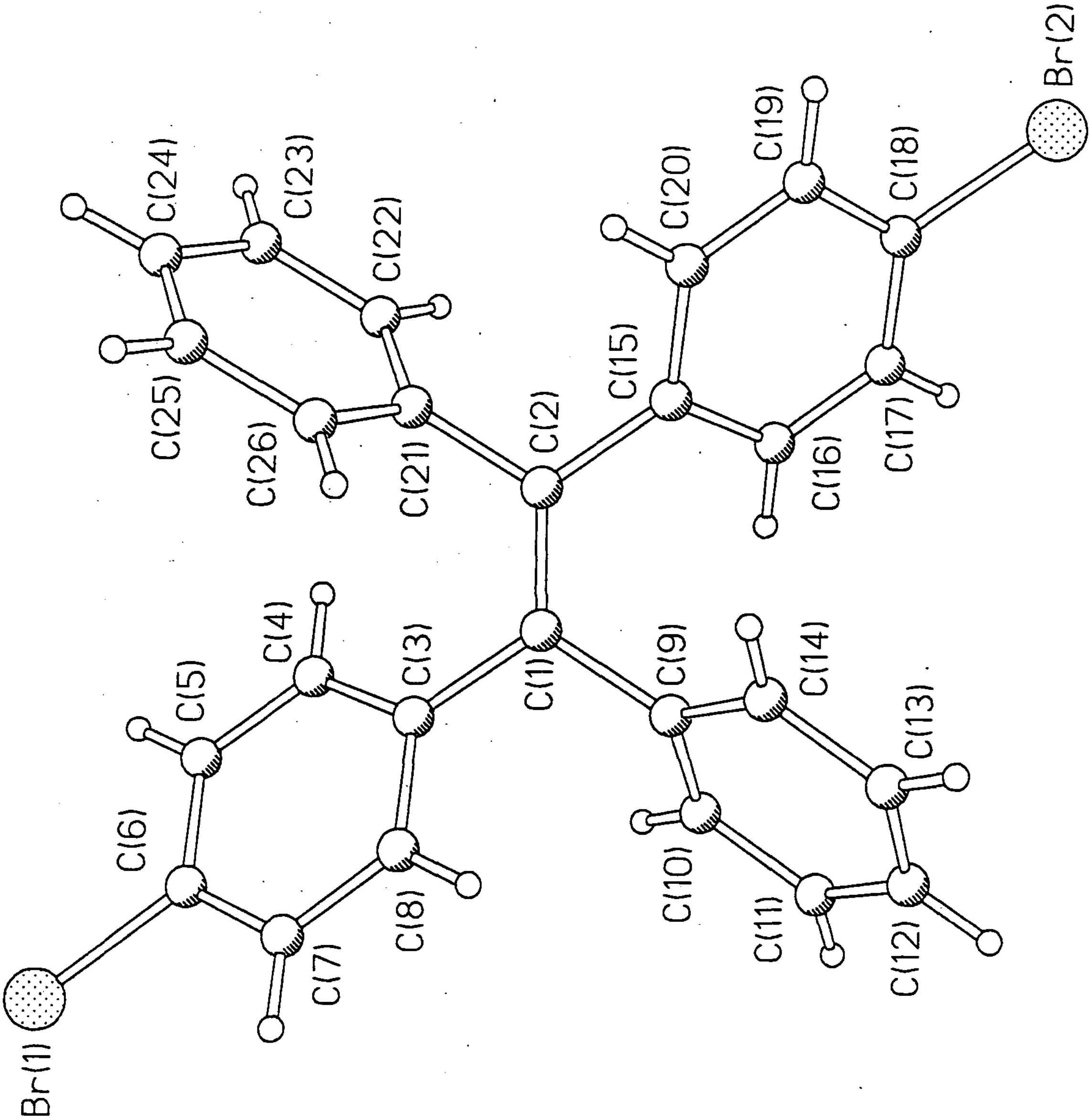


Table 1. Crystal data and structure refinement for 1.

Identification code	97srv082
Empirical formula	C26 H18 Br2
Formula weight	490.22
Temperature	295(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 10.692(1) A alpha = 90 deg. b = 9.191(1) A beta = 102.47(1) deg. c = 22.641(1) A gamma = 90 deg.
Volume	2172.4(3) A^3
Z	4
Density (calculated)	1.499 g/cm^3
Absorption coefficient	3.740 mm^-1
F(000)	976
Crystal size	0.28 x 0.20 x 0.06 mm
Theta range for data collection	1.84 to 25.00 deg.
Index ranges	-15<=h<=15, -12<=k<=12, -31<=l<=28
Reflections collected	12604
Independent reflections	3820 [R(int) = 0.0899]
Observed reflections, I>2sigma(I)	2270
Absorption correction	Integration
Max. and min. transmission	0.8104 and 0.4180
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3228 / 0 / 254
Goodness-of-fit on F^2	1.152
Final R indices [I>2sigma(I)]	R1 = 0.0619, wR2 = 0.0916
R indices (all data)	R1 = 0.1334, wR2 = 0.1259
Extinction coefficient	0.0011(2)
Largest diff. peak and hole	0.398 and -0.543 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	4739.7(7)	3235(1)	824.5(3)	76(1)
Br(2)	14537.9(7)	2210(1)	5435.9(3)	83(1)
C(1)	9009(6)	3400(6)	3151(2)	42(2)
C(2)	10282(5)	3532(6)	3172(2)	39(2)
C(3)	8004(5)	3438(6)	2577(3)	40(2)
C(4)	8189(6)	2770(6)	2053(3)	49(2)
C(5)	7225(6)	2737(7)	1529(3)	51(2)
C(6)	6062(6)	3369(7)	1535(3)	48(2)
C(7)	5848(6)	4045(7)	2043(3)	52(2)
C(8)	6816(6)	4058(6)	2561(3)	45(2)
C(9)	8469(5)	3240(7)	3709(3)	42(2)
C(10)	7640(6)	2127(7)	3770(3)	54(2)
C(11)	7117(6)	2038(8)	4278(3)	66(2)
C(12)	7414(7)	3089(11)	4721(3)	77(2)
C(13)	8229(6)	4206(9)	4671(3)	64(2)
C(14)	8765(5)	4273(7)	4169(3)	48(2)
C(15)	11303(5)	3238(6)	3729(2)	39(1)
C(16)	11177(5)	2125(6)	4132(3)	48(2)
C(17)	12135(6)	1826(7)	4634(3)	48(2)
C(18)	13242(5)	2628(7)	4738(3)	49(2)
C(19)	13411(6)	3721(7)	4350(3)	53(2)
C(20)	12445(5)	4014(7)	3849(3)	49(2)
C(21)	10759(5)	3989(7)	2630(3)	45(2)
C(22)	11604(6)	3122(8)	2407(3)	58(2)
C(23)	12048(6)	3512(10)	1899(3)	77(2)
C(24)	11638(8)	4778(13)	1602(4)	93(3)
C(25)	10834(8)	5675(10)	1823(4)	84(3)
C(26)	10385(6)	5293(7)	2333(3)	58(2)

Table 3. Bond lengths [A] and angles [deg] for 1.

Br(1)-C(6)	1.903(6)	Br(2)-C(18)	1.902(6)
C(1)-C(2)	1.357(7)	C(1)-C(3)	1.497(7)
C(1)-C(9)	1.504(8)	C(2)-C(21)	1.488(8)
C(2)-C(15)	1.505(7)	C(3)-C(8)	1.386(7)
C(3)-C(4)	1.388(8)	C(4)-C(5)	1.393(7)
C(5)-C(6)	1.375(8)	C(6)-C(7)	1.368(8)
C(7)-C(8)	1.386(7)	C(9)-C(10)	1.379(8)
C(9)-C(14)	1.395(8)	C(10)-C(11)	1.387(9)
C(11)-C(12)	1.380(10)	C(12)-C(13)	1.367(10)
C(13)-C(14)	1.380(8)	C(15)-C(20)	1.390(7)
C(15)-C(16)	1.396(8)	C(16)-C(17)	1.383(7)
C(17)-C(18)	1.371(8)	C(18)-C(19)	1.372(8)
C(19)-C(20)	1.386(7)	C(21)-C(22)	1.379(8)
C(21)-C(26)	1.390(8)	C(22)-C(23)	1.384(9)
C(23)-C(24)	1.368(11)	C(24)-C(25)	1.362(11)
C(25)-C(26)	1.388(10)		

C(2)-C(1)-C(3)	123.6(5)	C(2)-C(1)-C(9)	122.9(5)
C(3)-C(1)-C(9)	113.4(5)	C(1)-C(2)-C(21)	121.1(5)
C(1)-C(2)-C(15)	123.6(5)	C(21)-C(2)-C(15)	115.3(5)
C(8)-C(3)-C(4)	117.3(5)	C(8)-C(3)-C(1)	120.9(5)
C(4)-C(3)-C(1)	121.6(5)	C(3)-C(4)-C(5)	121.4(6)
C(6)-C(5)-C(4)	119.1(6)	C(7)-C(6)-C(5)	121.0(6)
C(7)-C(6)-Br(1)	120.8(5)	C(5)-C(6)-Br(1)	118.2(5)
C(6)-C(7)-C(8)	119.0(6)	C(3)-C(8)-C(7)	122.1(6)
C(10)-C(9)-C(14)	118.5(6)	C(10)-C(9)-C(1)	121.8(6)
C(14)-C(9)-C(1)	119.7(6)	C(9)-C(10)-C(11)	120.7(6)
C(12)-C(11)-C(10)	119.4(7)	C(13)-C(12)-C(11)	121.1(7)
C(12)-C(13)-C(14)	119.1(7)	C(13)-C(14)-C(9)	121.2(6)
C(20)-C(15)-C(16)	117.0(5)	C(20)-C(15)-C(2)	121.2(5)
C(16)-C(15)-C(2)	121.7(5)	C(17)-C(16)-C(15)	121.6(5)
C(18)-C(17)-C(16)	119.6(6)	C(17)-C(18)-C(19)	120.7(6)
C(17)-C(18)-Br(2)	118.8(5)	C(19)-C(18)-Br(2)	120.5(5)
C(18)-C(19)-C(20)	119.3(6)	C(19)-C(20)-C(15)	121.8(6)
C(22)-C(21)-C(26)	117.7(6)	C(22)-C(21)-C(2)	120.4(6)
C(26)-C(21)-C(2)	121.9(6)	C(21)-C(22)-C(23)	121.6(7)
C(24)-C(23)-C(22)	119.9(8)	C(25)-C(24)-C(23)	119.7(8)
C(24)-C(25)-C(26)	120.8(8)	C(25)-C(26)-C(21)	120.3(7)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 1.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	73(1)	76(1)	64(1)	-14(1)	-17(1)	16(1)
Br(2)	52(1)	134(1)	56(1)	20(1)	0(1)	-5(1)
C(1)	46(4)	43(4)	38(3)	0(3)	11(3)	-1(3)
C(2)	42(4)	34(4)	44(4)	-2(3)	13(3)	2(3)
C(3)	42(3)	34(4)	43(4)	-3(3)	10(3)	-1(3)
C(4)	43(4)	48(4)	54(4)	-5(3)	8(3)	-3(3)
C(5)	54(4)	56(4)	43(4)	-9(3)	13(3)	-8(3)
C(6)	44(4)	45(4)	52(4)	-4(3)	0(3)	-3(3)
C(7)	50(4)	50(4)	55(4)	-3(3)	6(3)	8(3)
C(8)	53(4)	44(4)	40(4)	-10(3)	13(3)	4(3)
C(9)	31(3)	46(4)	47(4)	4(3)	2(3)	5(3)
C(10)	43(4)	61(5)	54(4)	-2(4)	5(3)	-6(3)
C(11)	37(4)	85(6)	74(5)	18(5)	11(4)	-12(4)
C(12)	48(4)	134(8)	49(5)	15(5)	11(4)	9(5)
C(13)	52(4)	94(6)	47(4)	-13(4)	11(4)	20(4)
C(14)	42(4)	50(4)	49(4)	-1(3)	3(3)	1(3)
C(15)	40(3)	43(4)	32(3)	0(3)	8(3)	4(3)
C(16)	36(3)	49(4)	58(4)	3(3)	6(3)	-5(3)
C(17)	51(4)	48(4)	49(4)	12(3)	17(3)	5(3)
C(18)	37(3)	65(5)	43(4)	-4(3)	4(3)	0(3)
C(19)	44(4)	66(5)	48(4)	-1(4)	6(3)	-10(3)
C(20)	48(4)	57(4)	43(4)	3(3)	11(3)	-3(3)
C(21)	31(3)	61(4)	40(4)	8(3)	1(3)	-11(3)
C(22)	50(4)	74(5)	54(4)	4(4)	16(3)	-8(4)
C(23)	45(4)	132(8)	57(5)	-6(5)	17(4)	-17(5)
C(24)	69(6)	159(11)	49(5)	19(6)	6(5)	-46(6)
C(25)	79(6)	89(7)	73(6)	49(5)	-10(5)	-41(5)
C(26)	46(4)	56(5)	70(5)	13(4)	3(4)	-7(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

	x	y	z	U(eq)
H(4)	8974(6)	2335(6)	2050(3)	58
H(5)	7365(6)	2290(7)	1181(3)	61
H(7)	5066(6)	4490(7)	2040(3)	63
H(8)	6662(6)	4496(6)	2909(3)	54
H(10)	7432(6)	1430(7)	3467(3)	64
H(11)	6568(6)	1277(8)	4320(3)	79
H(12)	7054(7)	3038(11)	5059(3)	92
H(13)	8422(6)	4913(9)	4972(3)	77
H(14)	9335(5)	5019(7)	4137(3)	57
H(16)	10432(5)	1569(6)	4061(3)	58
H(17)	12028(6)	1084(7)	4898(3)	58
H(19)	14164(6)	4261(7)	4422(3)	64
H(20)	12565(5)	4750(7)	3584(3)	59
H(22)	11882(6)	2252(8)	2603(3)	70
H(23)	12625(6)	2916(10)	1759(3)	93
H(24)	11905(8)	5025(13)	1250(4)	112
H(25)	10585(8)	6556(10)	1630(4)	101
H(26)	9830(6)	5913(7)	2476(3)	70

Table 1. Crystal data and structure refinement for 1.

Identification code	97srv081
Empirical formula	C16 H14 Br2
Formula weight	366.09
Temperature	295(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 12.226(1) A alpha = 90 deg. b = 15.976(1) A beta = 98.38(1) deg. c = 15.792(1) A gamma = 90 deg.
Volume	3051.6(4) A^3
Z	8
Density (calculated)	1.594 g/cm^3
Absorption coefficient	5.294 mm^-1
F(000)	1440
Crystal size	0.35 x 0.35 x 0.25 mm
Theta range for data collection	1.82 to 25.00 deg.
Index ranges	-17<=h<=17, -22<=k<=21, -22<=l<=14
Reflections collected	17930
Independent reflections	5367 [R(int) = 0.0822]
Observed reflections, I>2sigma(I)	2682
Absorption correction	Semi-empirical (on Laue equivalents)
Max. and min. transmission	0.2912 and 0.1848
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4184 / 0 / 326
Goodness-of-fit on F^2	1.143
Final R indices [I>2sigma(I)]	R1 = 0.0672, wR2 = 0.0999
R indices (all data)	R1 = 0.1604, wR2 = 0.1472
Extinction coefficient	0.0008(1)
Largest diff. peak and hole	0.456 and -0.445 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	2429(1)	8526(1)	5126(1)	100(1)
Br(2)	2590(1)	3470(1)	5510(1)	97(1)
C(1)	221(6)	6565(6)	7798(5)	64(2)
C(2)	337(6)	5743(6)	7911(5)	65(2)
C(3)	-434(7)	7120(5)	8316(5)	87(3)
C(4)	-132(7)	5255(6)	8619(5)	97(3)
C(5)	755(6)	7028(5)	7147(5)	59(2)
C(6)	151(7)	7545(6)	6550(5)	83(3)
C(7)	646(8)	7980(5)	5950(5)	82(3)
C(8)	1759(8)	7906(5)	5939(5)	69(2)
C(9)	2381(6)	7416(5)	6533(5)	64(2)
C(10)	1884(6)	6980(4)	7128(5)	58(2)
C(11)	903(6)	5205(5)	7332(5)	58(2)
C(12)	575(6)	5202(5)	6455(5)	68(2)
C(13)	1083(6)	4696(5)	5927(5)	71(2)
C(14)	1929(6)	4185(4)	6258(6)	63(2)
C(15)	2293(7)	4175(5)	7118(6)	75(2)
C(16)	1761(7)	4678(5)	7646(5)	70(2)
Br(3)	2380(1)	940(1)	4776(1)	114(1)
Br(4)	2825(1)	6087(1)	4816(1)	94(1)
C(17)	4715(6)	3824(6)	2215(5)	67(2)
C(18)	4605(6)	2987(5)	2189(5)	64(2)
C(19)	5314(7)	4304(6)	1576(5)	96(3)
C(20)	5023(7)	2450(6)	1520(5)	95(3)
C(21)	4052(6)	2520(5)	2821(5)	60(2)
C(22)	3207(7)	1961(5)	2556(5)	72(2)
C(23)	2690(7)	1489(5)	3130(6)	79(2)
C(24)	3050(7)	1590(5)	3981(6)	72(2)
C(25)	3907(7)	2117(5)	4276(5)	72(2)
C(26)	4394(6)	2587(5)	3700(5)	68(2)
C(27)	4241(7)	4368(5)	2840(5)	61(2)
C(28)	3128(6)	4372(5)	2905(5)	66(2)
C(29)	2715(6)	4880(5)	3488(5)	66(2)
C(30)	3410(7)	5398(4)	4015(5)	62(2)
C(31)	4509(7)	5413(5)	3960(5)	69(2)
C(32)	4933(7)	4905(5)	3371(5)	74(2)

Table 3. Bond lengths [A] and angles [deg] for 1.

Br(1)-C(8)	1.900(8)	Br(2)-C(14)	1.905(8)
C(1)-C(2)	1.329(10)	C(1)-C(5)	1.491(10)
C(1)-C(3)	1.513(10)	C(2)-C(11)	1.497(10)
C(2)-C(4)	1.542(10)	C(5)-C(6)	1.383(10)
C(5)-C(10)	1.388(9)	C(6)-C(7)	1.384(10)
C(7)-C(8)	1.369(10)	C(8)-C(9)	1.365(10)
C(9)-C(10)	1.379(9)	C(11)-C(16)	1.379(10)
C(11)-C(12)	1.384(9)	C(12)-C(13)	1.373(10)
C(13)-C(14)	1.361(10)	C(14)-C(15)	1.365(10)
C(15)-C(16)	1.387(10)	Br(3)-C(24)	1.904(8)
Br(4)-C(30)	1.893(7)	C(17)-C(18)	1.343(10)
C(17)-C(27)	1.493(10)	C(17)-C(19)	1.536(10)
C(18)-C(21)	1.486(10)	C(18)-C(20)	1.507(9)
C(21)-C(22)	1.384(10)	C(21)-C(26)	1.395(10)
C(22)-C(23)	1.398(10)	C(23)-C(24)	1.363(10)
C(24)-C(25)	1.371(10)	C(25)-C(26)	1.380(10)
C(27)-C(28)	1.379(9)	C(27)-C(32)	1.396(10)
C(28)-C(29)	1.377(9)	C(29)-C(30)	1.377(10)
C(30)-C(31)	1.358(10)	C(31)-C(32)	1.391(10)
C(2)-C(1)-C(5)	122.3(7)	C(2)-C(1)-C(3)	124.1(7)
C(5)-C(1)-C(3)	113.7(7)	C(1)-C(2)-C(11)	122.4(7)
C(1)-C(2)-C(4)	123.6(8)	C(11)-C(2)-C(4)	114.0(7)
C(6)-C(5)-C(10)	116.9(7)	C(6)-C(5)-C(1)	121.5(7)
C(10)-C(5)-C(1)	121.6(7)	C(7)-C(6)-C(5)	121.6(8)
C(8)-C(7)-C(6)	120.0(8)	C(9)-C(8)-C(7)	119.8(7)
C(9)-C(8)-Br(1)	120.8(7)	C(7)-C(8)-Br(1)	119.4(7)
C(8)-C(9)-C(10)	120.0(7)	C(9)-C(10)-C(5)	121.7(7)
C(16)-C(11)-C(12)	116.9(8)	C(16)-C(11)-C(2)	121.7(7)
C(12)-C(11)-C(2)	121.4(7)	C(13)-C(12)-C(11)	121.2(8)
C(14)-C(13)-C(12)	120.4(8)	C(13)-C(14)-C(15)	120.5(8)
C(13)-C(14)-Br(2)	119.2(7)	C(15)-C(14)-Br(2)	120.2(7)
C(14)-C(15)-C(16)	118.6(8)	C(11)-C(16)-C(15)	122.4(8)
C(18)-C(17)-C(27)	123.5(7)	C(18)-C(17)-C(19)	122.1(8)
C(27)-C(17)-C(19)	114.3(8)	C(17)-C(18)-C(21)	122.2(7)
C(17)-C(18)-C(20)	123.1(8)	C(21)-C(18)-C(20)	114.7(7)
C(22)-C(21)-C(26)	116.9(8)	C(22)-C(21)-C(18)	121.0(7)
C(26)-C(21)-C(18)	122.0(8)	C(21)-C(22)-C(23)	122.7(8)
C(24)-C(23)-C(22)	117.6(8)	C(23)-C(24)-C(25)	121.9(8)
C(23)-C(24)-Br(3)	118.6(7)	C(25)-C(24)-Br(3)	119.5(7)
C(24)-C(25)-C(26)	119.5(8)	C(25)-C(26)-C(21)	121.2(8)
C(28)-C(27)-C(32)	118.1(7)	C(28)-C(27)-C(17)	122.3(7)
C(32)-C(27)-C(17)	119.6(7)	C(29)-C(28)-C(27)	121.0(7)
C(28)-C(29)-C(30)	120.3(7)	C(31)-C(30)-C(29)	120.0(7)
C(31)-C(30)-Br(4)	120.4(6)	C(29)-C(30)-Br(4)	119.6(6)
C(30)-C(31)-C(32)	120.1(7)	C(31)-C(32)-C(27)	120.5(7)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 1. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	145(1)	82(1)	79(1)	7(1)	32(1)	-24(1)
Br(2)	88(1)	84(1)	124(1)	-6(1)	31(1)	5(1)
C(1)	52(5)	85(6)	55(5)	-4(5)	6(4)	-1(5)
C(2)	60(5)	78(6)	57(5)	2(5)	9(4)	-19(5)
C(3)	86(7)	104(7)	73(6)	-9(5)	16(5)	2(5)
C(4)	102(7)	118(8)	74(6)	16(5)	22(5)	-30(6)
C(5)	58(5)	64(5)	55(5)	-3(4)	8(4)	2(4)
C(6)	69(6)	109(7)	69(6)	17(5)	6(5)	26(5)
C(7)	109(8)	79(6)	57(6)	14(5)	11(5)	25(6)
C(8)	87(7)	58(5)	64(6)	-9(4)	20(5)	-8(5)
C(9)	65(5)	63(5)	65(5)	-6(4)	13(5)	-2(4)
C(10)	54(5)	57(5)	62(5)	4(4)	1(4)	2(4)
C(11)	56(5)	56(5)	61(5)	17(4)	-1(4)	-14(4)
C(12)	55(5)	92(6)	54(5)	5(5)	3(4)	6(5)
C(13)	57(5)	94(7)	61(5)	1(5)	4(5)	-1(5)
C(14)	51(5)	51(5)	88(7)	8(4)	16(5)	-12(4)
C(15)	71(6)	57(5)	93(7)	25(5)	-4(5)	-3(4)
C(16)	88(7)	58(5)	60(5)	16(4)	-4(5)	-13(5)
Br(3)	122(1)	96(1)	127(1)	33(1)	33(1)	12(1)
Br(4)	123(1)	82(1)	79(1)	-10(1)	23(1)	21(1)
C(17)	48(5)	94(7)	60(5)	5(5)	8(4)	6(5)
C(18)	54(5)	72(6)	63(5)	-11(5)	-1(4)	15(5)
C(19)	90(7)	114(8)	87(7)	-1(6)	21(5)	-4(6)
C(20)	106(7)	109(7)	72(6)	-21(5)	19(5)	42(6)
C(21)	66(6)	63(5)	52(5)	-2(4)	7(4)	17(5)
C(22)	72(6)	58(5)	82(6)	-17(5)	2(5)	13(5)
C(23)	79(6)	56(5)	97(7)	-15(5)	3(6)	2(5)
C(24)	76(6)	54(5)	84(6)	-5(5)	4(5)	20(5)
C(25)	74(6)	82(6)	56(5)	-2(5)	-3(5)	23(5)
C(26)	60(5)	63(5)	79(6)	-4(5)	2(5)	15(4)
C(27)	64(6)	60(5)	58(5)	-9(4)	10(4)	4(4)
C(28)	50(5)	64(5)	82(6)	-7(4)	3(4)	2(4)
C(29)	54(5)	57(5)	89(6)	-2(5)	17(5)	7(4)
C(30)	77(6)	49(5)	61(5)	3(4)	16(5)	2(4)
C(31)	78(6)	67(5)	63(5)	-2(4)	10(5)	-20(5)
C(32)	66(6)	84(6)	78(6)	1(5)	28(5)	-5(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

	x	y	z	U(eq)
H(3A)	-1077(7)	7326(5)	7955(5)	131
H(3B)	13(7)	7582(5)	8549(5)	131
H(3C)	-658(7)	6798(5)	8775(5)	131
H(4A)	428(7)	4885(6)	8894(5)	146
H(4B)	-765(7)	4935(6)	8375(5)	146
H(4C)	-344(7)	5641(6)	9033(5)	146
H(6)	-603(7)	7609(6)	6561(5)	99
H(7)	213(8)	8311(5)	5548(5)	98
H(9)	3141(6)	7377(5)	6537(5)	77
H(10)	2317(6)	6643(4)	7523(5)	70
H(12)	-4(6)	5548(5)	6224(5)	81
H(13)	849(6)	4704(5)	5340(5)	85
H(15)	2888(7)	3840(5)	7340(6)	90
H(16)	1986(7)	4660(5)	8234(5)	84
H(19A)	5814(7)	4702(6)	1878(5)	145
H(19B)	4779(7)	4593(6)	1175(5)	145
H(19C)	5720(7)	3919(6)	1274(5)	145
H(20A)	4577(7)	1954(6)	1432(5)	143
H(20B)	5778(7)	2296(6)	1707(5)	143
H(20C)	4974(7)	2756(6)	993(5)	143
H(22)	2971(7)	1901(5)	1972(5)	86
H(23)	2126(7)	1116(5)	2930(6)	94
H(25)	4161(7)	2160(5)	4858(5)	86
H(26)	4961(6)	2957(5)	3900(5)	82
H(28)	2650(6)	4026(5)	2551(5)	79
H(29)	1962(6)	4875(5)	3522(5)	79
H(31)	4977(7)	5763(5)	4316(5)	83
H(32)	5684(7)	4925(5)	3331(5)	89

Appendix 3 Analytical data for Chapter 4

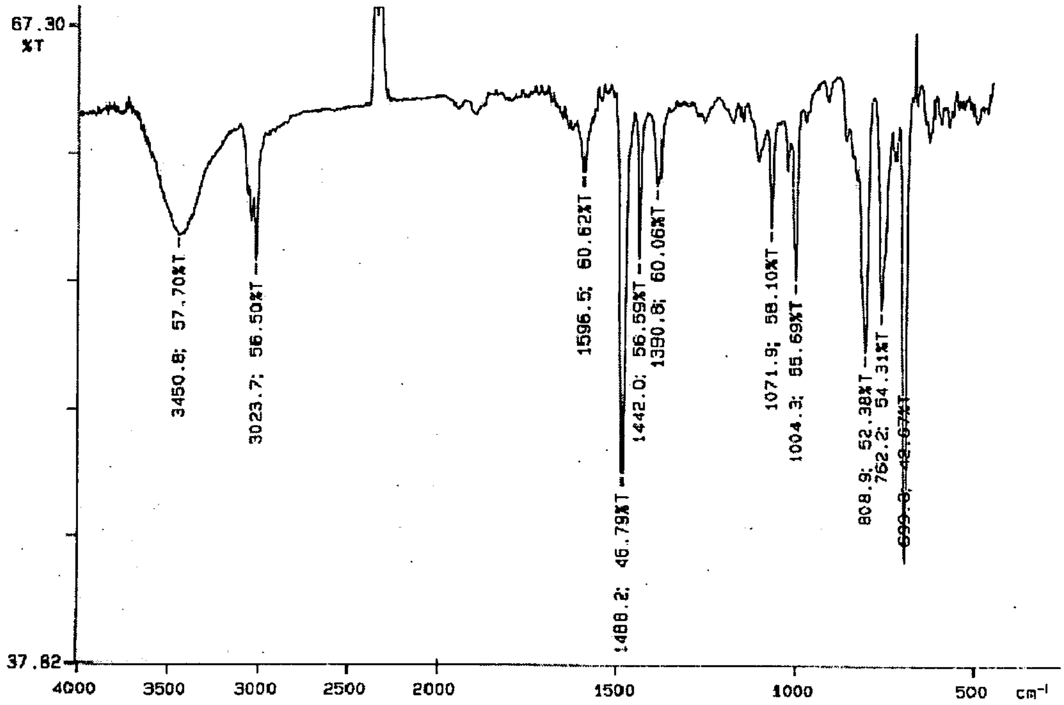
Appendix 3.1 FTIR spectra

Appendix 3.2 ^{1}H Nmr spectra

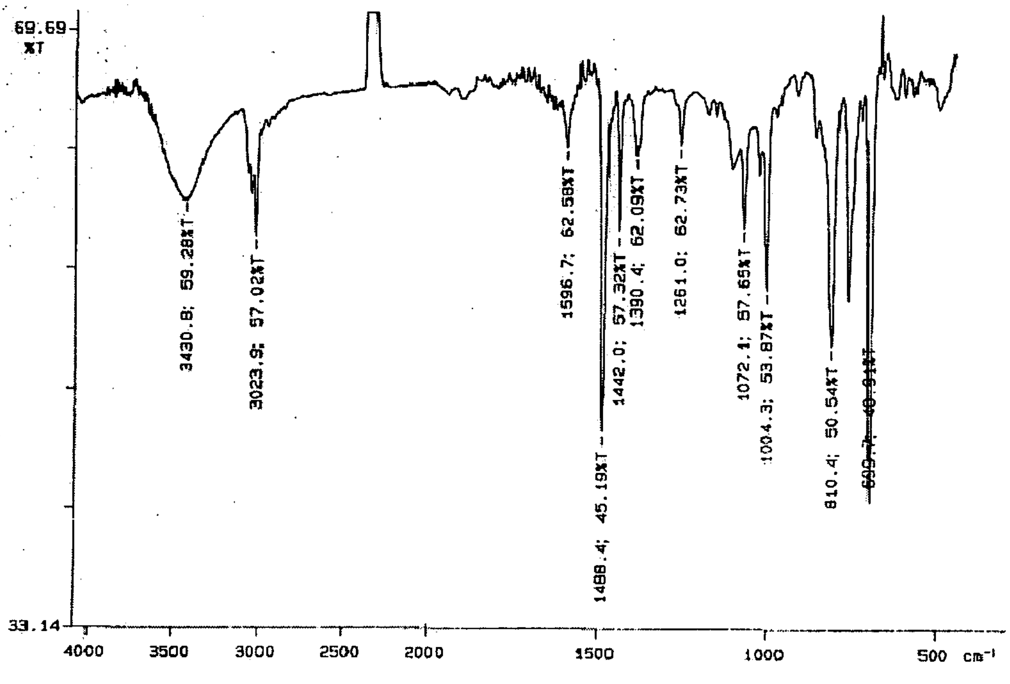
Appendix 3.3 ^{13}C Nmr spectra

Appendix 3.4 GPC traces

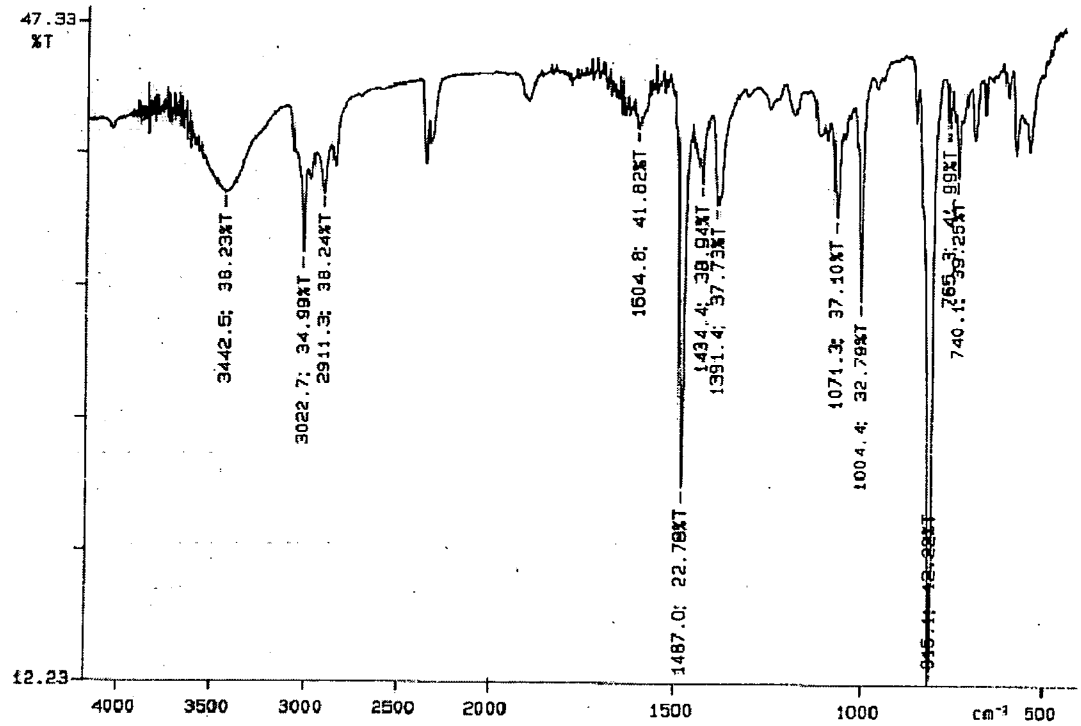
Appendix 3.5 DSC traces



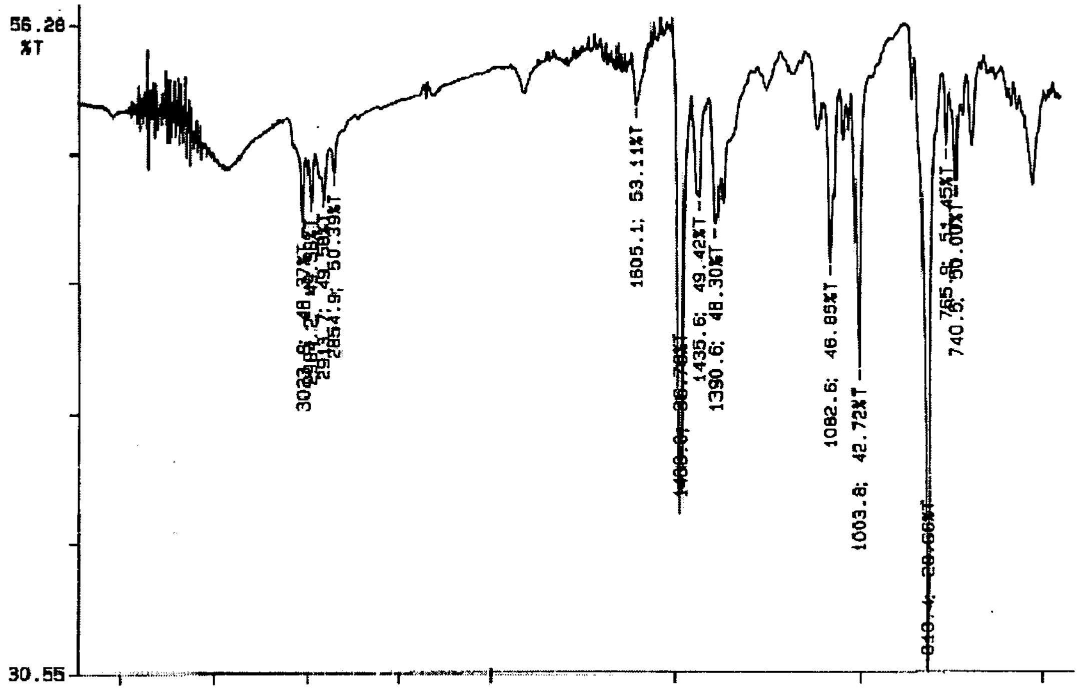
Appendix 3.1.1 FTIR spectrum of P3PV-DP (48% *cis*, M_n=1500)



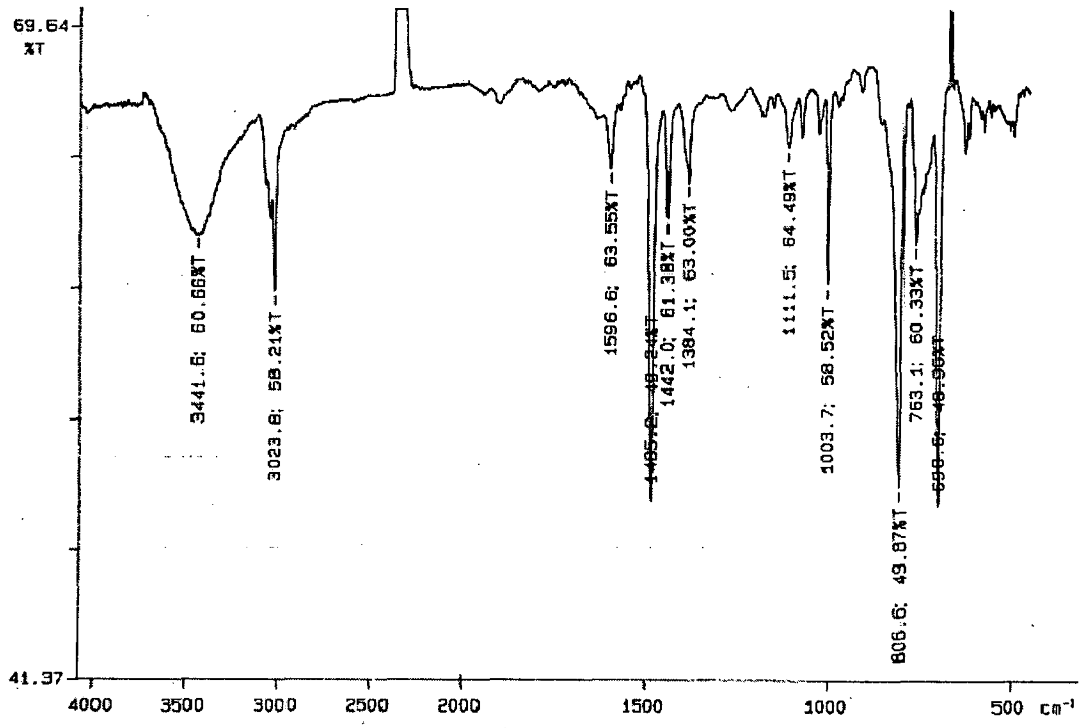
Appendix 3.1.2 FTIR spectrum of P3PV-DP (30% *cis*, M_n=1200)



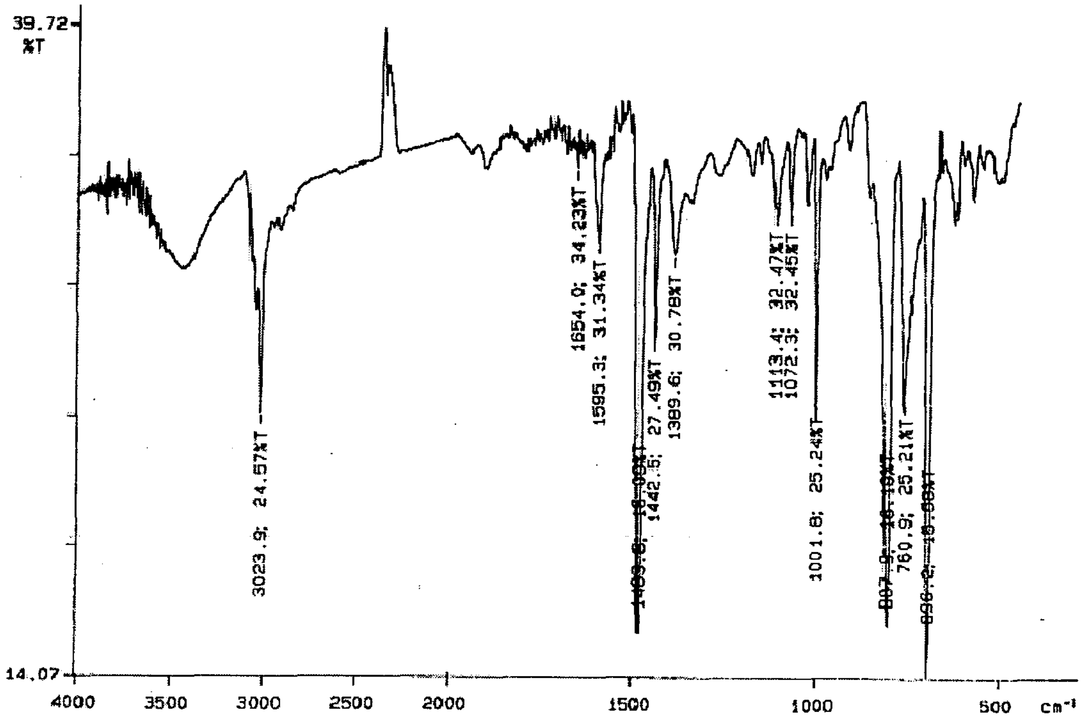
Appendix 3.1.3 FTIR spectrum of P3PV-DMe (98% *cis*, M_n=1600)



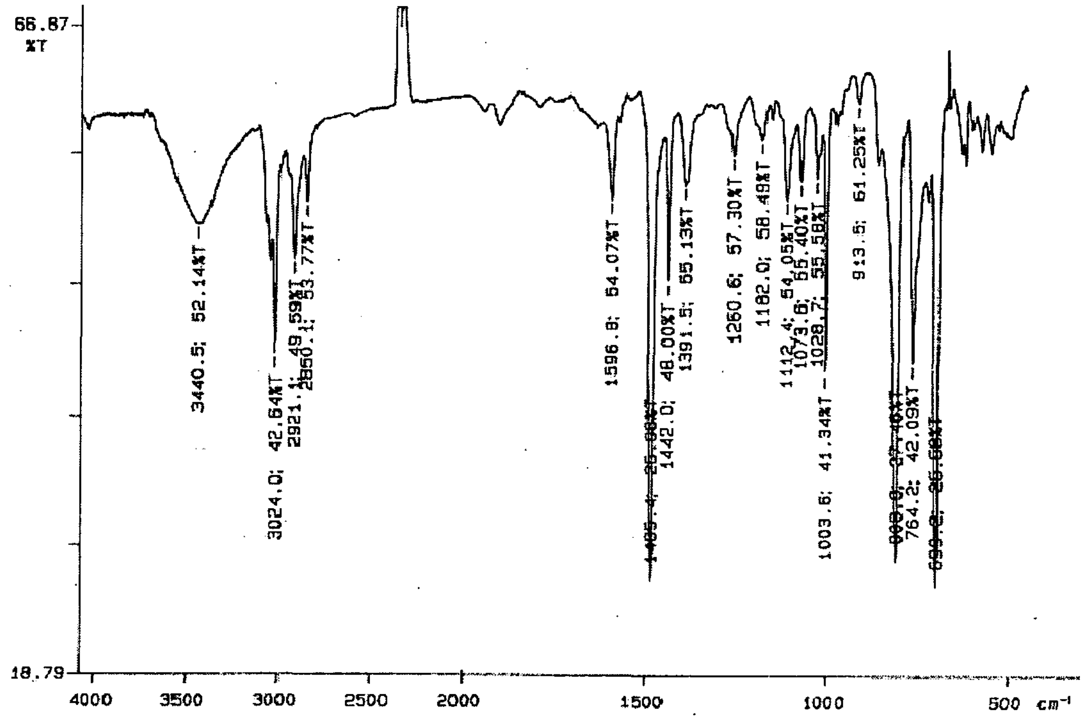
Appendix 3.1.4 FTIR spectrum of P3PV-DMe (0% *cis*, M_n=1250)



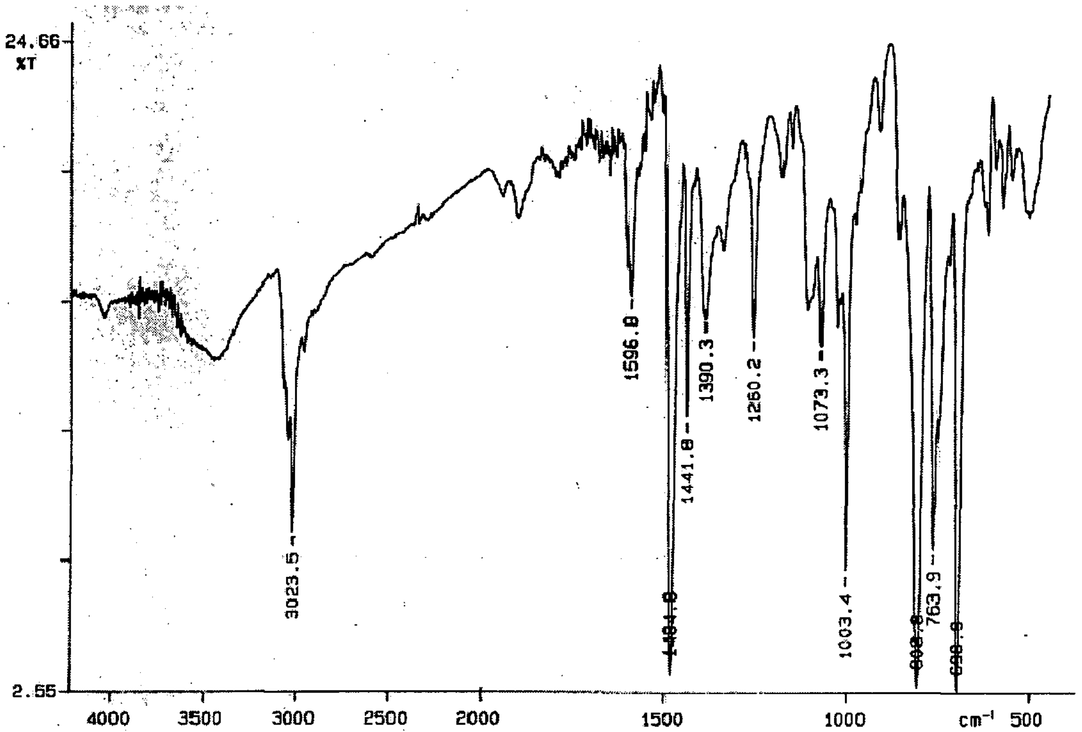
Appendix 3.1.5 FTIR spectrum of P4PV-DP (97% *cis*, M_n=3850)



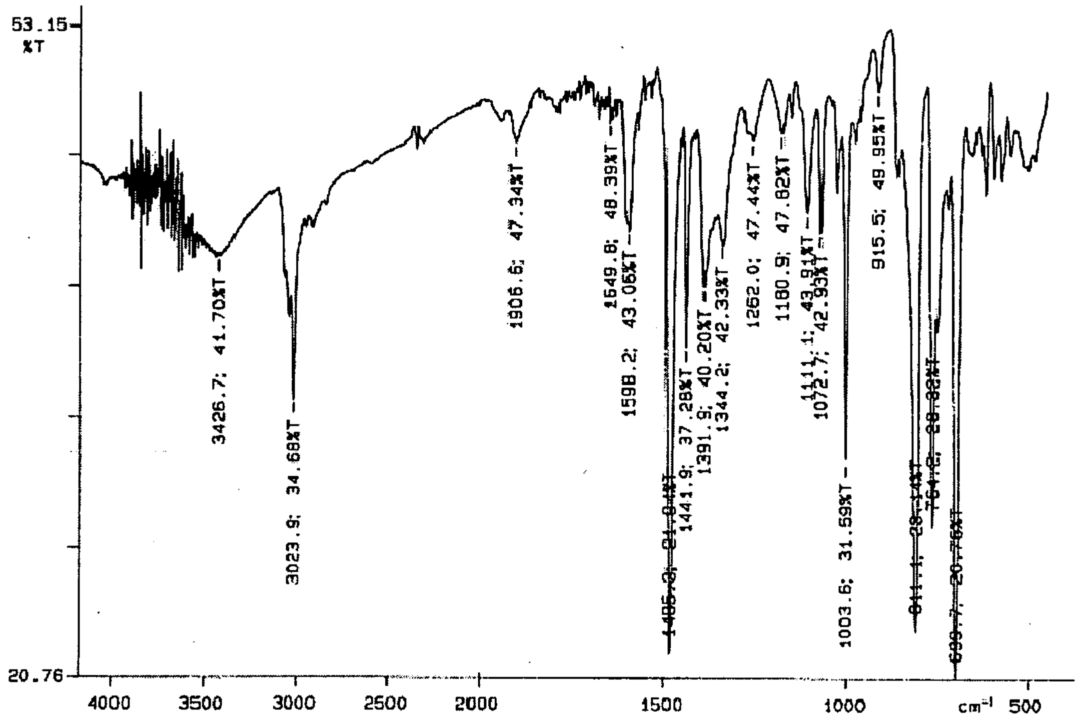
Appendix 3.1.6 FTIR spectrum of P4PV-DP (62% *cis*, M_n=5000)



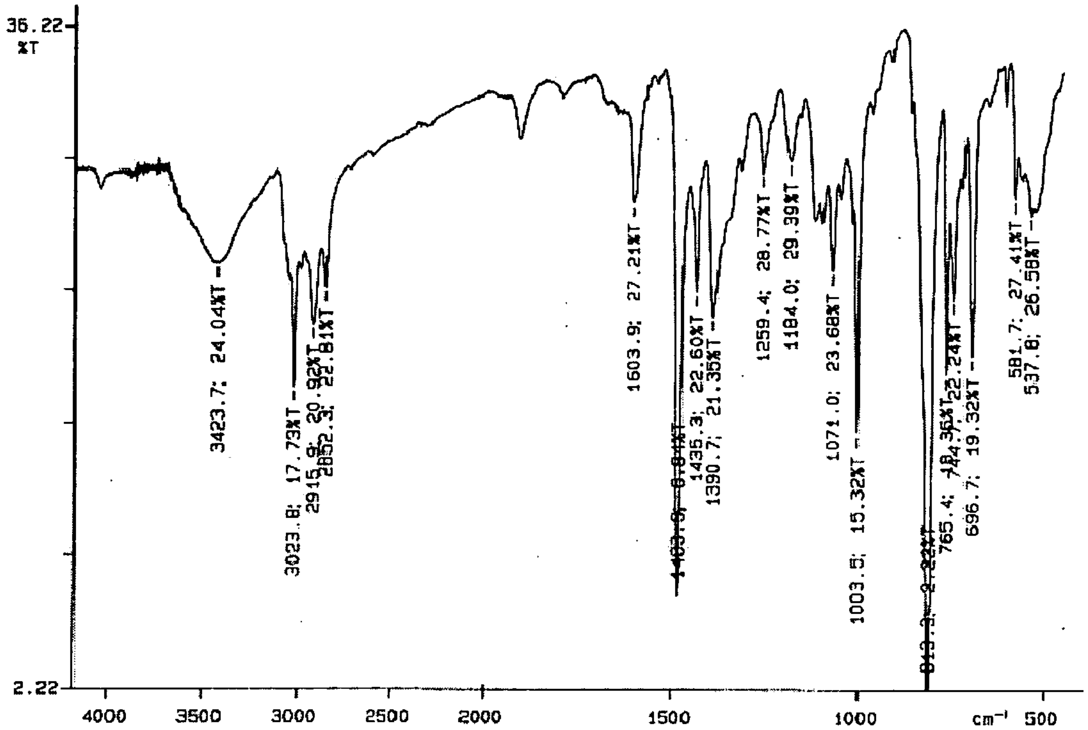
Appendix 3.1.7 FTIR spectrum of P4PV-DP (48% *cis*, M_n=4200)



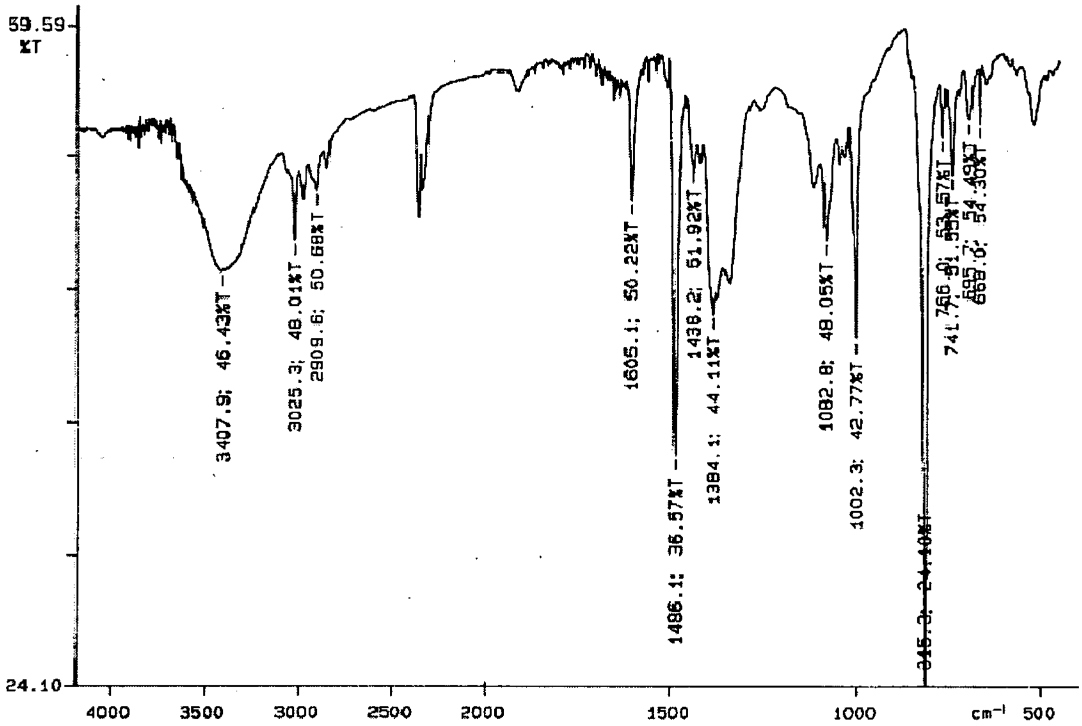
Appendix 3.1.8 FTIR spectrum of P4PV-DP (32% *cis*, M_n=2800)



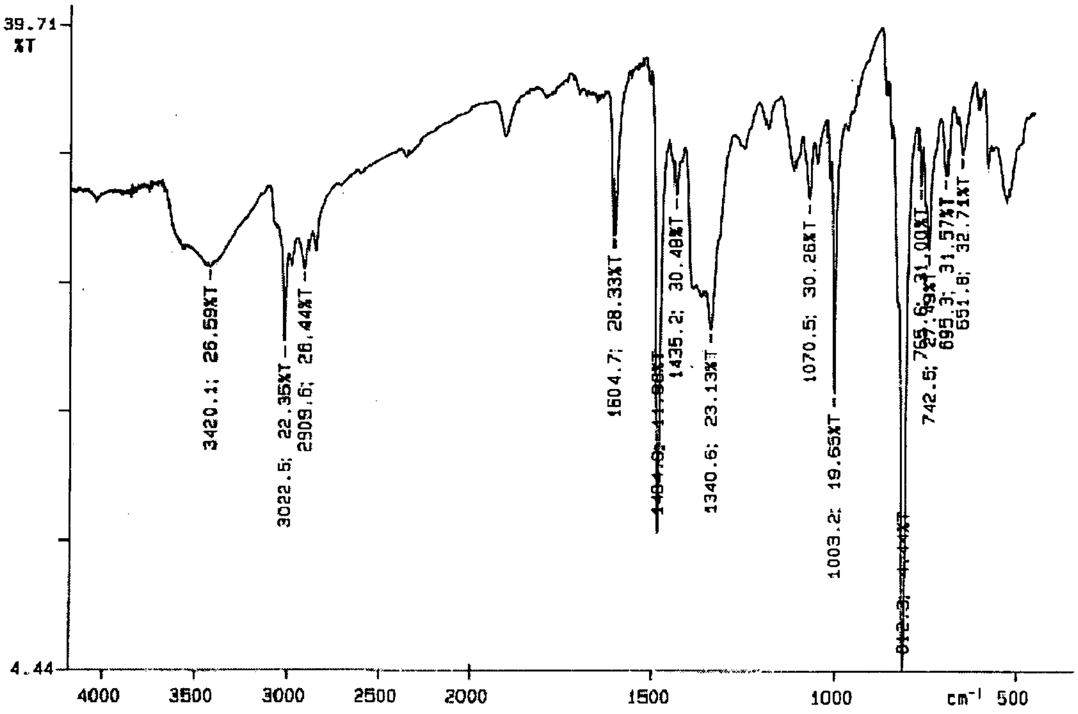
Appendix 3.1.9 FTIR spectrum of P4PV-DP (2% *cis*, M_n=1800)



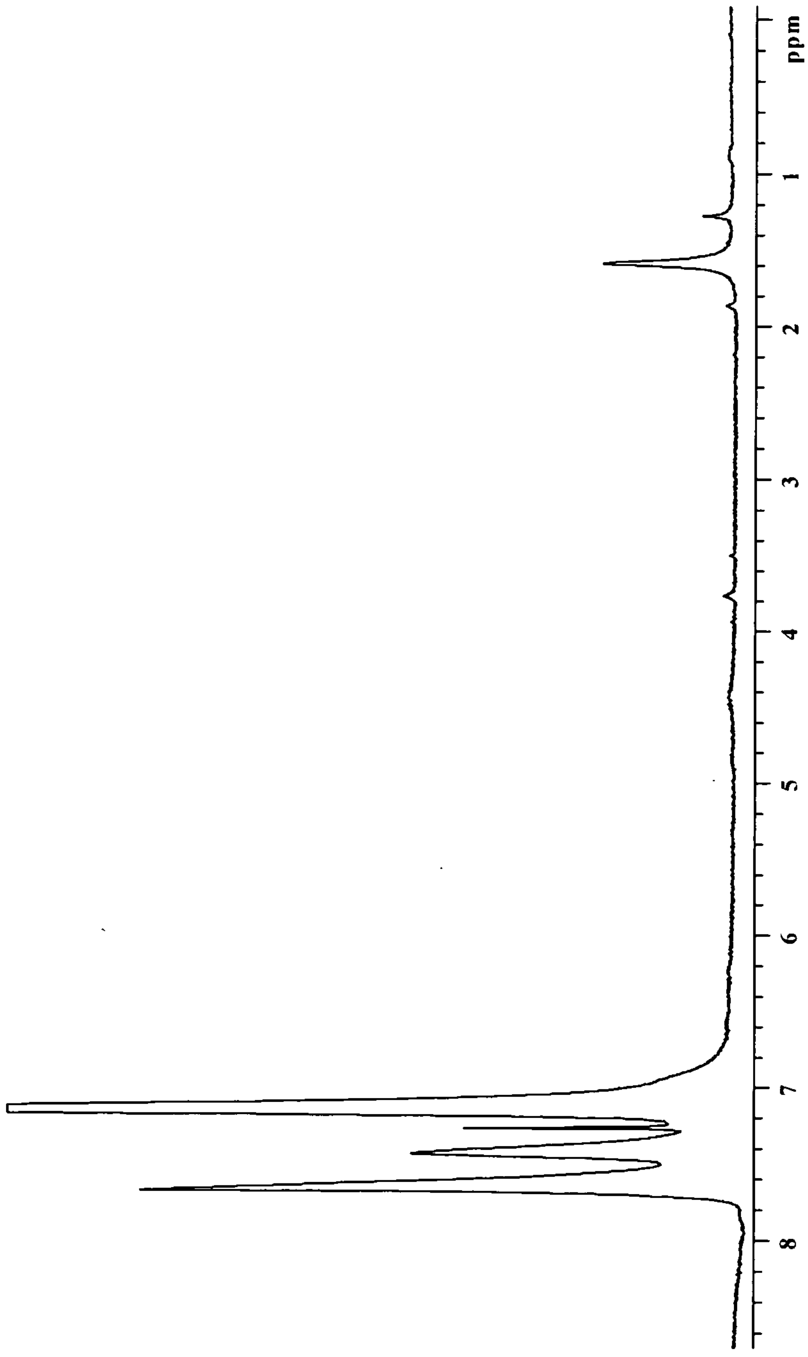
Appendix 3.1.10 FTIR spectrum of P4PV-DMe (98% *cis*)



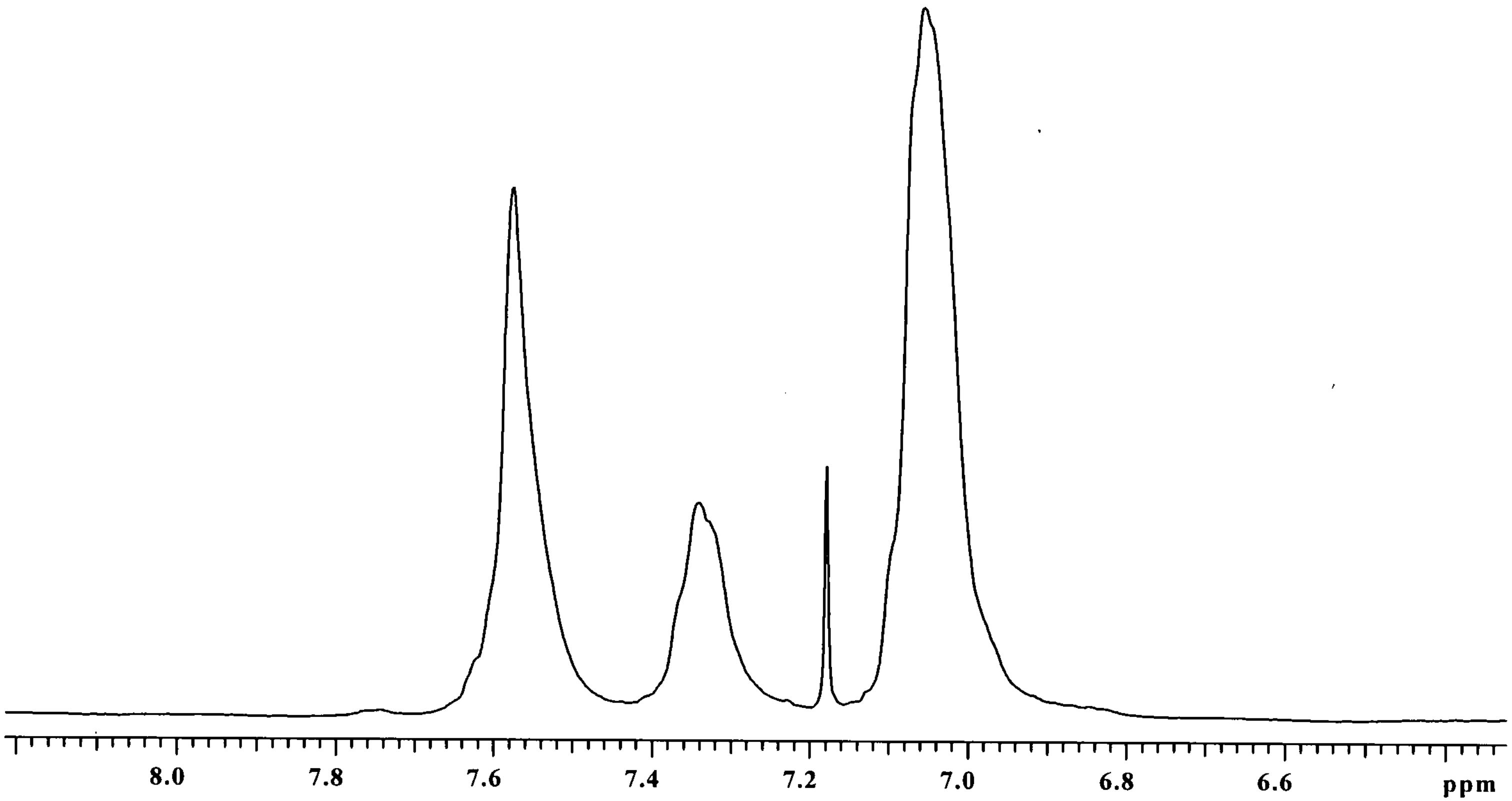
Appendix 3.1.11 FTIR spectrum of P4PV-DMe (2% *cis*)



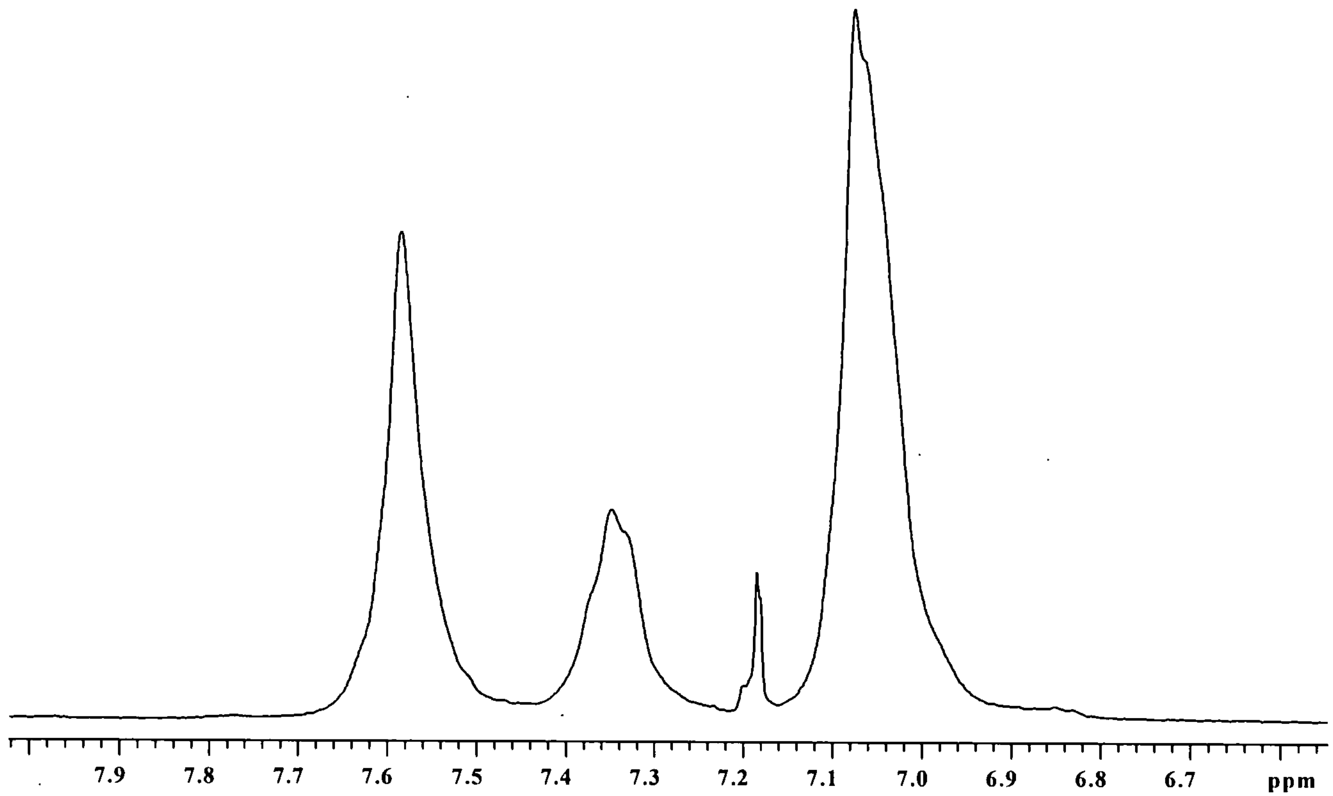
Appendix 3.1.12 FTIR spectrum of P4PV-DMe (80% *cis*, M_n=1100)



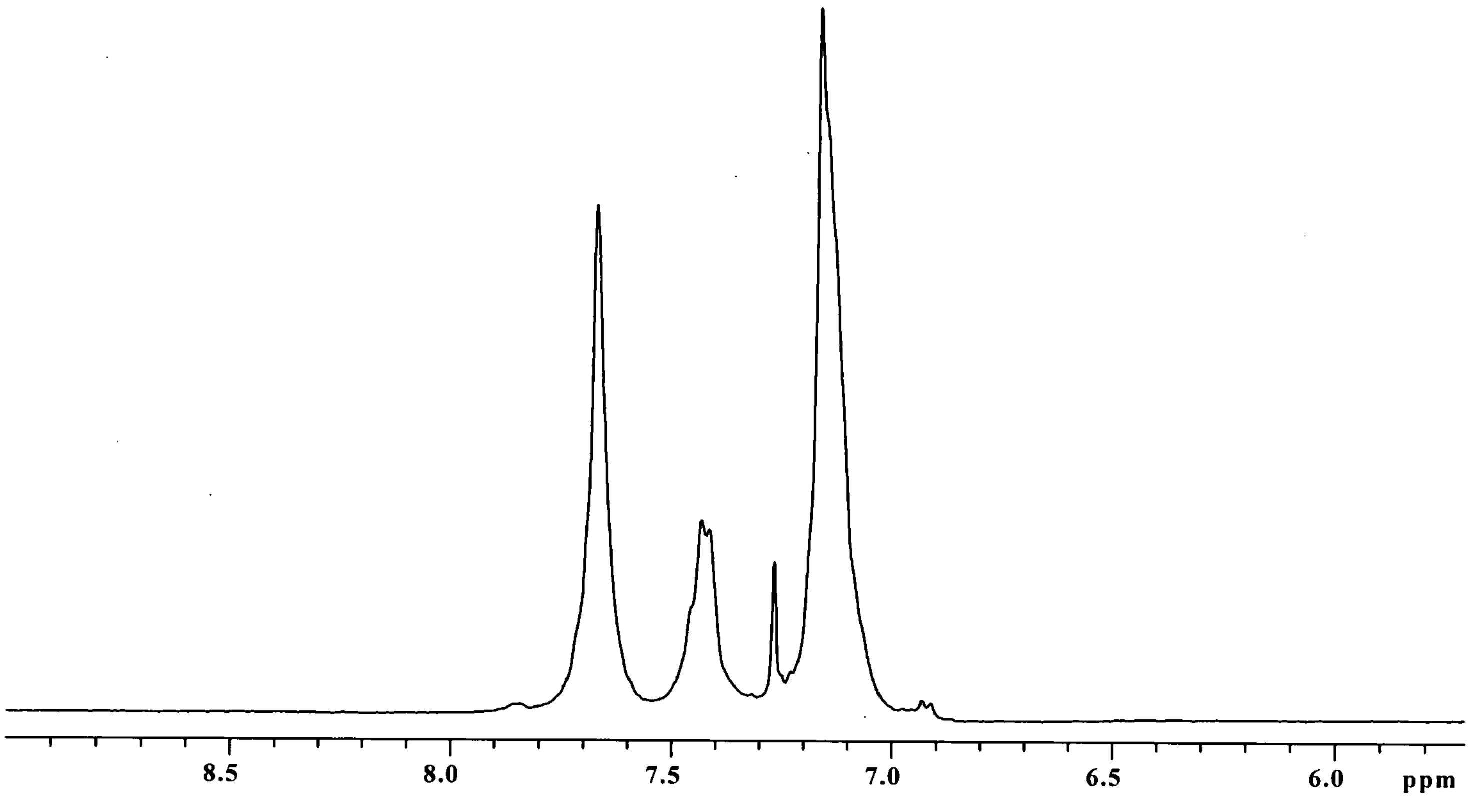
Appendix 3.2.1 ^{1}H Nmr spectrum of poly(tetra-*p*-phenylene diphenylvinylene) (97% *cis*, M_n=2900).



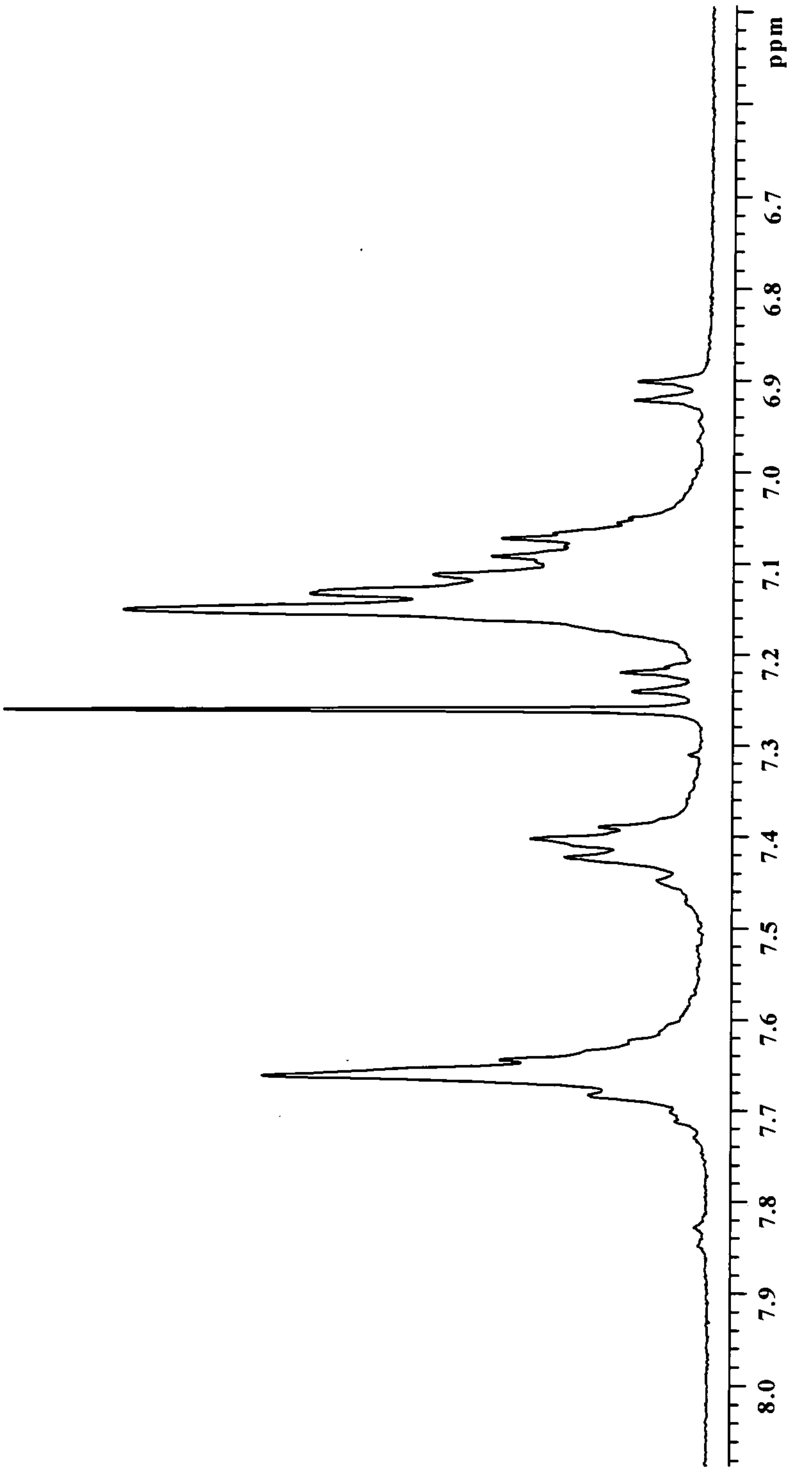
Appendix 3.2.2 ^{1}H Nmr spectrum of poly(tetra-*p*-phenylene diphenylvinylene) (62% *cis*, M_n=5000).



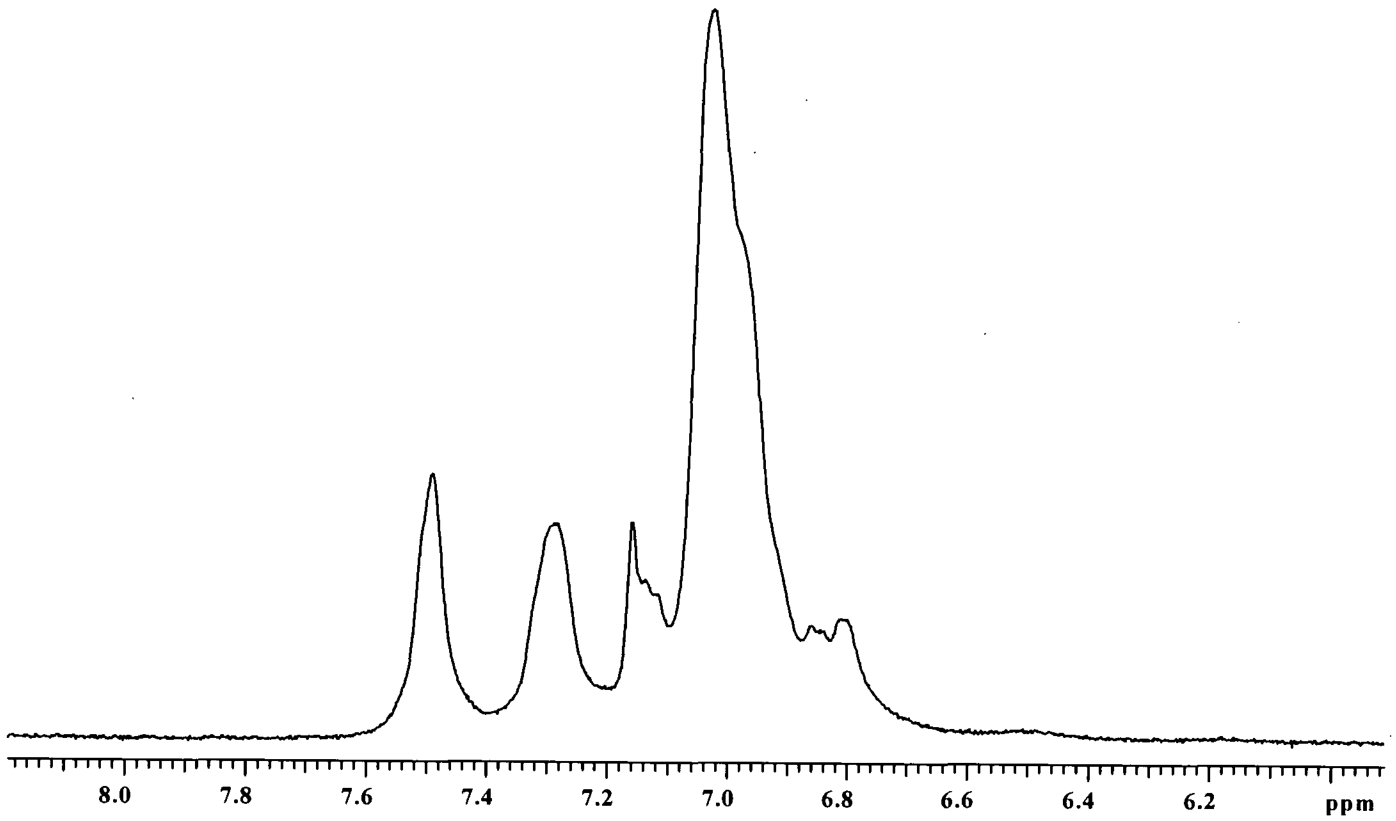
Appendix 3.2.3 ^{1}H Nmr spectrum of poly(tetra-*p*-phenylene diphenylvinylene) (48% *cis*, M_n=4200).



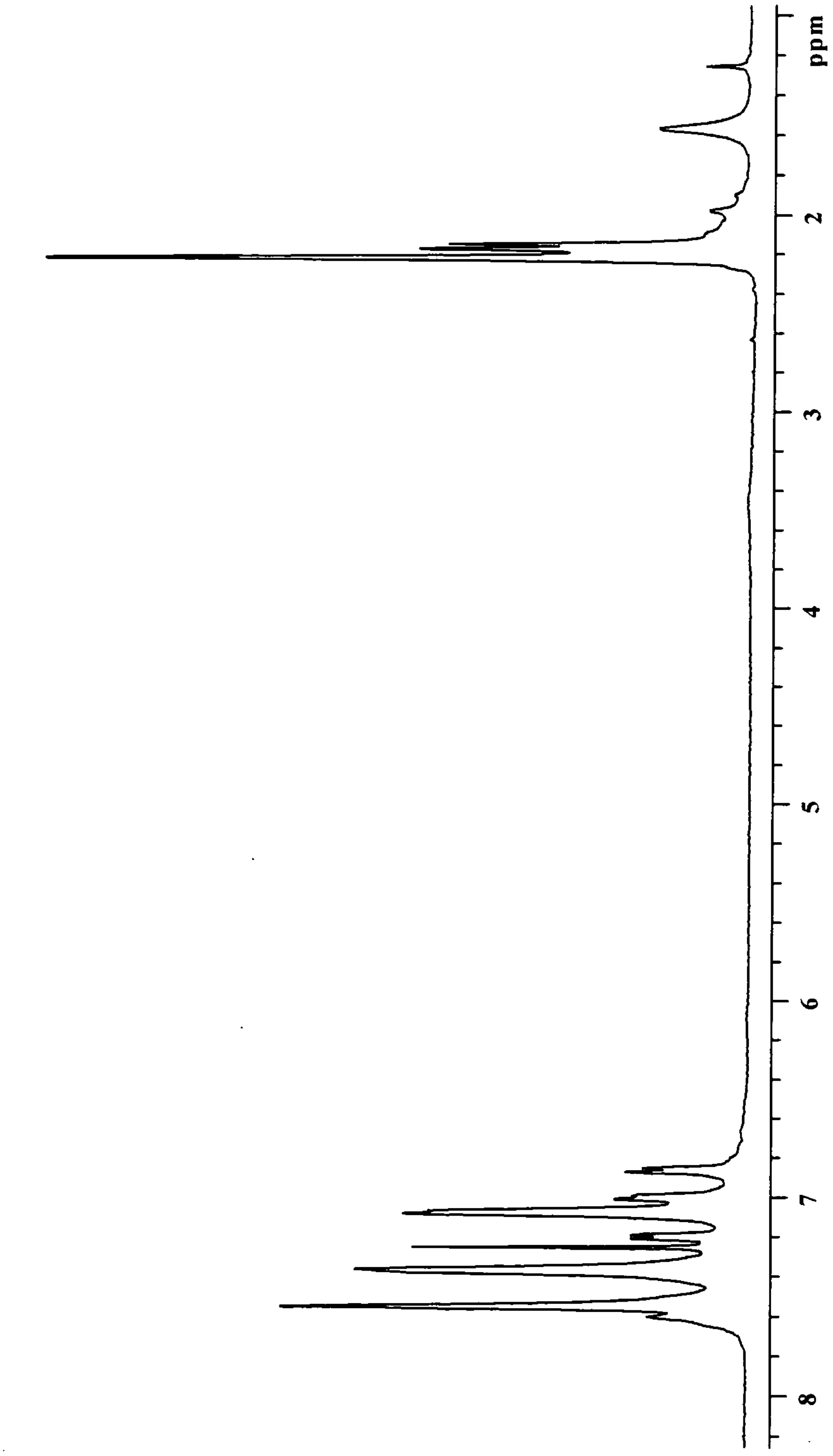
Appendix 3.2.4 ^{1}H Nmr spectrum of poly(tetra-*p*-phenylene diphenylvinylene) (32% *cis*, M_n=2800).



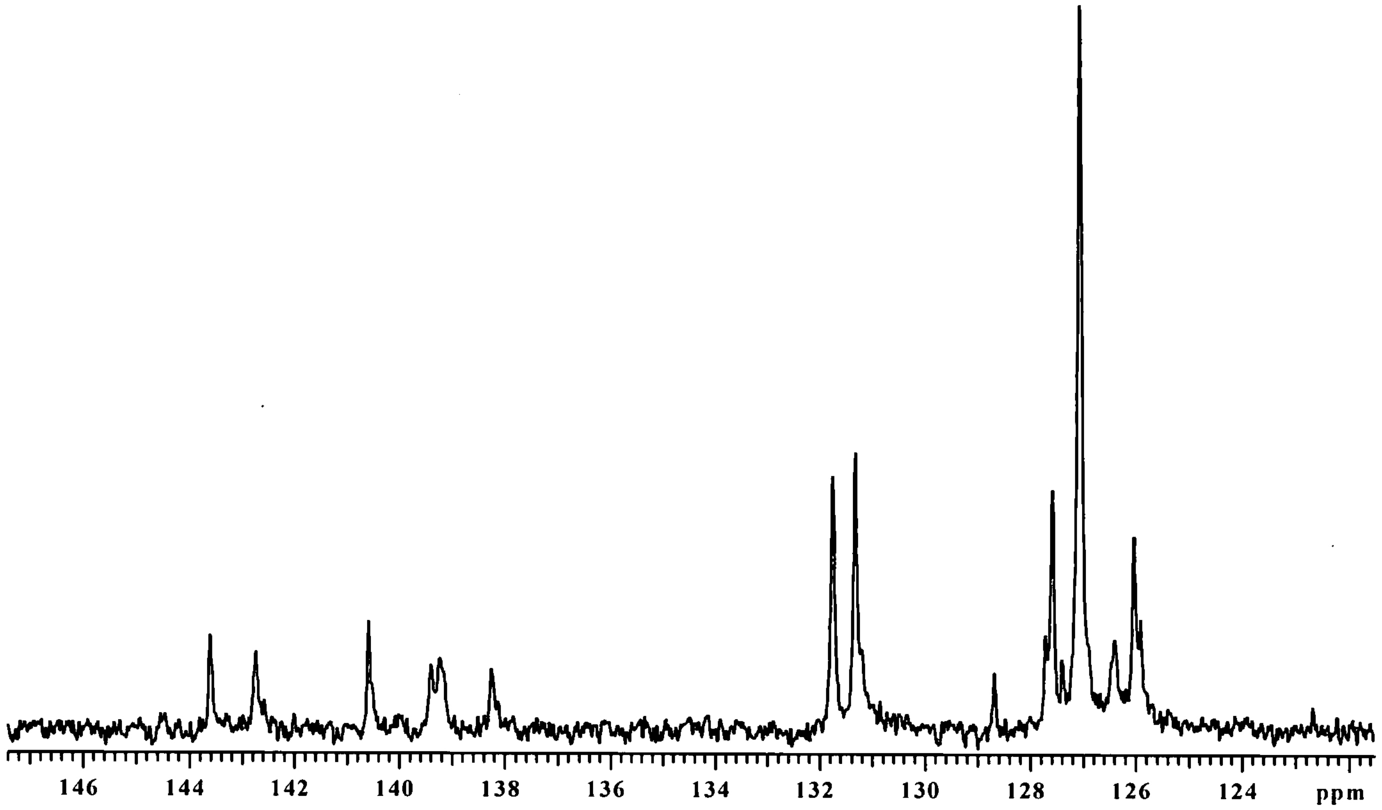
Appendix 3.2.5 ^{1}H Nmr spectrum of poly(tetra-*p*-phenylene diphenylvinylene) (2% *cis*, M_n=1800).



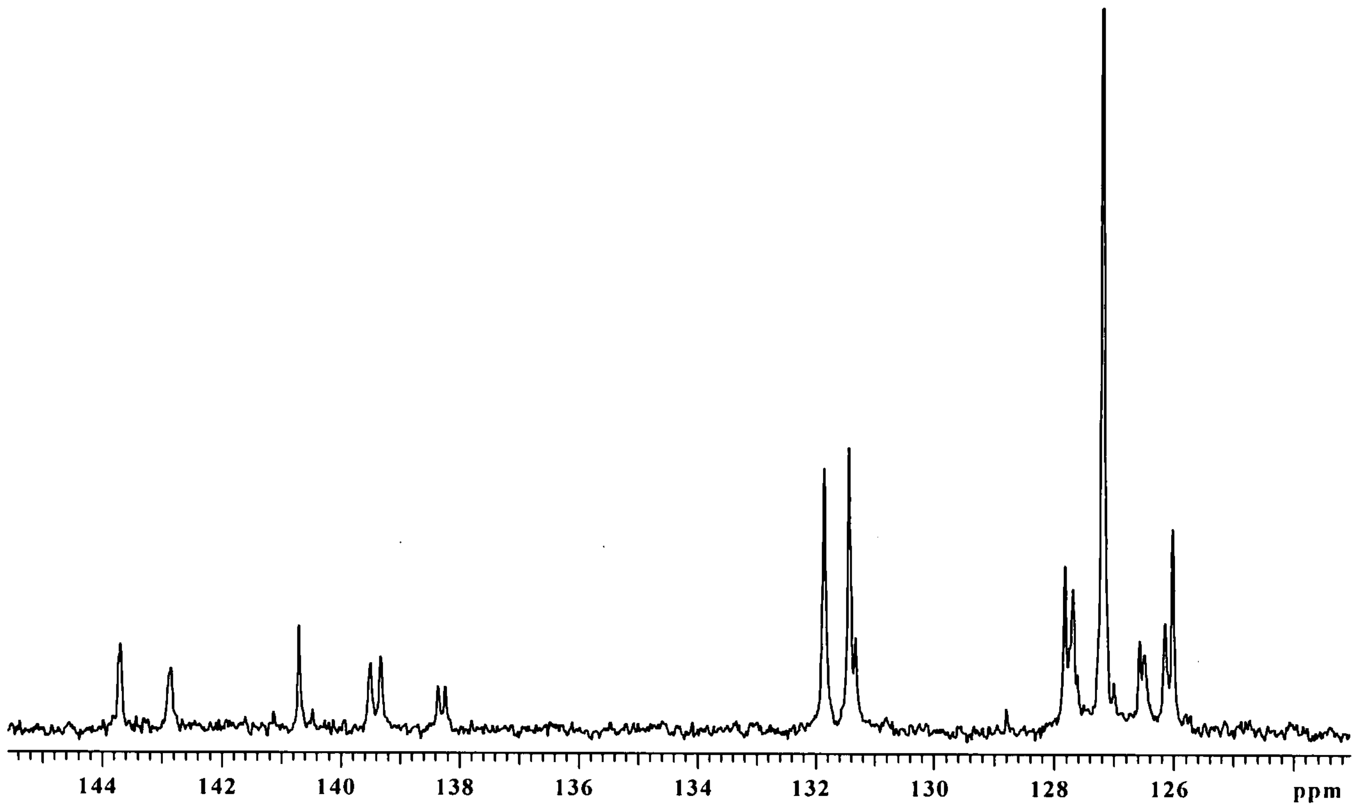
Appendix 3.2.6 ^{1}H Nmr spectrum of poly(tri-*p*-phenylene diphenylvinylene) (48% *cis*, M_n=1500).



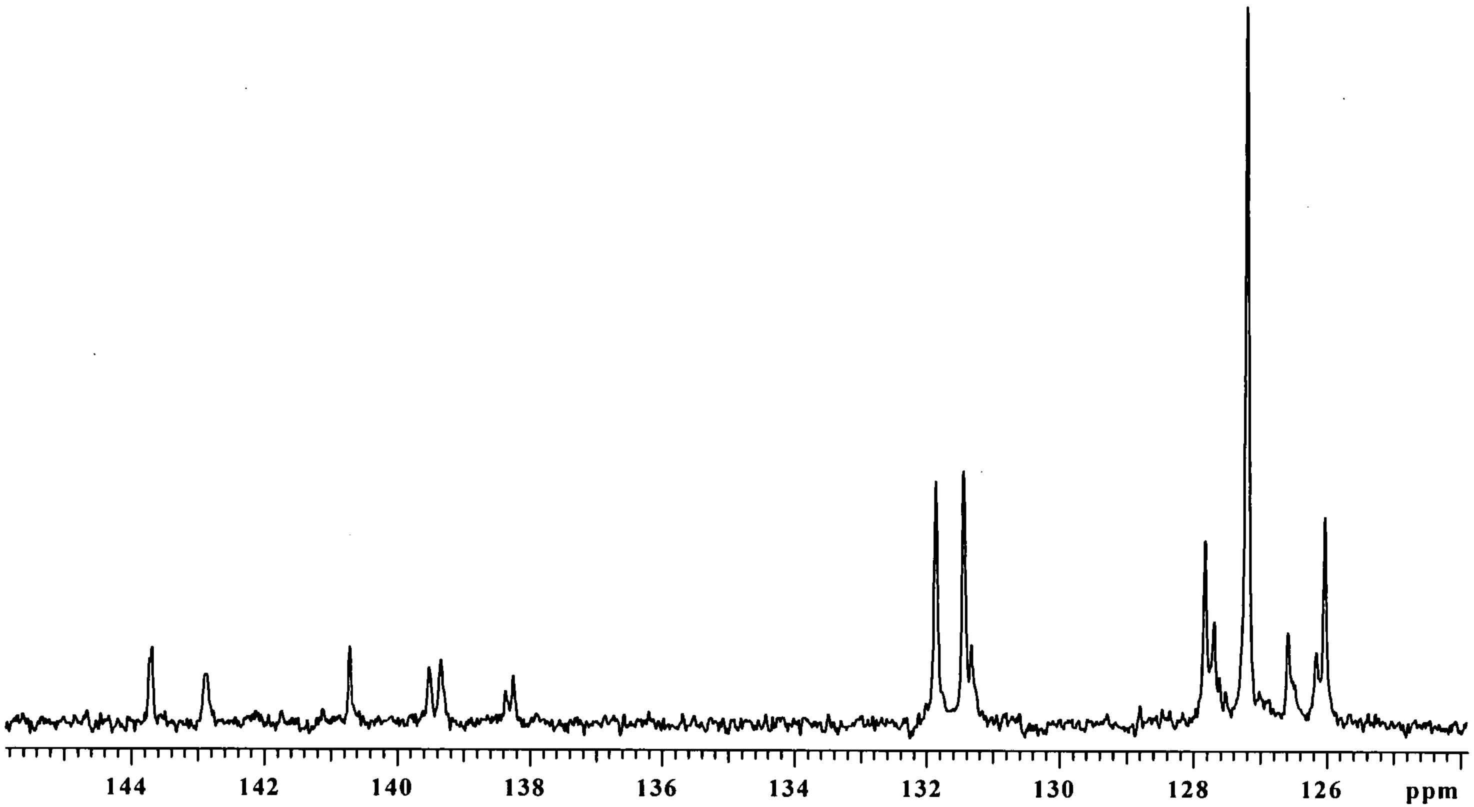
Appendix 3.2.7 ^{1}H Nmr spectrum of poly(tri-*p*-phenylene dimethylvinylene) (98% *cis*, M_n=1600).



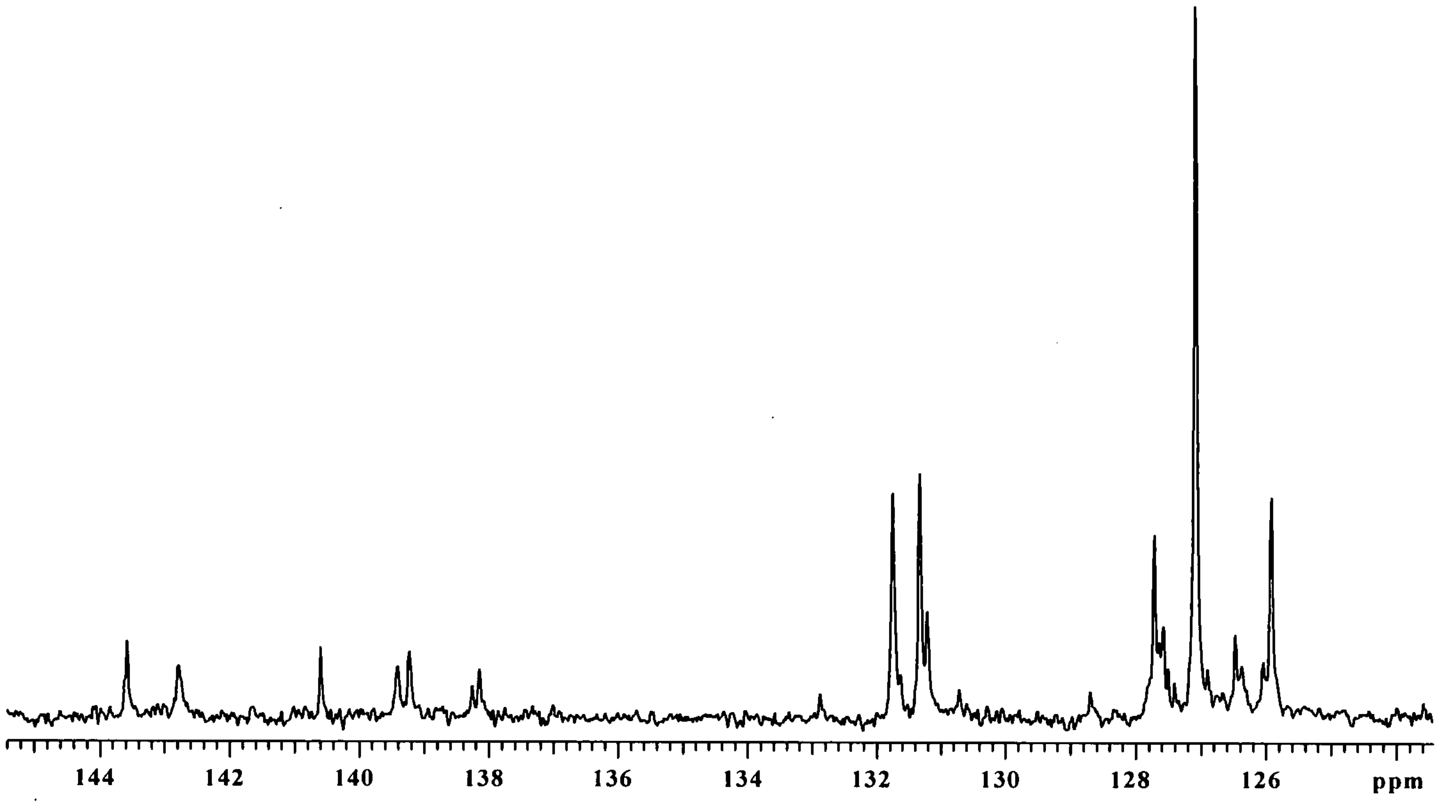
Appendix 3.3.1 ^{13}C Nmr spectrum of poly(tetra-*p*-phenylene diphenylvinylene) (97% *cis*, M_n=3850).



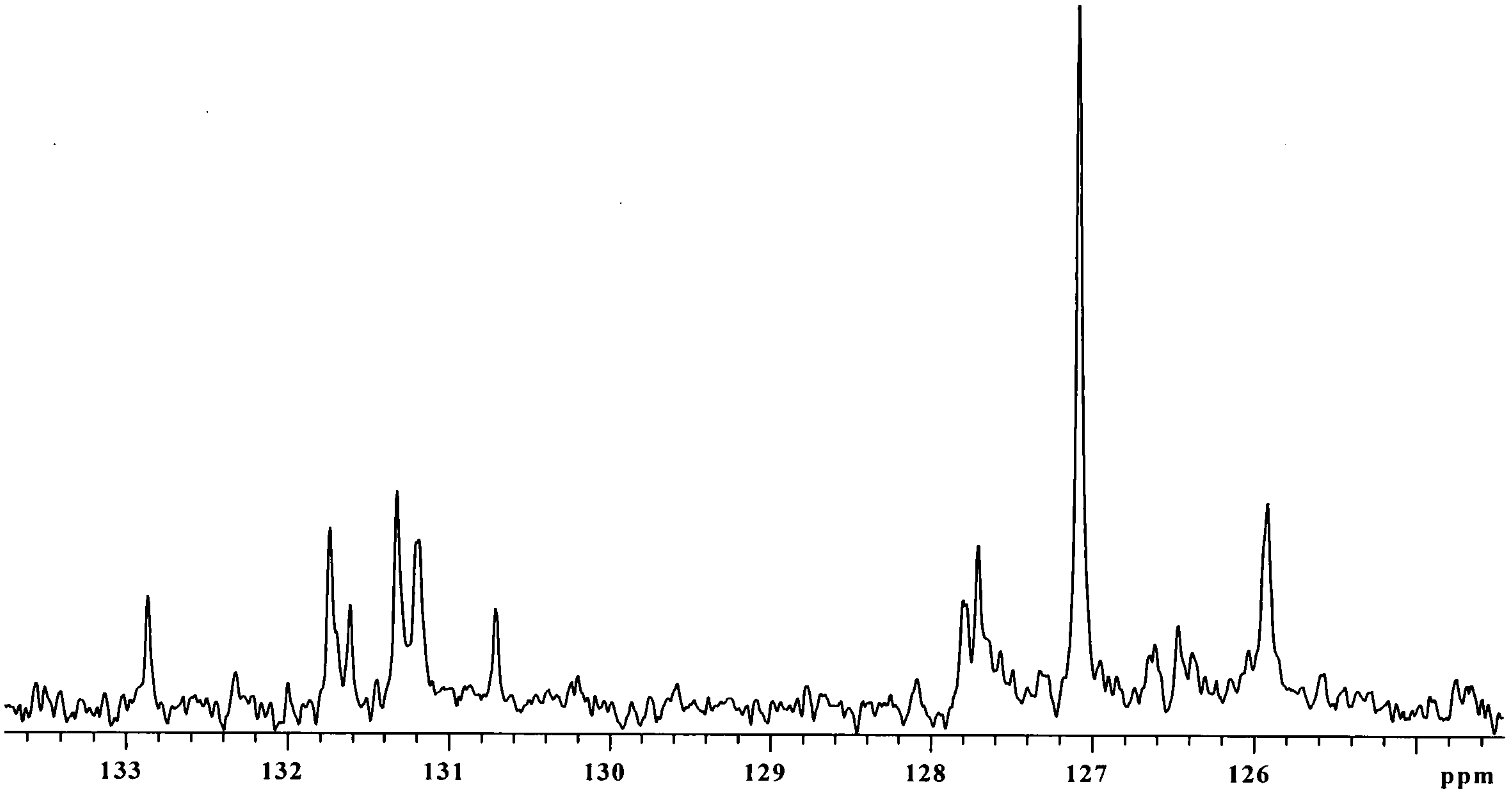
Appendix 3.3.2 ^{13}C Nmr spectrum of poly(tetra-*p*-phenylene diphenylvinylene) (62% *cis*, M_n=5000).



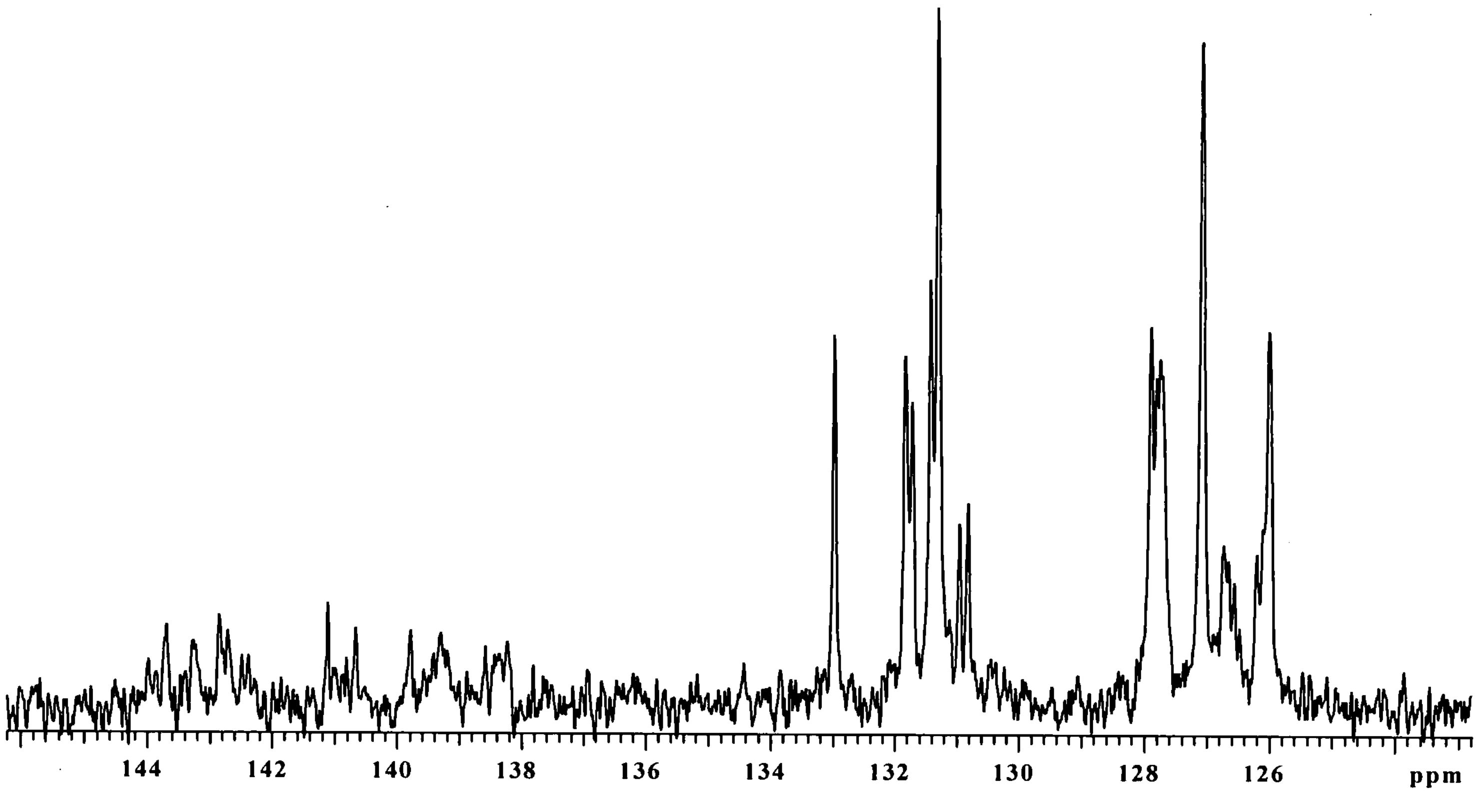
Appendix 3.3.3 ^{13}C Nmr spectrum of poly(tetra-*p*-phenylene diphenylvinylene) (48% *cis*, M_n=4200).



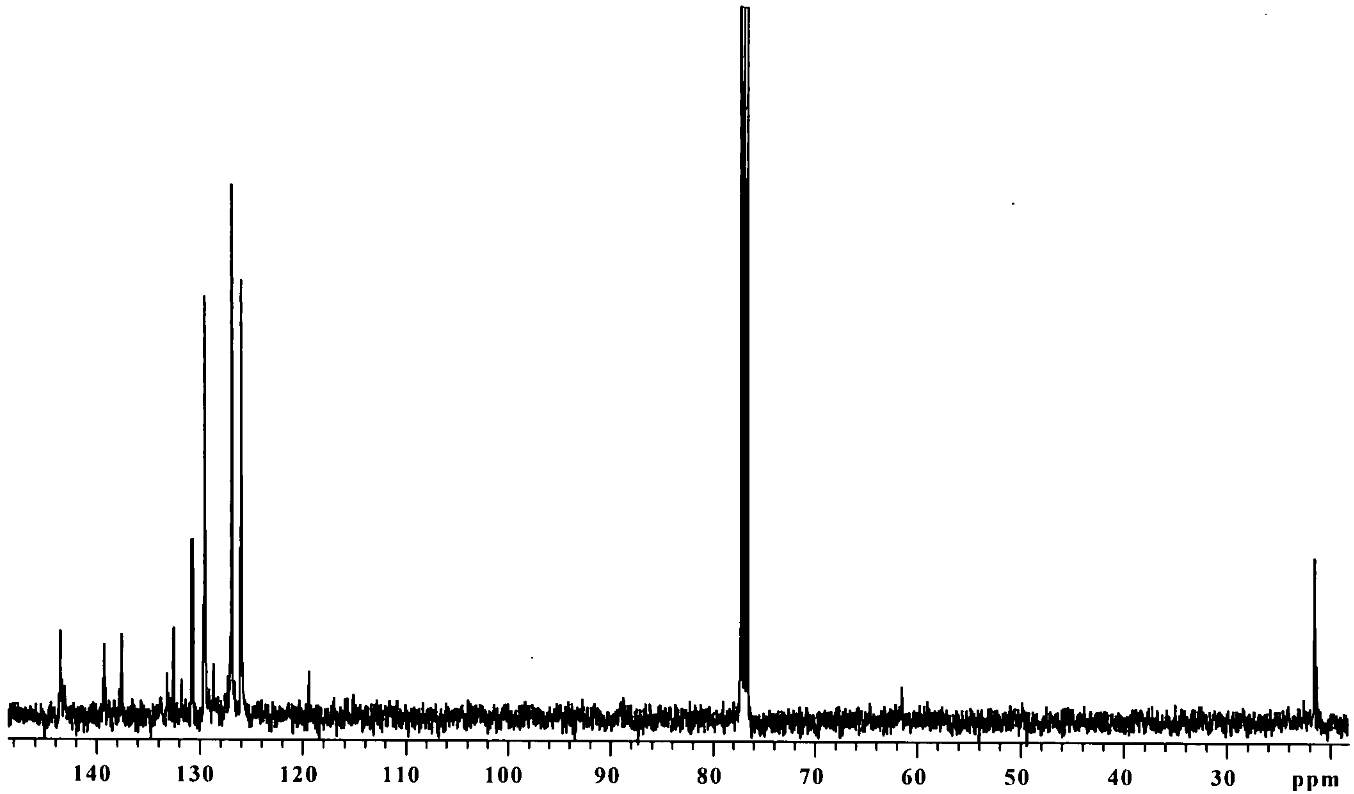
Appendix 3.3.4 ^{13}C Nmr spectrum of poly(tetra-*p*-phenylene diphenylvinylene) (32% *cis*, M_n=2800).



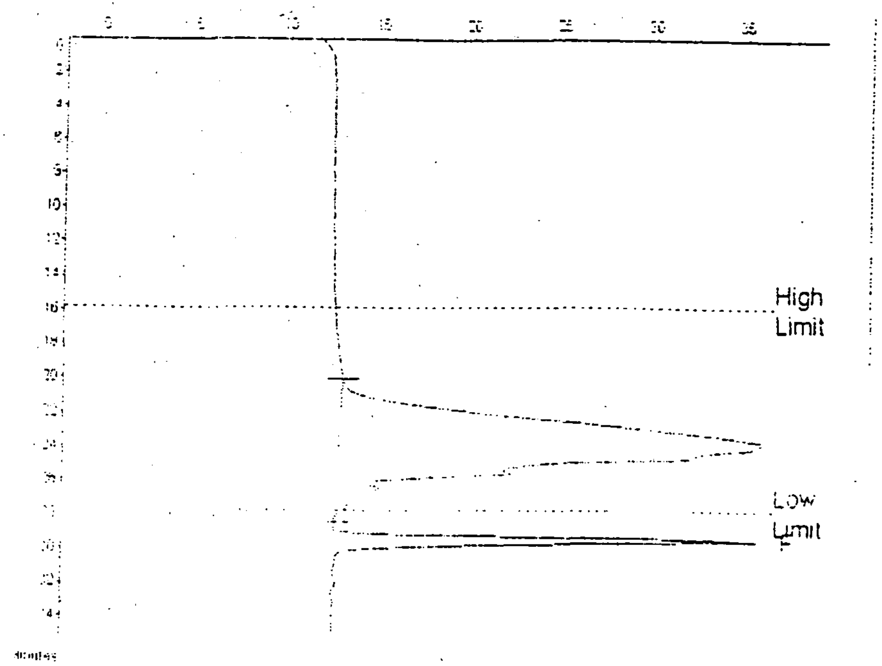
Appendix 3.3.5 ^{13}C Nmr spectrum of poly(tetra-*p*-phenylene diphenylvinylene) (2% *cis*, M_n=1800).



Appendix 3.3.6 ^{13}C Nmr spectrum of poly(tri-*p*-phenylene diphenylvinylene) (48% *cis*, M_n=1500).

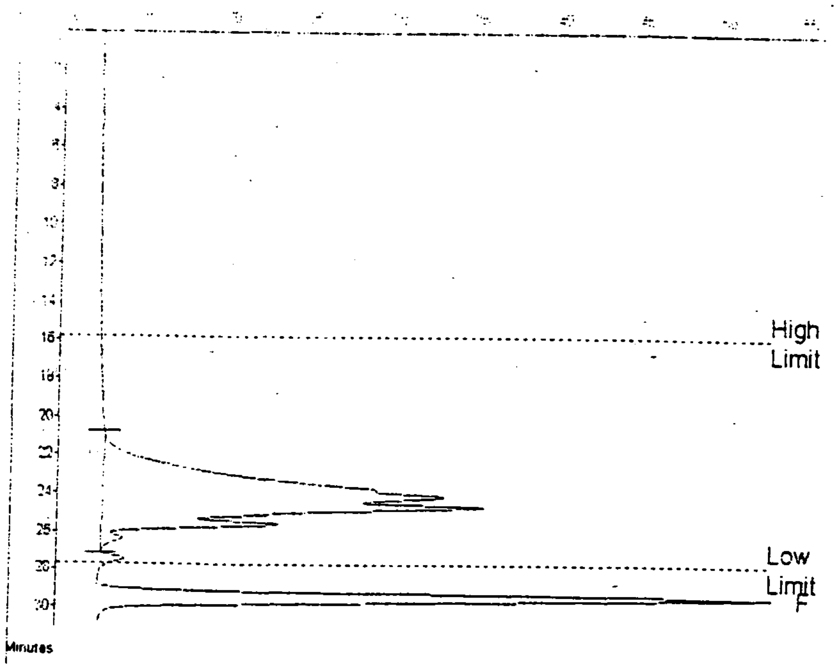


Appendix 3.3.7 ^{13}C Nmr spectrum of poly(tri-*p*-phenylene dimethylvinylene) (98% *cis*, M_n=1600).



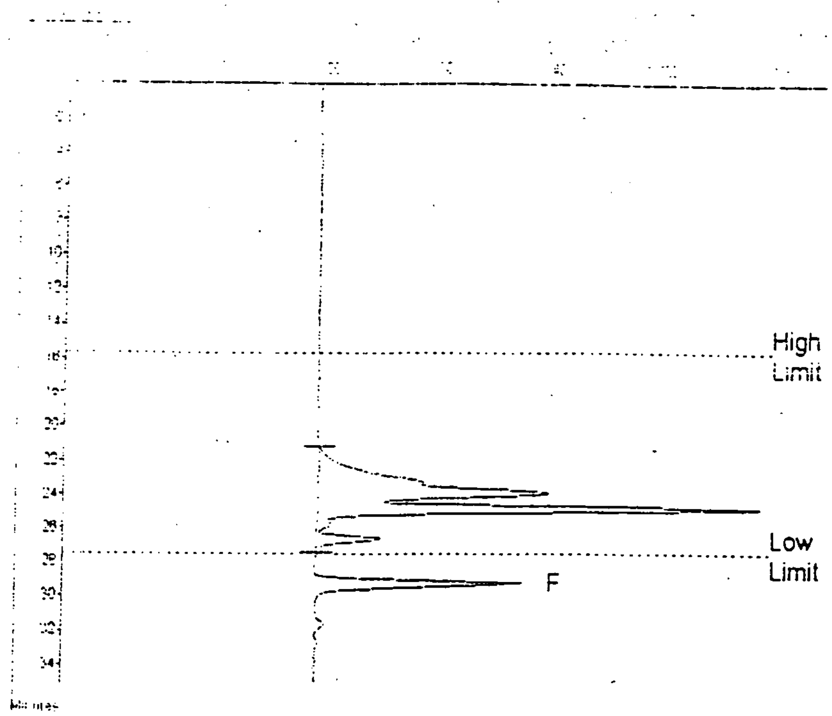
M_p=	1582	M_z=	446
M_n=	1120	M_{z+1}=	5579
M_w=	1974	M_v=	1812
Polydispersity=	1.762		

Appendix 3.4.1 GPC trace of poly(tri-*p*-phenylene dimethylvinylene) (80% *cis*).



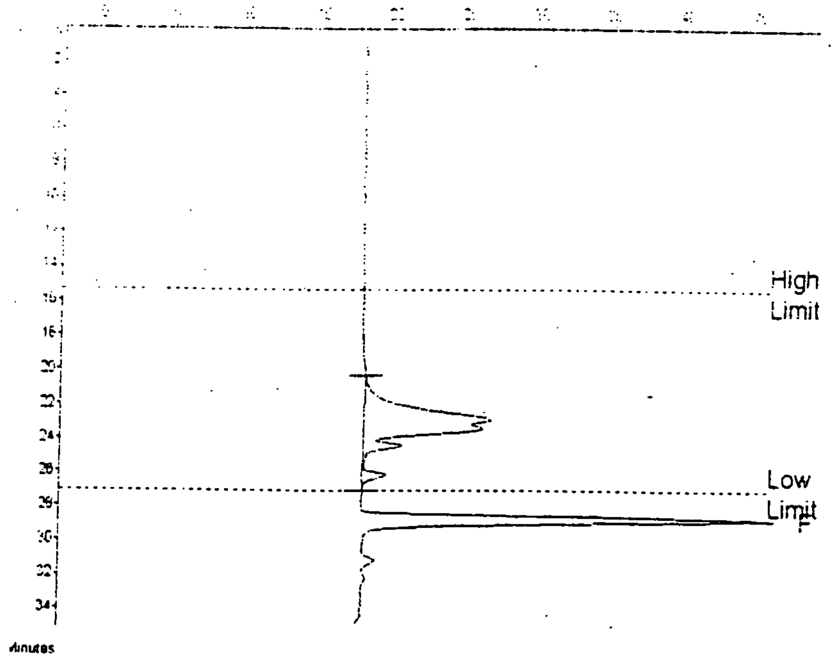
M_p=	890	M_z=	2078
M_n=	1002	M_{z+1}=	3130
M_w=	1402	M_v=	1326
Polydispersity=	1.399		

Appendix 3.4.2 GPC trace of poly(tri-*p*-phenylene dimethylvinylene) (98% *cis*).



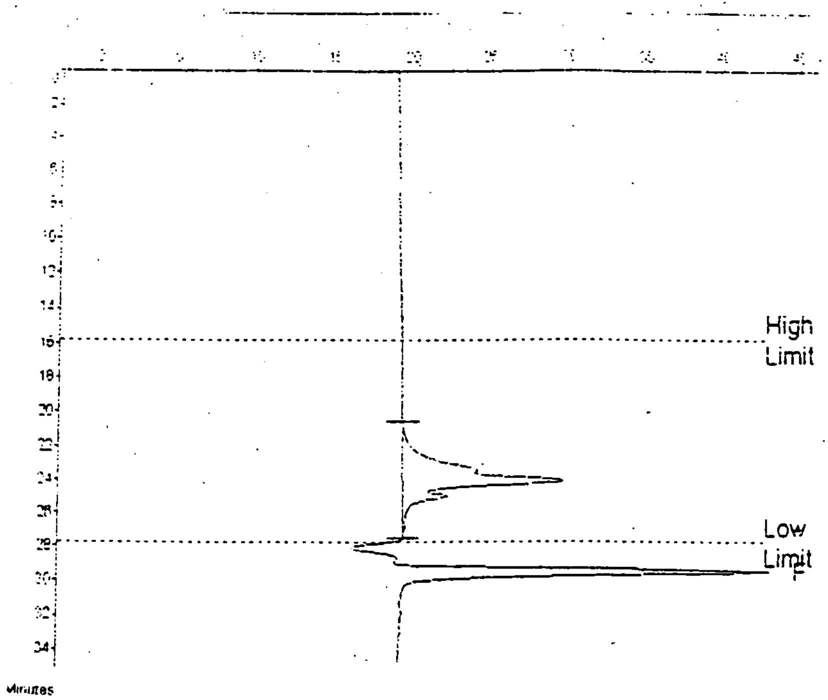
M_p= 719 M_z= 1721
M_n= 799 M_{z+1}= 2535
M_w= 1163 M_v= 1099
Polydispersity= 1.456

Appendix 3.4.3 GPC trace of poly(tri-*p*-phenylene diphenylvinylene) (48% *cis*).



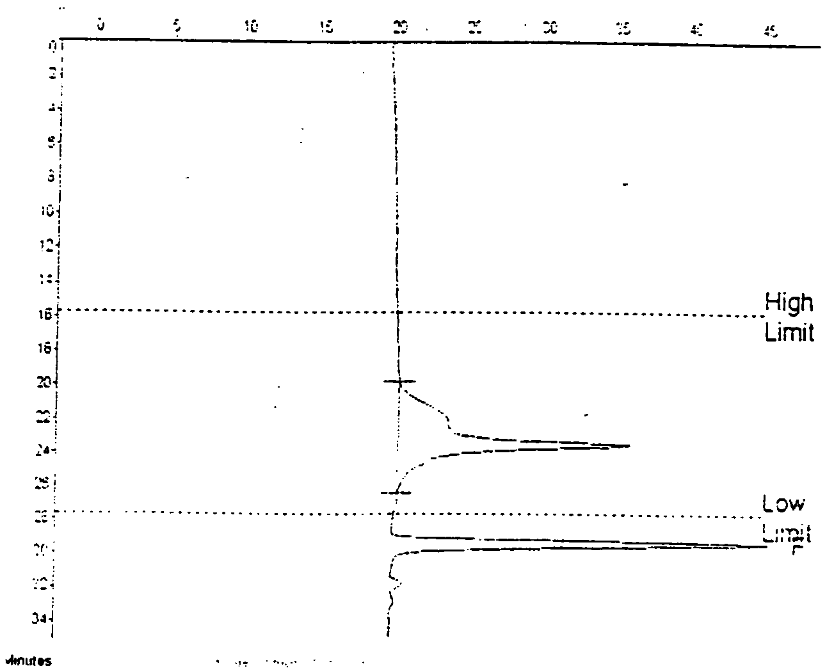
M_p= 1919 M_z= 2431
M_n= 1187 M_{z+1}= 3258
M_w= 1811 M_v= 1717
Polydispersity= 1.526

Appendix 3.4.4 GPC trace of poly(tri-*p*-phenylene diphenylvinylene) (62% *cis*).



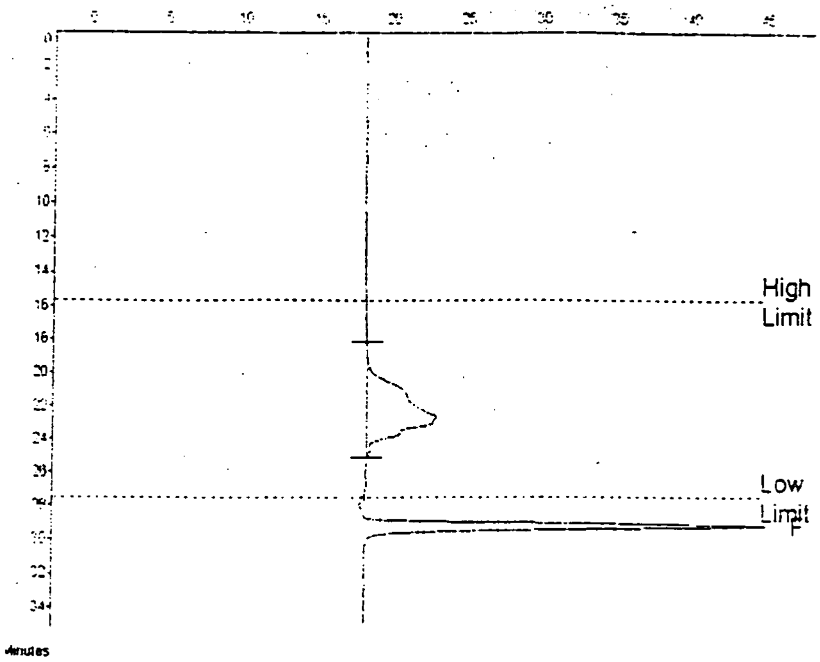
M_p=	1288	M_z=	2316
M_n=	1226	M_{z+1}=	3536
M_w=	1639	M_v=	1565
Polydispersity=	1.337		

Appendix 3.4.5 GPC trace of poly(tri-*p*-phenylene diphenylvinylene) (37% *cis*).



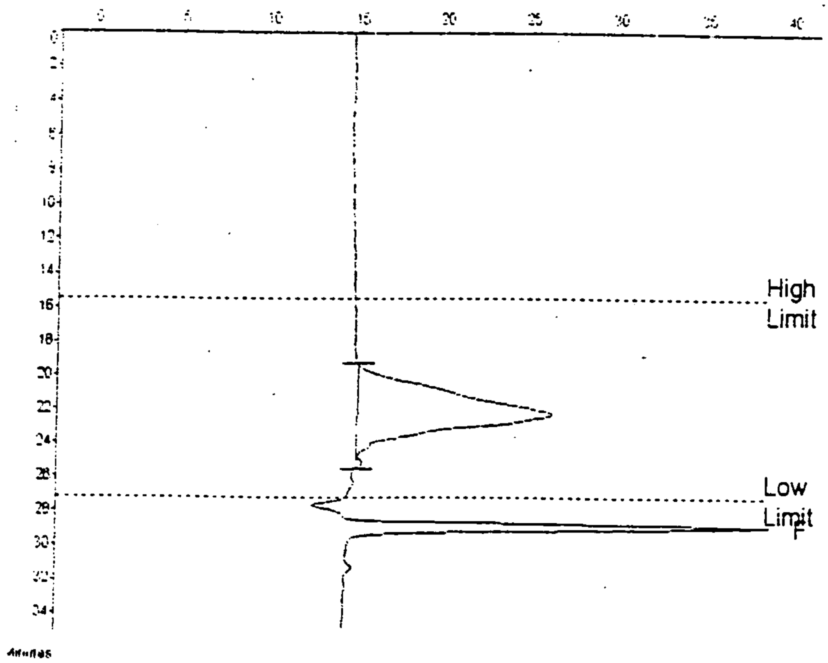
M_p=	1758	M_z=	5436
M_n=	1809	M_{z+1}=	8940
M_w=	2947	M_v=	2696
Polydispersity=	1.629		

Appendix 3.4.6 GPC trace of poly(tetra-*p*-phenylene diphenylvinylene) (2% *cis*).



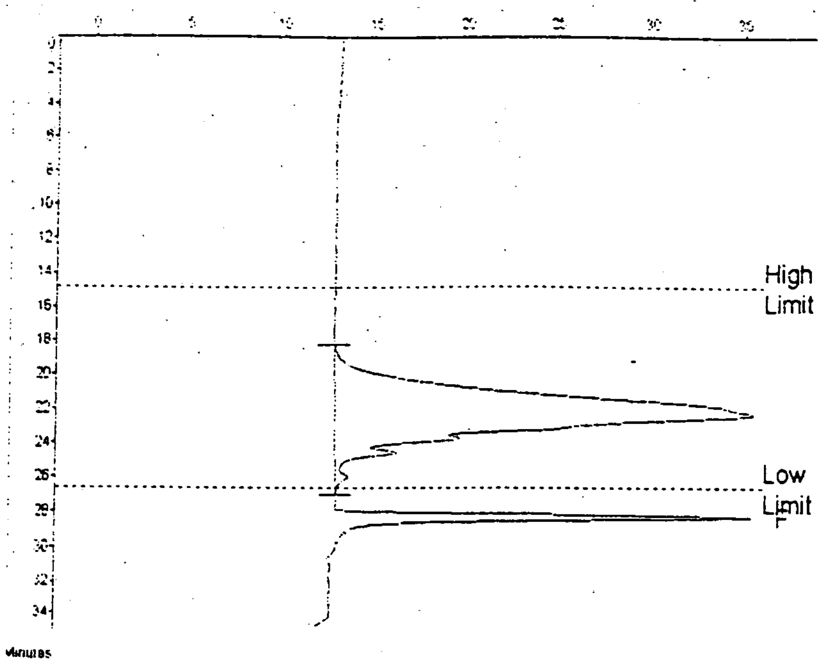
M_p= 2789 M_z= 8967
M_n= 2898 M_{z+1}= 17271
M_w= 4832 M_v= 4423
Polydispersity= 1.667

Appendix 3.4.7 GPC trace of poly(tetra-*p*-phenylene diphenylvinylene) (98% *cis*).



M_p= 3030 M_z= 7152
M_n= 2823 M_{z+1}= 10454
M_w= 4478 M_v= 4166
Polydispersity= 1.586

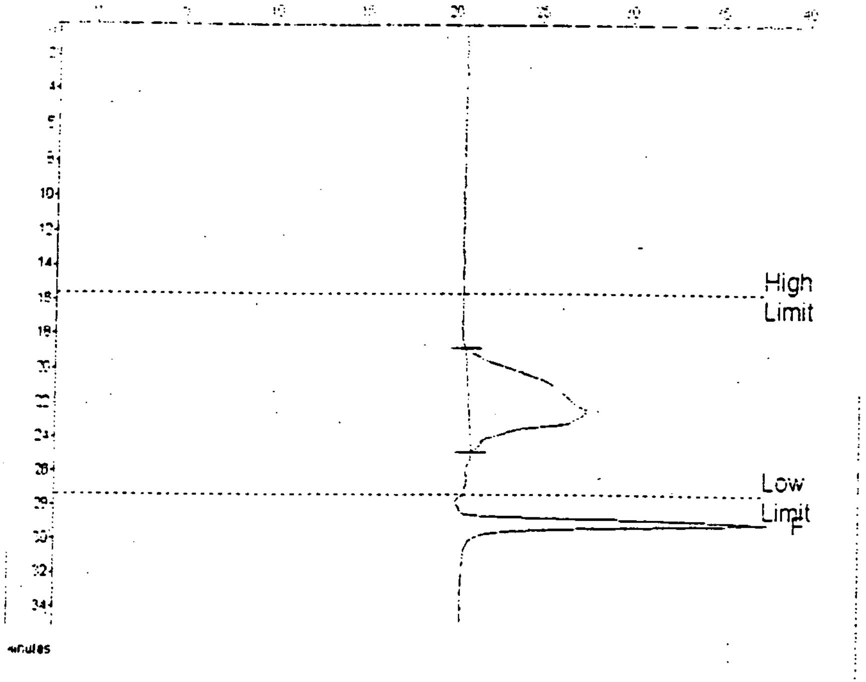
Appendix 3.4.8 GPC trace of poly(tetra-*p*-phenylene diphenylvinylene) (62% *cis*).



M_p=	2079	M_z=	5490
M_n=	1609	M_{z+1}=	10558
M_w=	2921	M_v=	2671

Polydispersity= 1.816

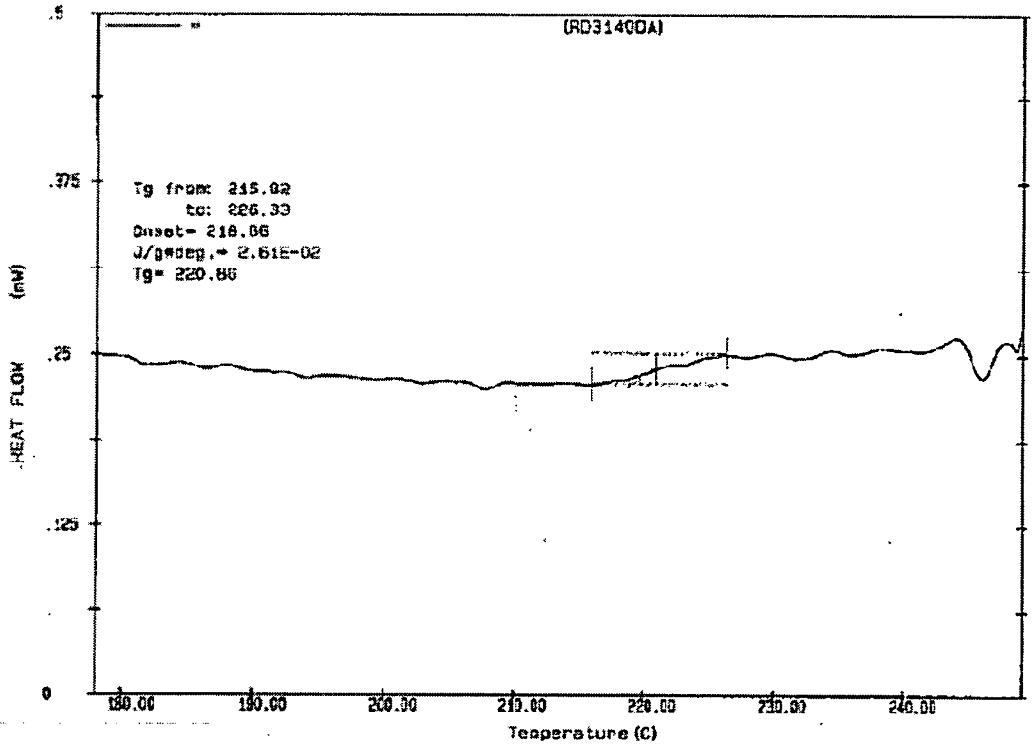
Appendix 3.4.9 GPC trace of poly(tetra-*p*-phenylene diphenylvinylene) (48% *cis*).



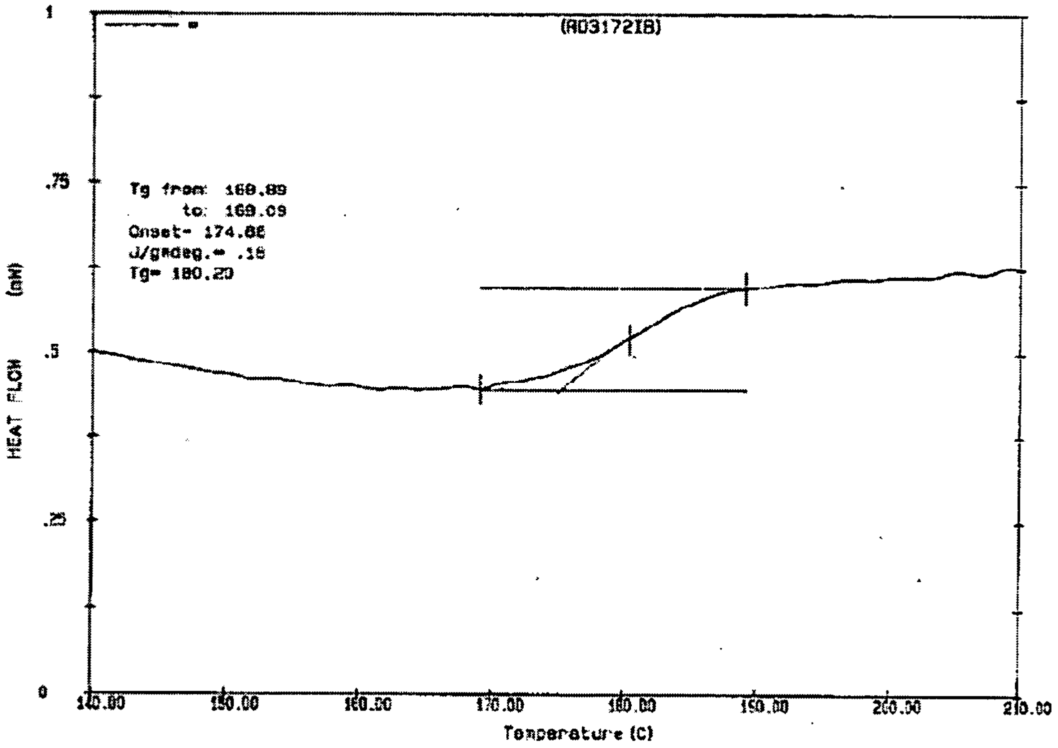
M_p=	3075	M_z=	11739
M_n=	3246	M_{z+1}=	17889
M_w=	6205	M_v=	5505

Polydispersity= 1.911

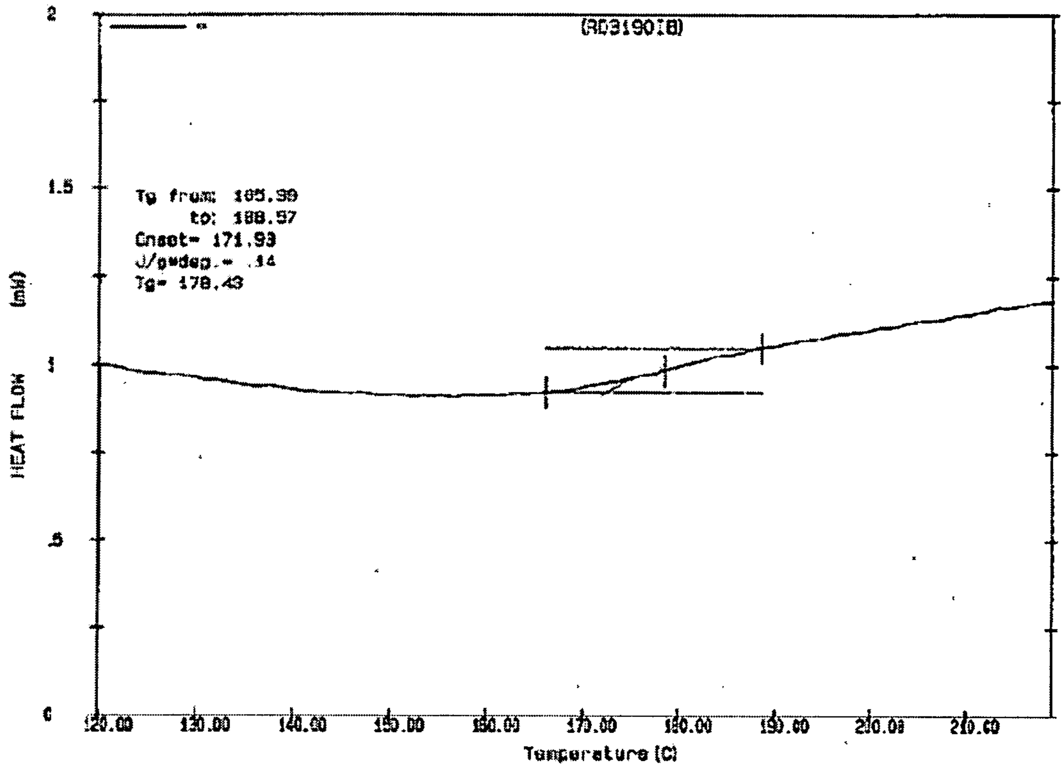
Appendix 3.4.10 GPC trace of poly(tetra-*p*-phenylene diphenylvinylene) (32% *cis*).



Appendix 3.5.1 DSC trace of poly(tetra-*p*-phenylene diphenylvinylene) (48% *cis*, M_n=4200)



Appendix 3.5.2 DSC trace of poly(tri-*p*-phenylene diphenylvinylene) (48% *cis*, M_n=1500)



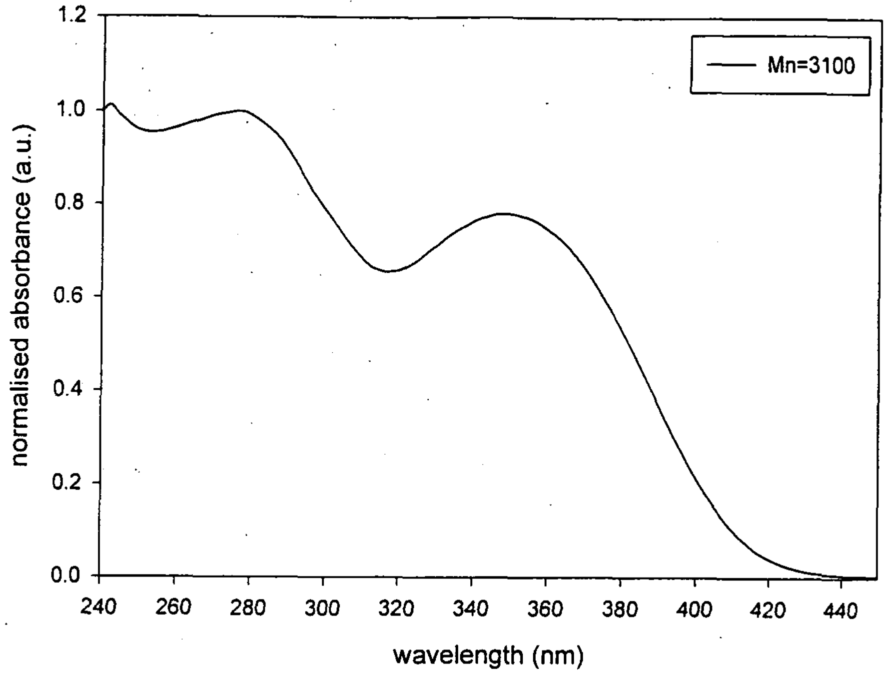
Appendix 3.5.3 DSC trace of poly(tri-*p*-phenylene dimethylvinylene) (80% *cis*, M_n=1900)

Appendix 4 Analytical data for Chapter 5

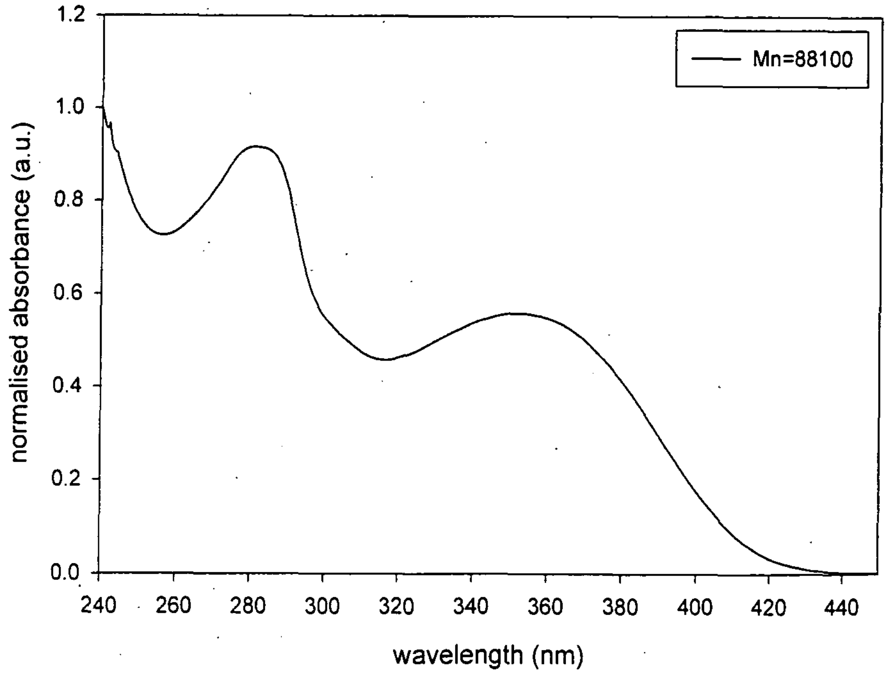
Appendix 4.1 UV-visible absorption spectra

Appendix 4.2 Photoluminescence (PL) spectra

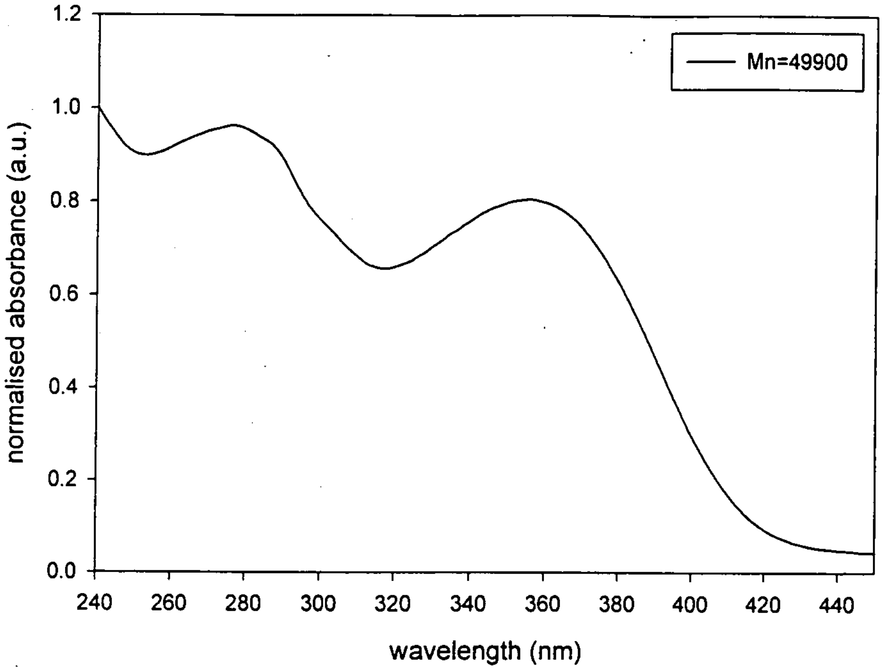
Appendix 4.3 Experimental methods for photoluminescence and photoluminescence efficiency



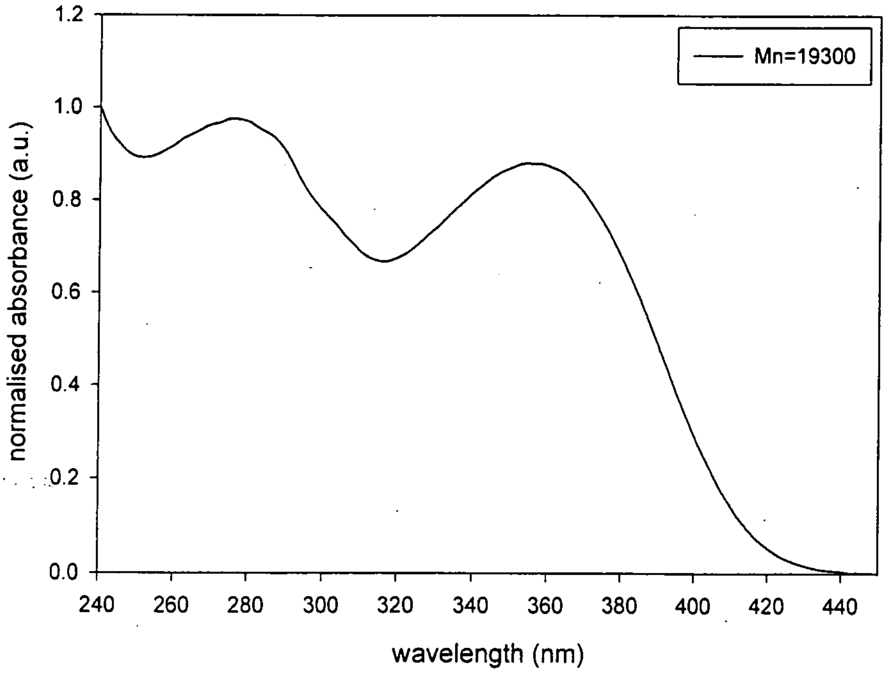
Appendix 4.1.1 UV-visible absorption spectrum of PDPV (pristine)



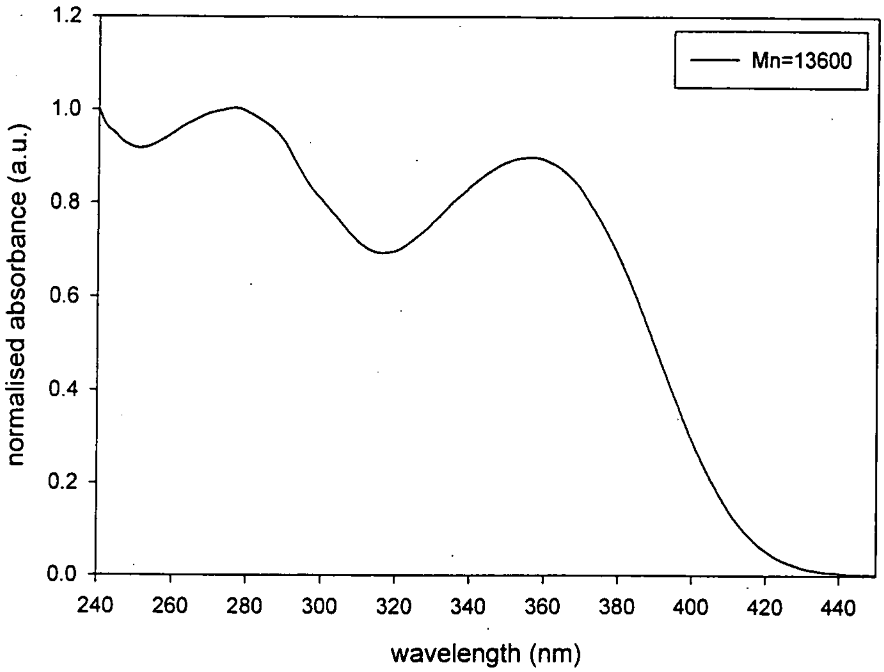
Appendix 4.1.2 UV-visible absorption spectrum of PDPV (fraction 1)



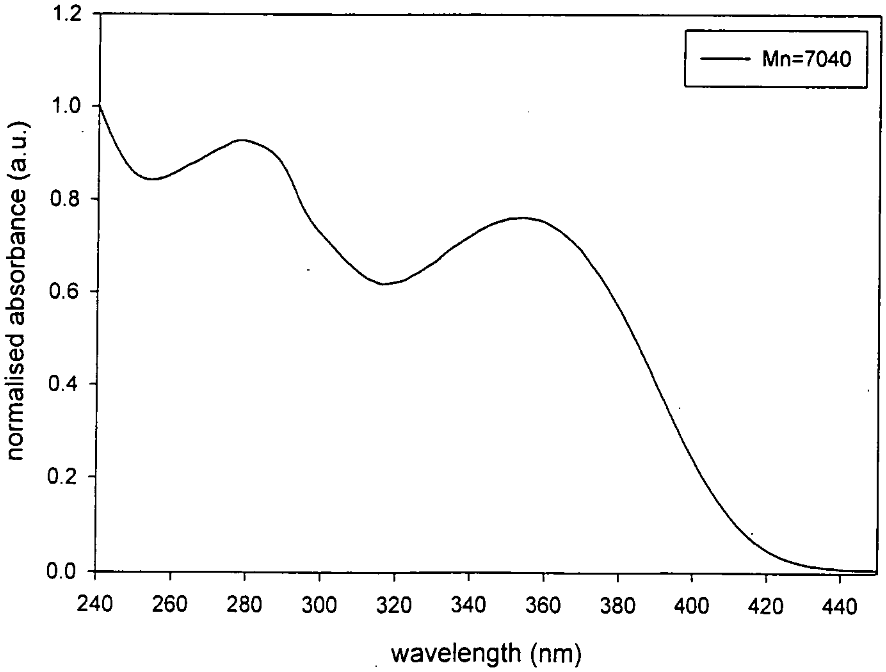
Appendix 4.1.3 UV-visible absorption spectrum of PDPV (fraction 2)



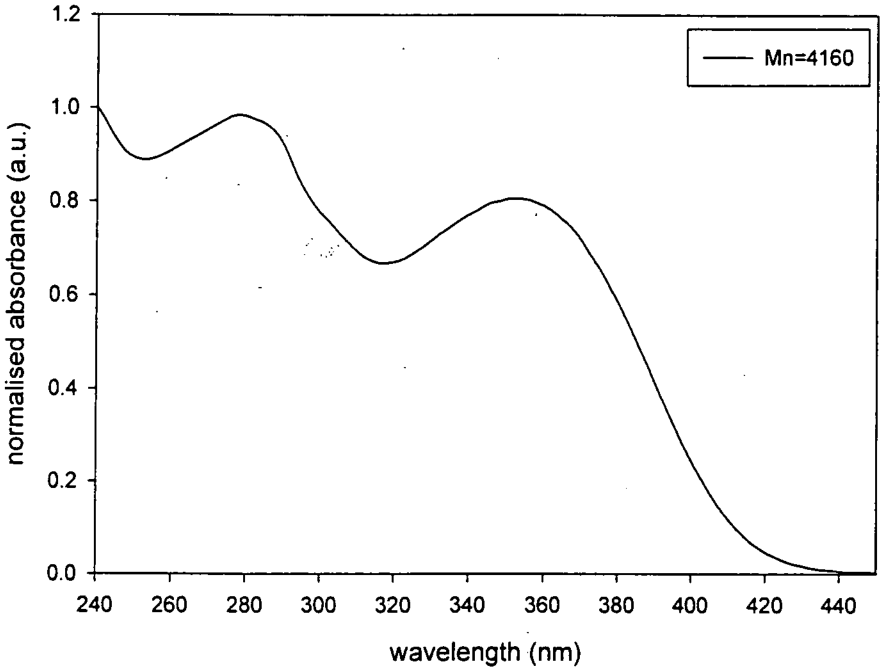
Appendix 4.1.4 UV-visible absorption spectrum of PDPV (fraction 4).



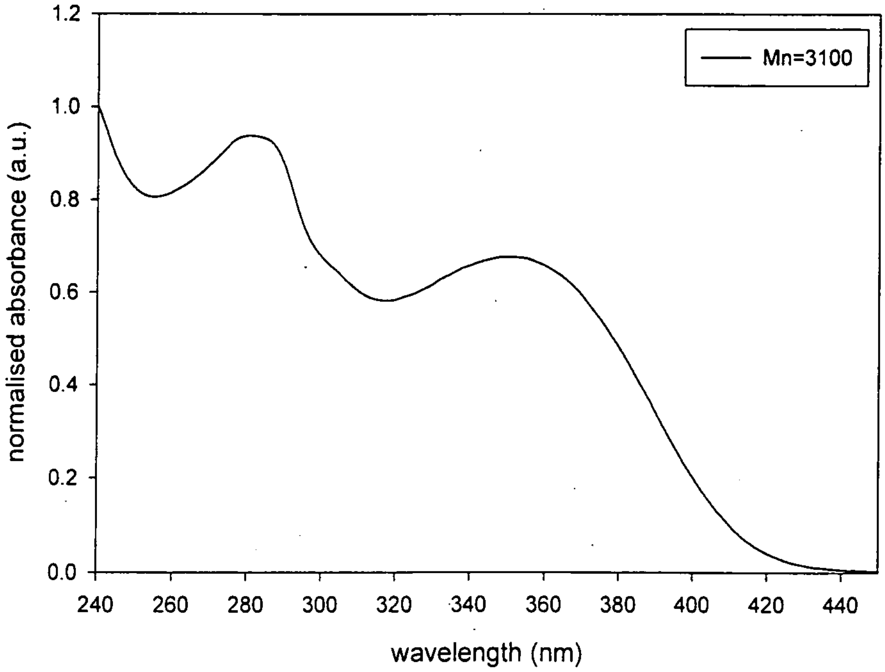
Appendix 4.1.5 UV-visible absorption spectrum of PDPV (fraction 6)



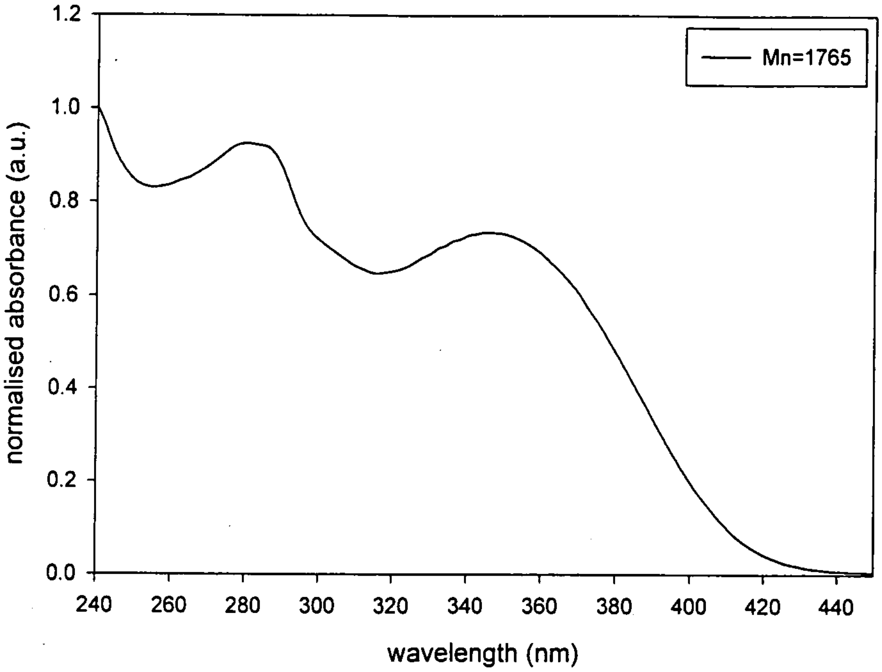
Appendix 4.1.6 UV-visible absorption spectrum of PDPV (fraction 8)



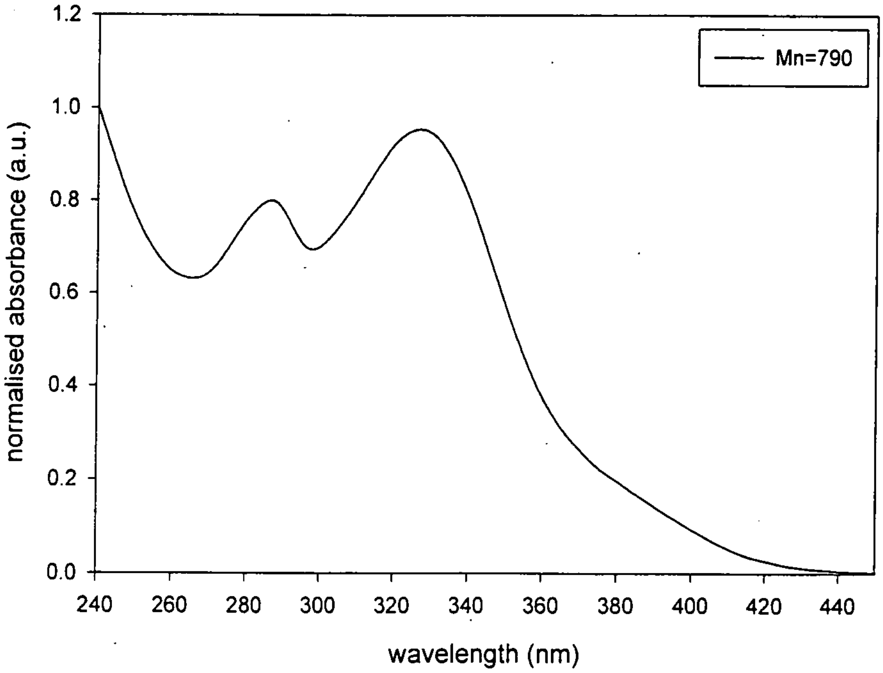
Appendix 4.1.7 UV-visible absorption spectrum of PDPV (fraction 10)



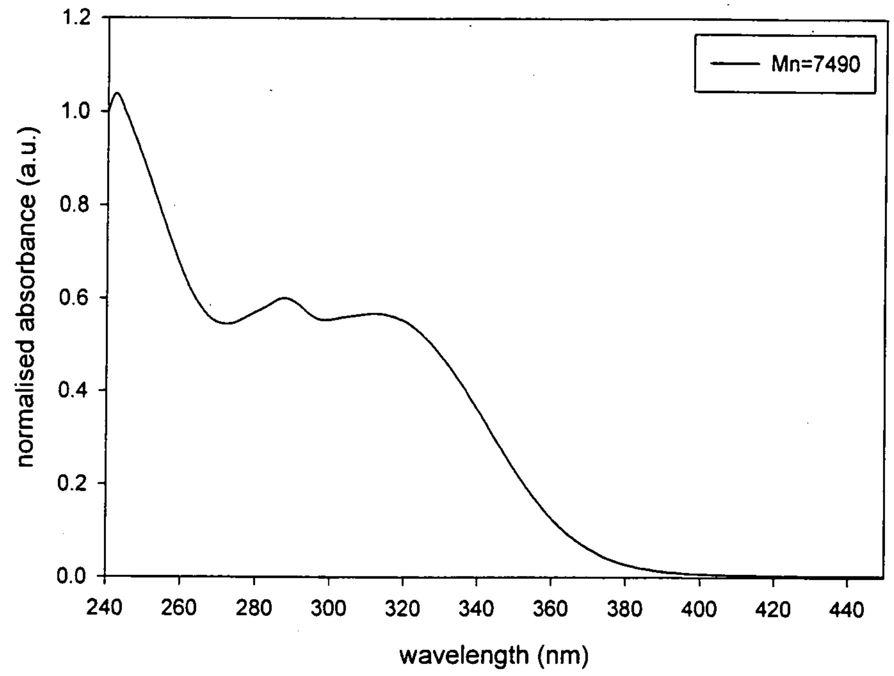
Appendix 4.1.8 UV-visible absorption spectrum of PDPV (fraction 13)



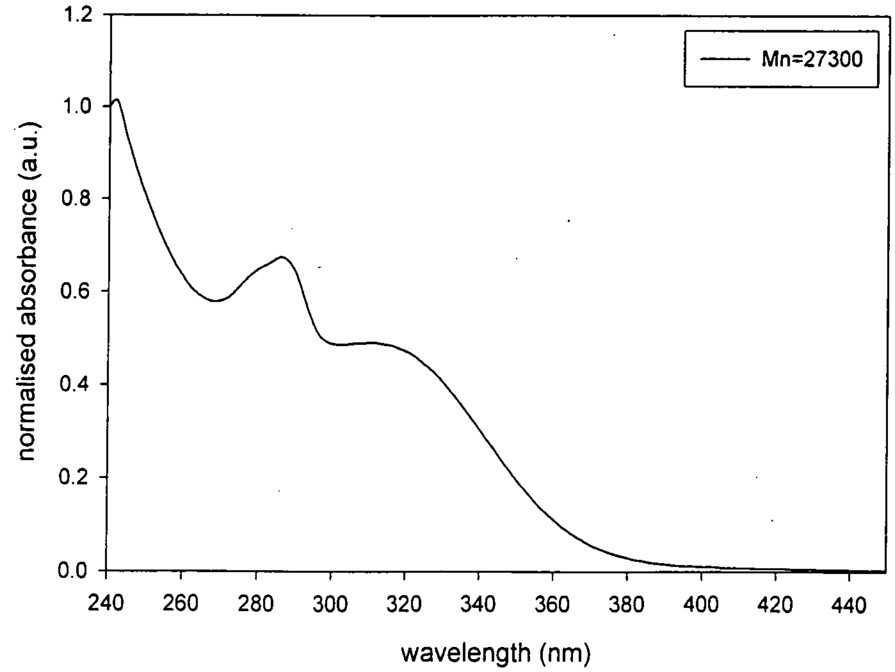
Appendix 4.1.9 UV-visible absorption spectrum of PDPV (fraction 16)



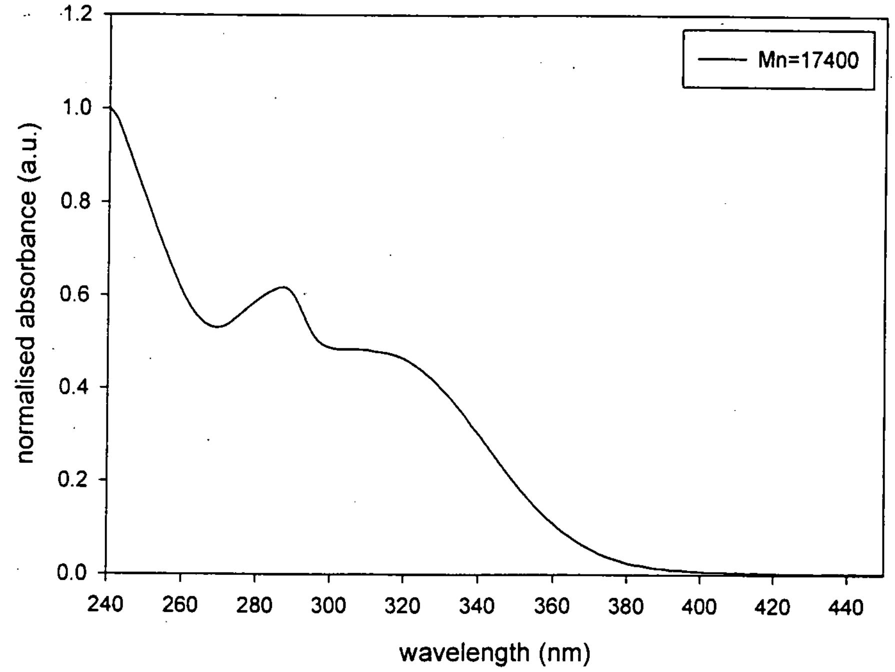
Appendix 4.1.10 UV-visible absorption spectrum of PDPV (fraction 18)



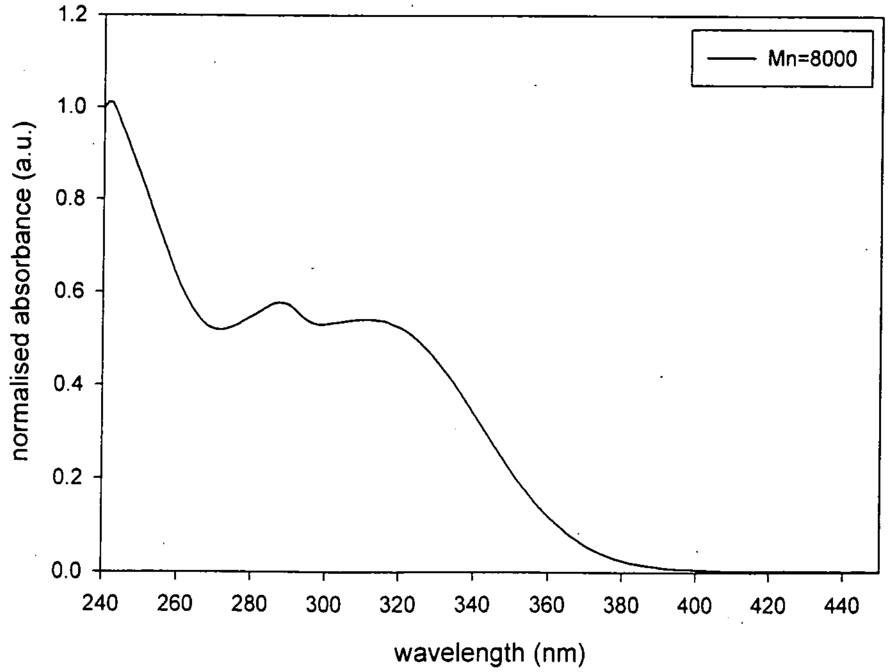
Appendix 4.1.11 UV-visible absorption spectrum of *m*-PPV-DP (pristine)



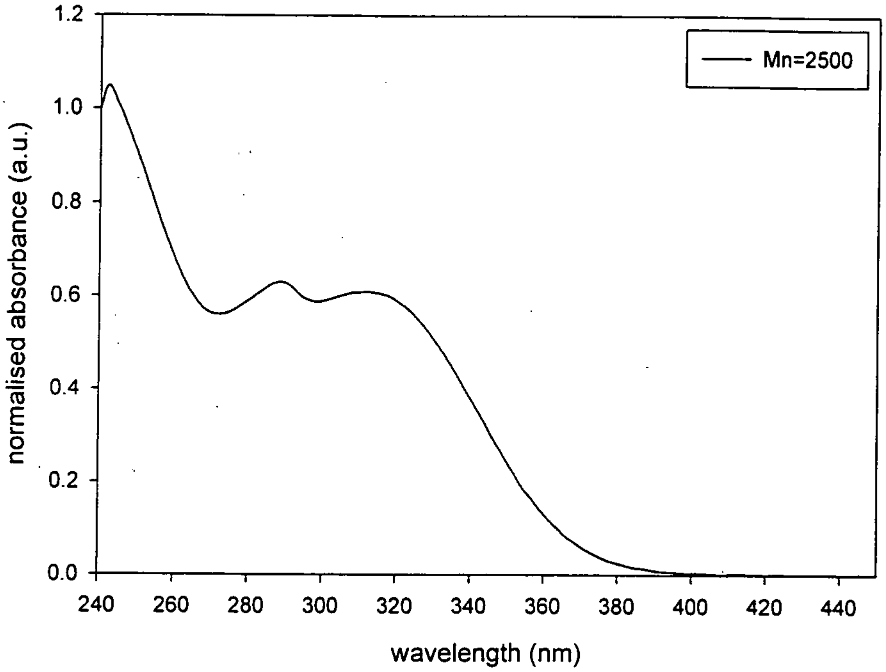
Appendix 4.1.12 UV-visible absorption spectrum of *m*-PPV-DP (fraction 1)



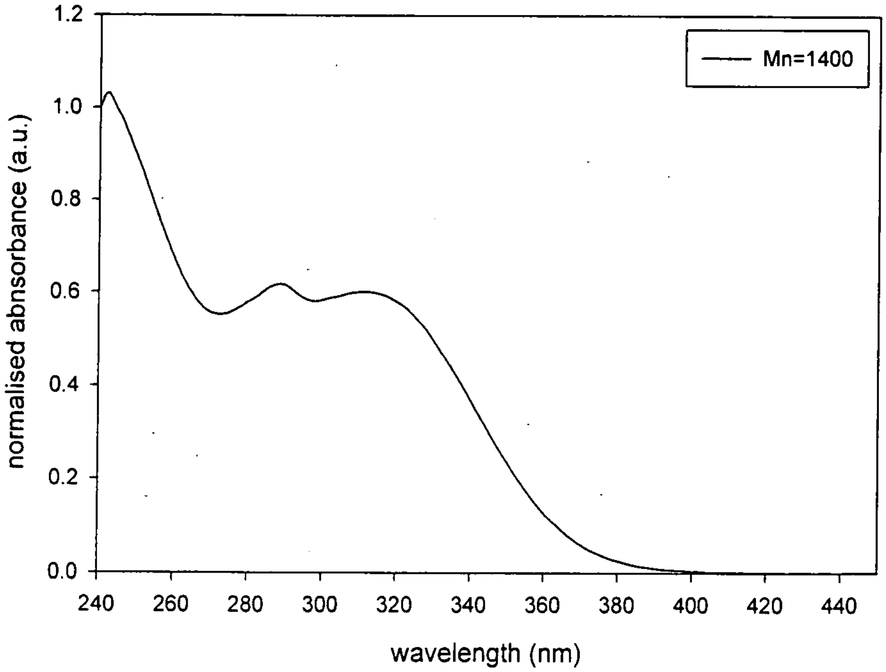
Appendix 4.1.13 UV-visible absorption spectrum of *m*-PPV-DP (fraction 3)



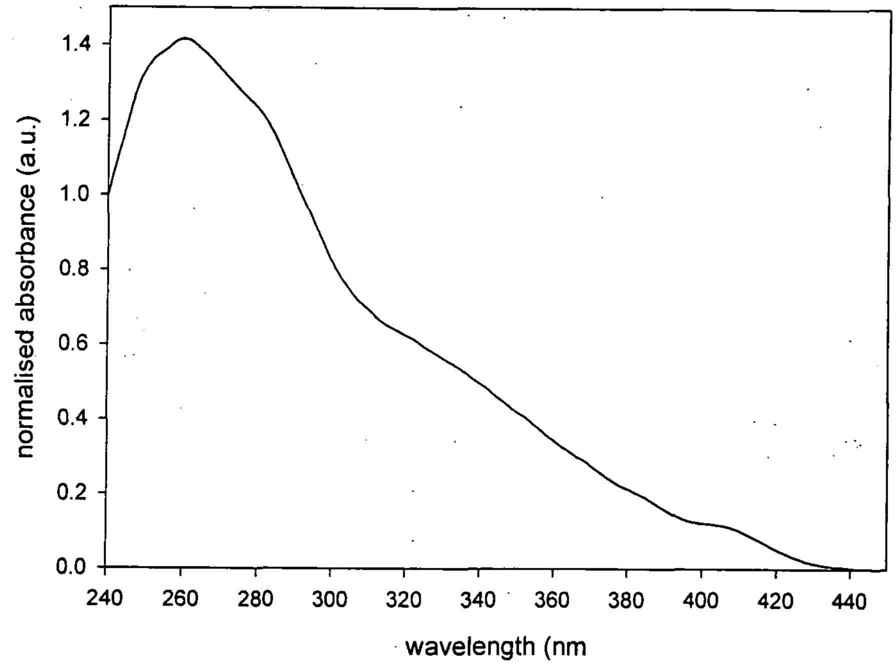
Appendix 4.1.14 UV-visible absorption spectrum of *m*-PPV-DP (fraction 6)



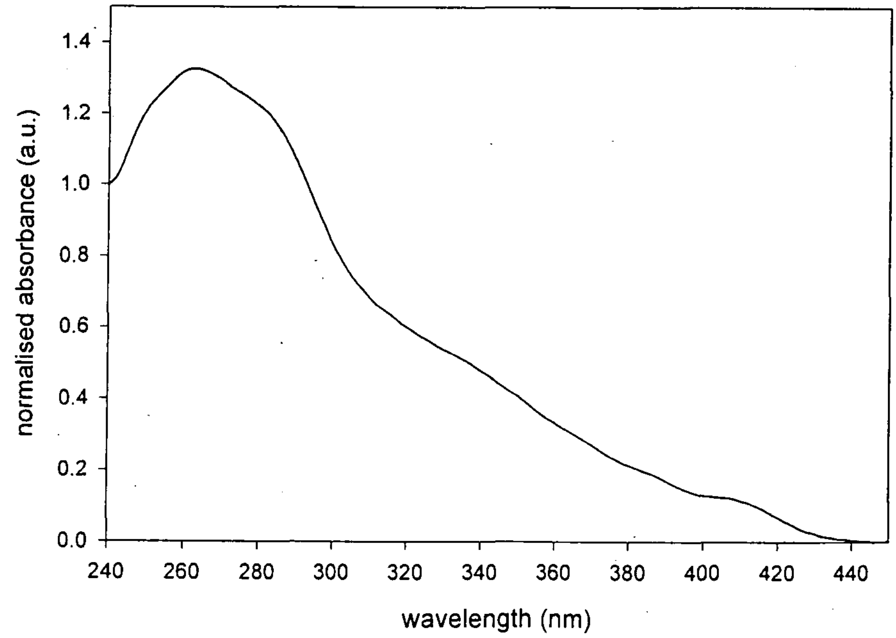
Appendix 4.1.15 UV-visible absorption spectrum of *m*-PPV-DP (fraction 8)



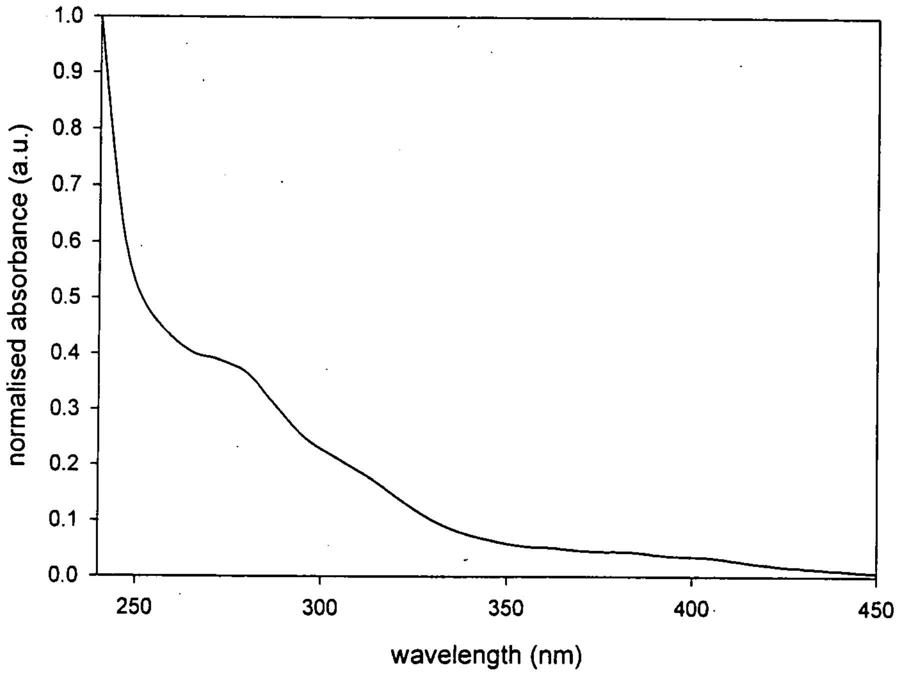
Appendix 4.1.16 UV-visible absorption spectrum of *m*-PPV-DP (fraction 11)



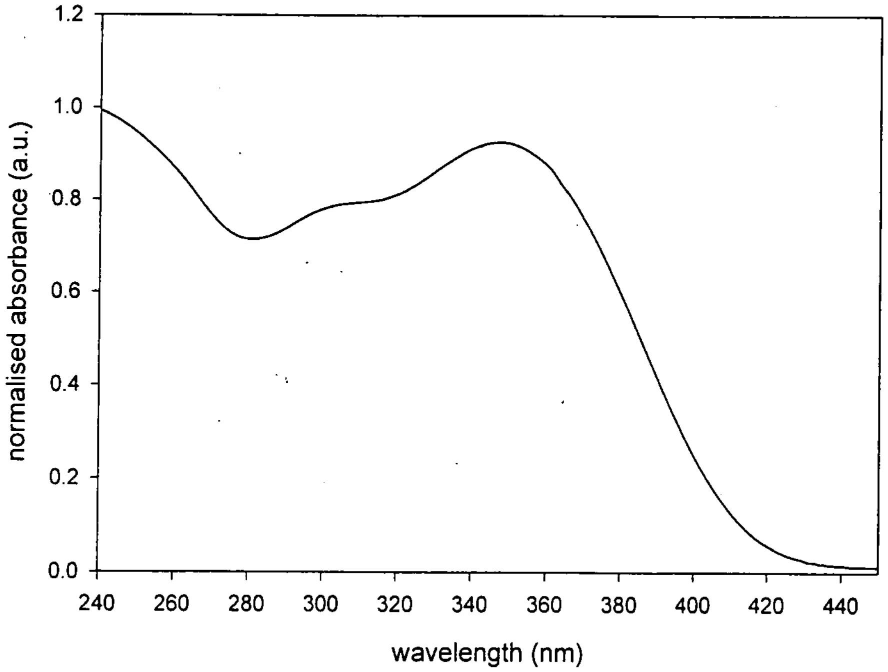
Appendix 4.1.17 UV-visible absorption spectrum of PDPV-DF (M_n=3000)



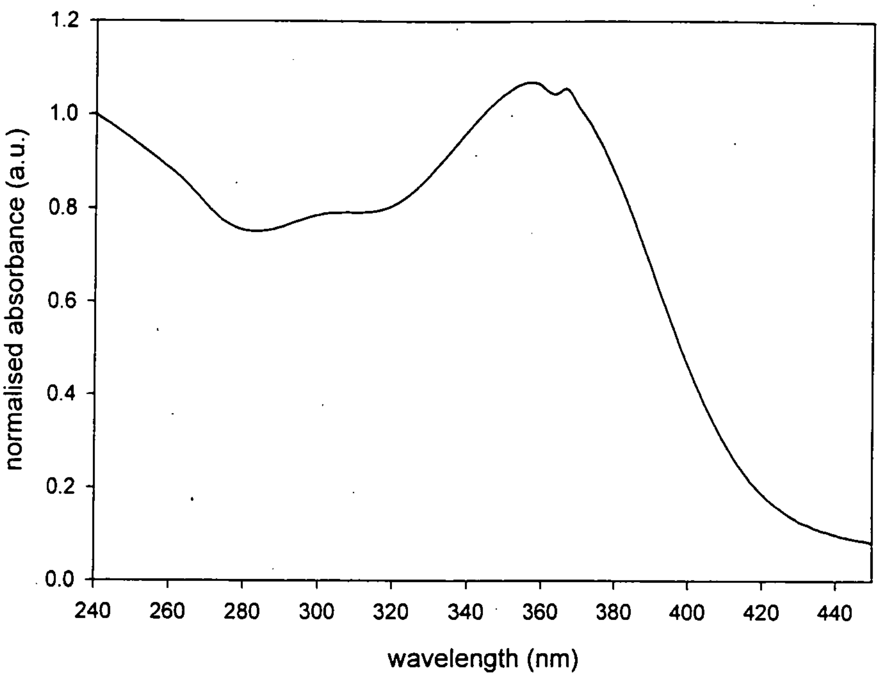
Appendix 4.1.18 UV-visible absorption spectrum of PDPV-DF (M_n=5500)



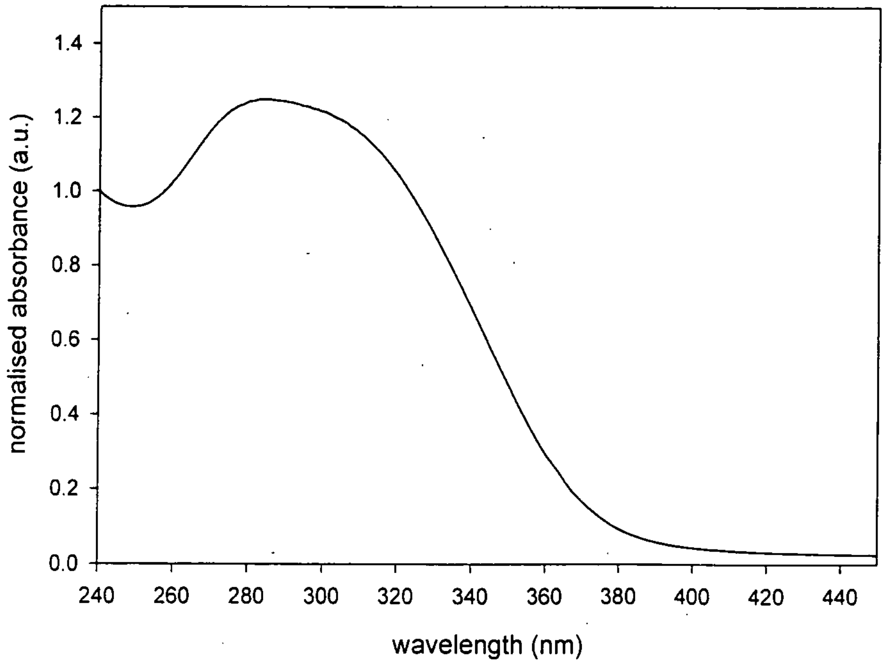
Appendix 4.1.19 UV-visible absorption spectrum of m-PPV-DM (M_n=1000)



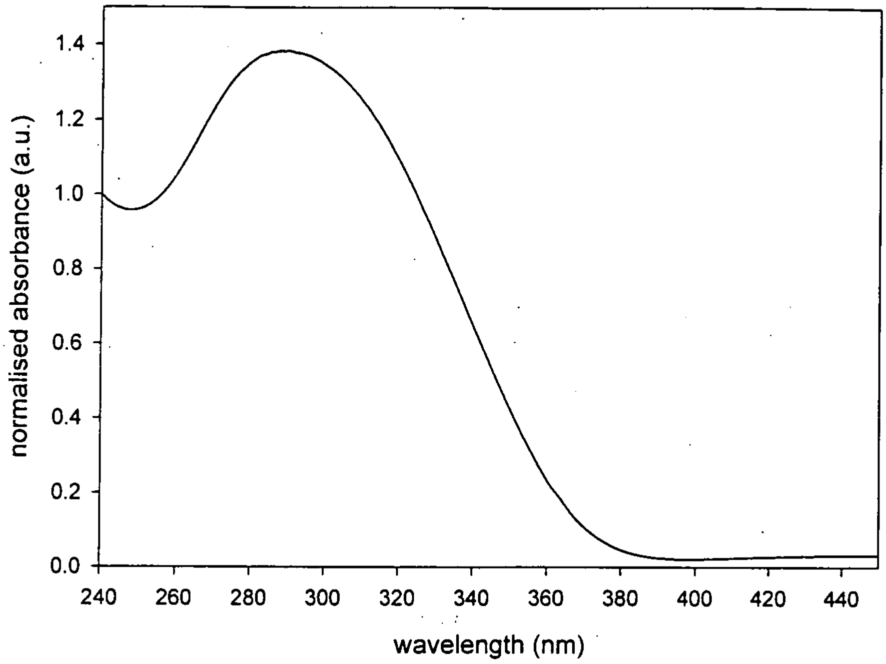
Appendix 4.1.20 UV-visible absorption spectrum of P3PV-DP (48% *cis*, M_n=1530)



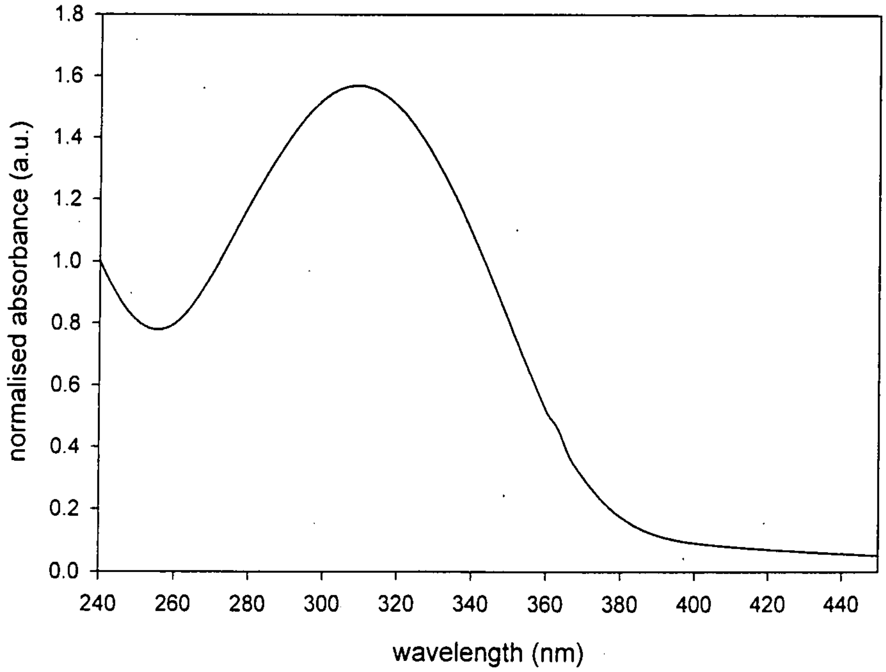
Appendix 4.1.21 UV-visible absorption spectrum of P3PV-DP (30% *cis*, M_n=1230)



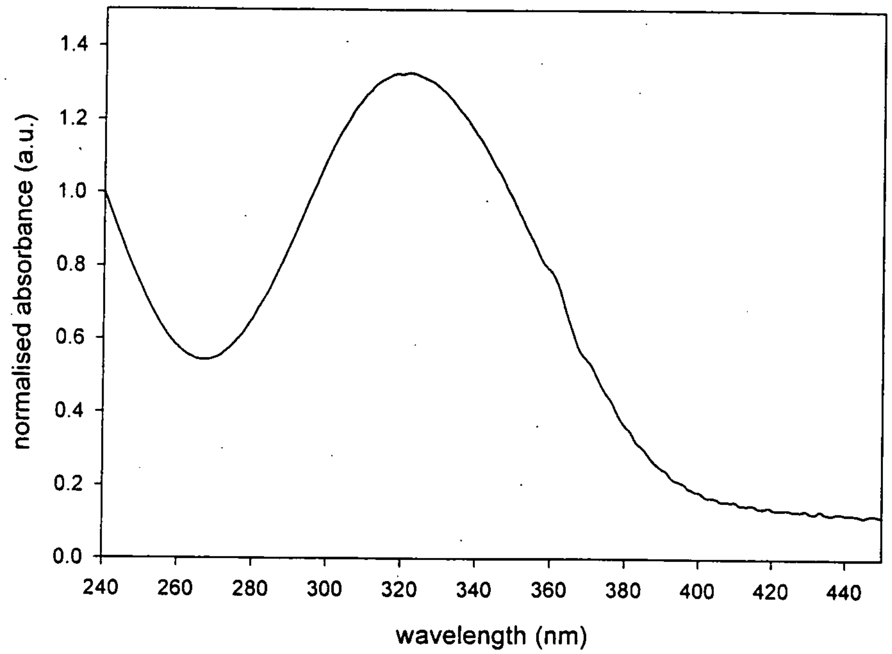
Appendix 4.1.22 UV-visible absorption spectrum of PDMeV (98% *cis*, M_n=2650)



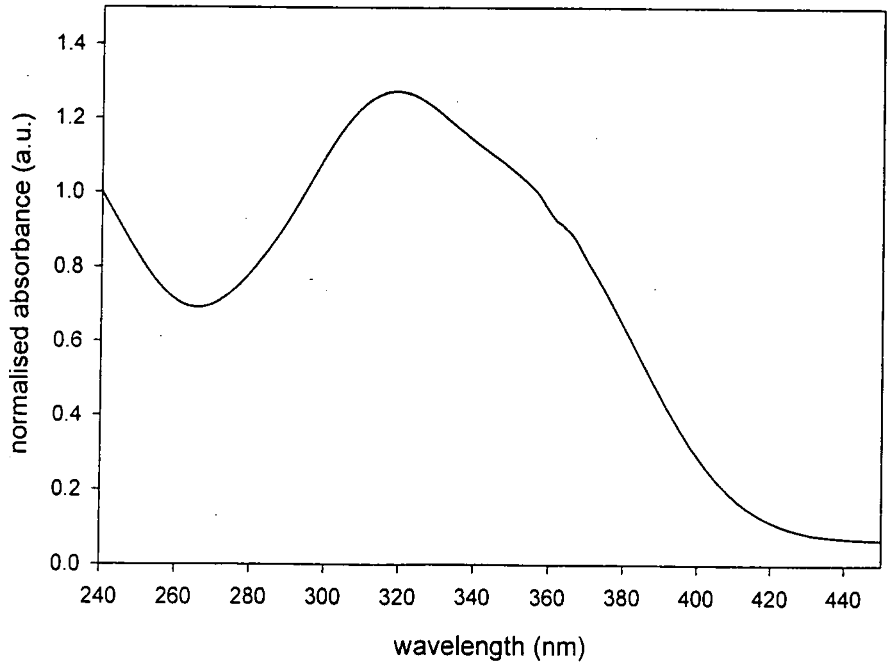
Appendix 4.1.23 UV-visible absorption spectrum of PDMeV (80% *cis*, M_n=1300)



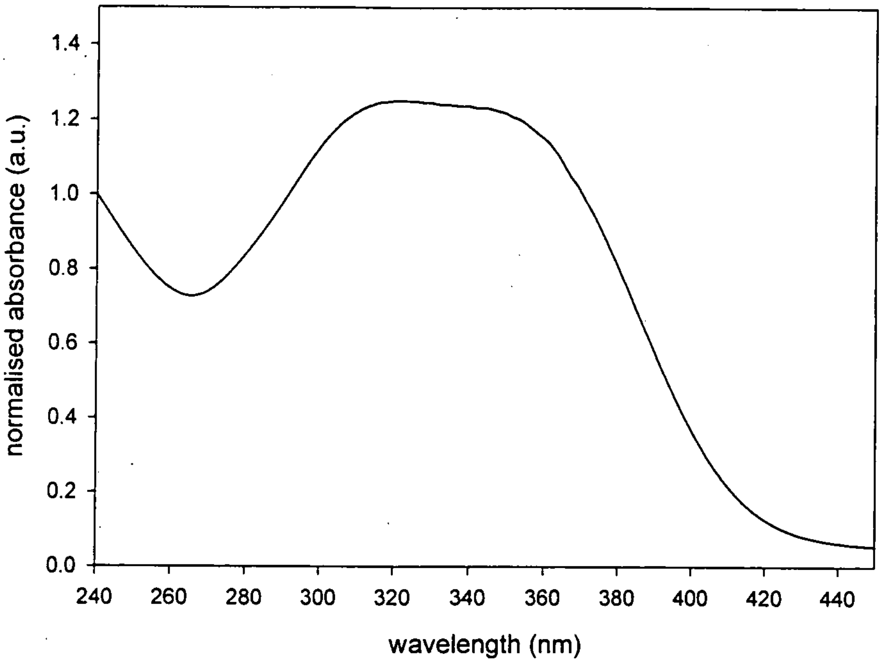
Appendix 4.1.24 UV-visible absorption spectrum of P3PV-DMe (80% *cis*, M_n=1880)



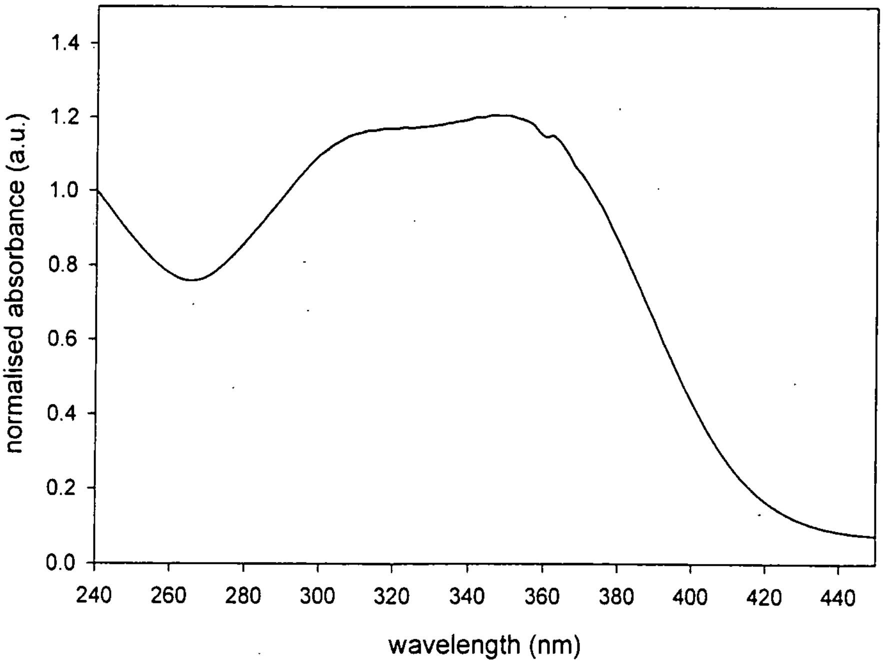
Appendix 4.1.25 UV-visible absorption spectrum of P4PV-DMe (98% *cis*)



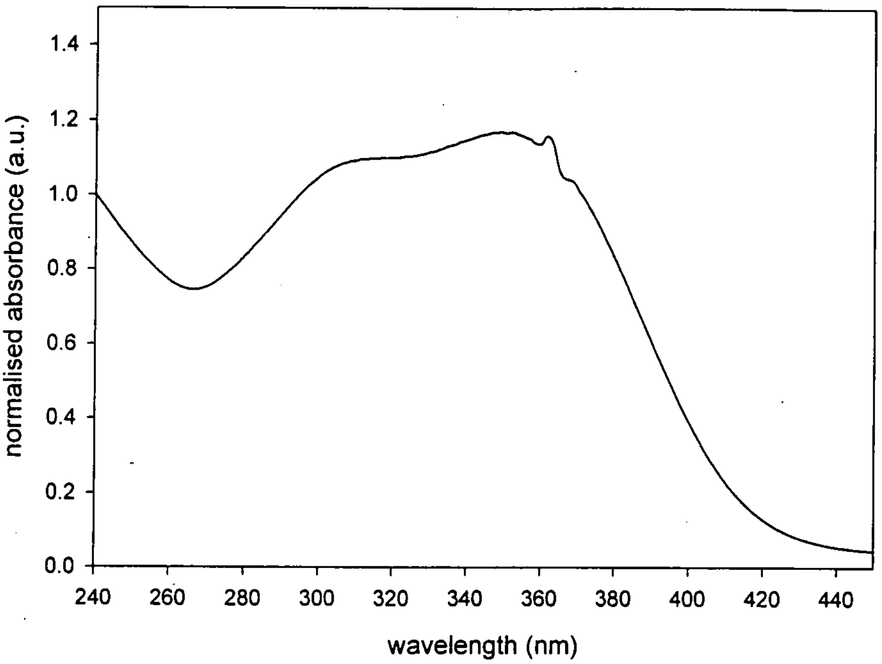
Appendix 4.1.26 UV-visible absorption spectrum of P4PV-DP (97% *cis*, M_n=2900)



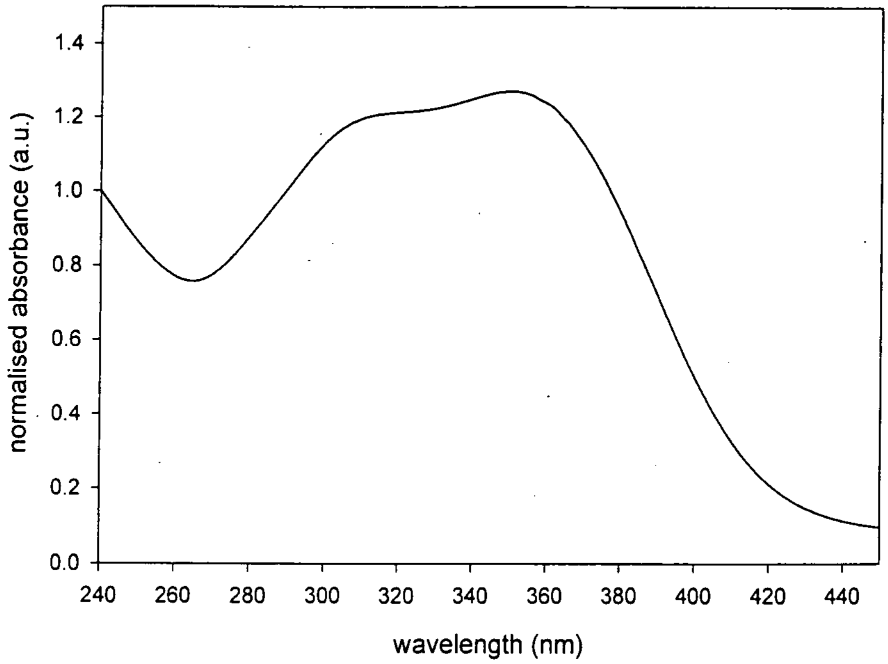
Appendix 4.1.27 UV-visible absorption spectrum of P4PV-DP (62% *cis*, M_n=5000)



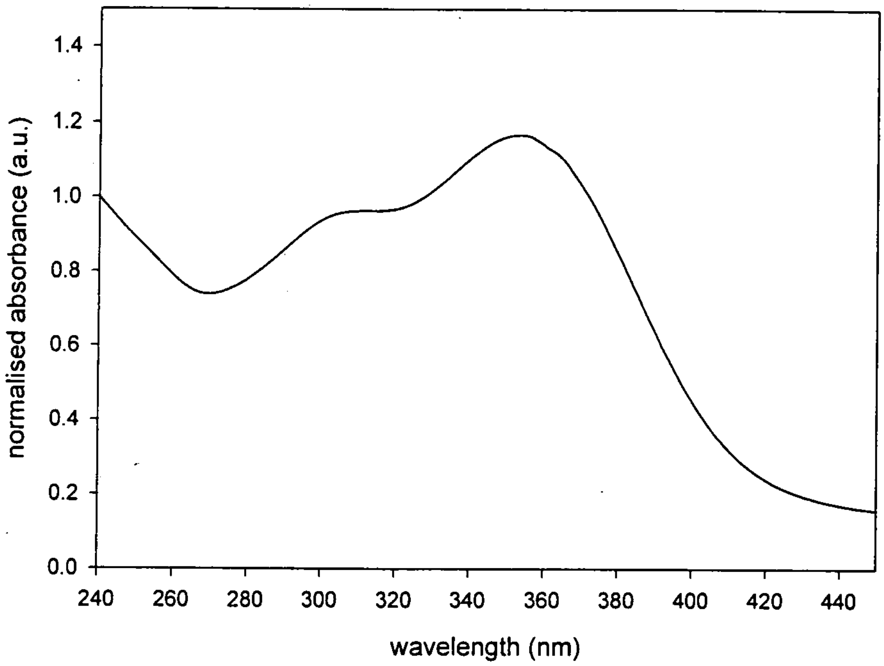
Appendix 4.1.28 UV-visible absorption spectrum of P4PV-DP (48% *cis*, M_n=4200)



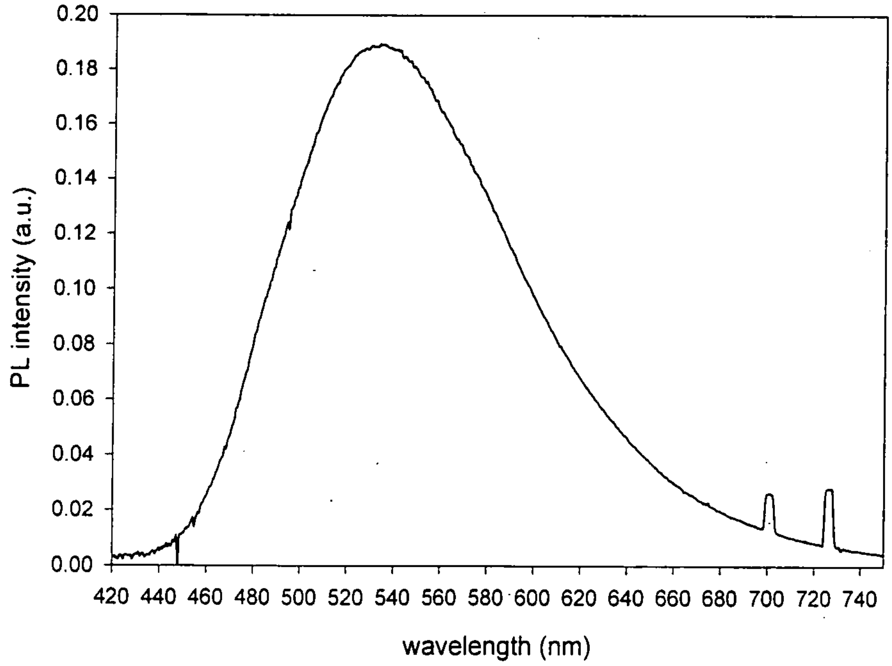
Appendix 4.1.29 UV-visible absorption spectrum of P4PV-DP (32% *cis*, M_n=2800)



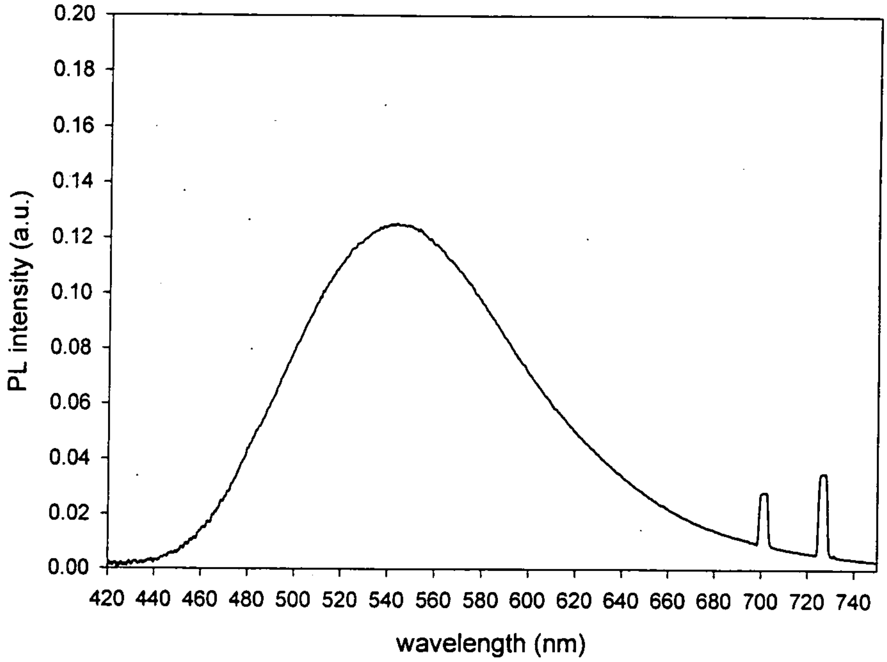
Appendix 4.1.30 UV-visible absorption spectrum of P4PV-DP (32% *cis*, M_n=16300)



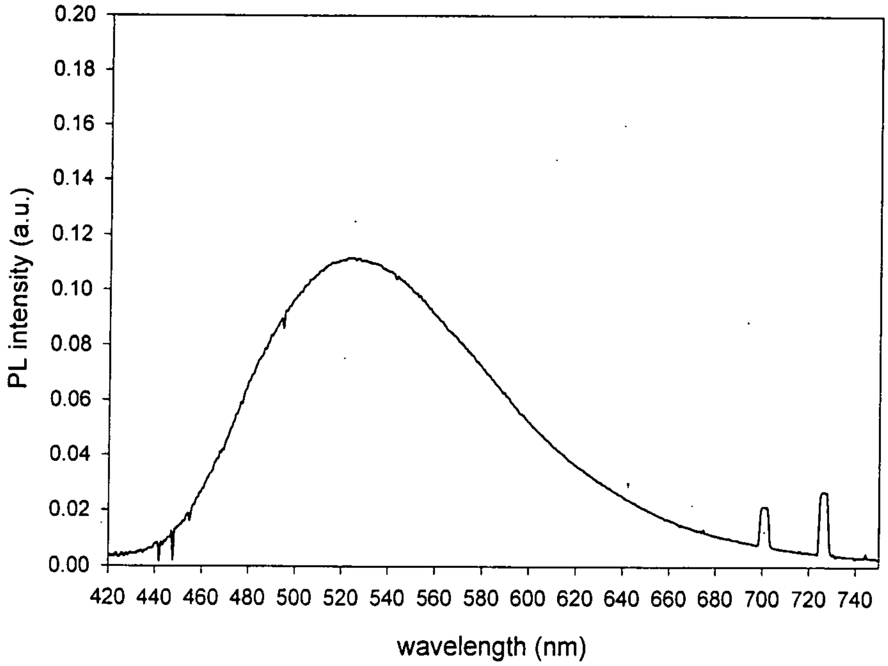
Appendix 4.1.31 UV-visible absorption spectrum of P4PV-DP (2% *cis*, M_n=1810)



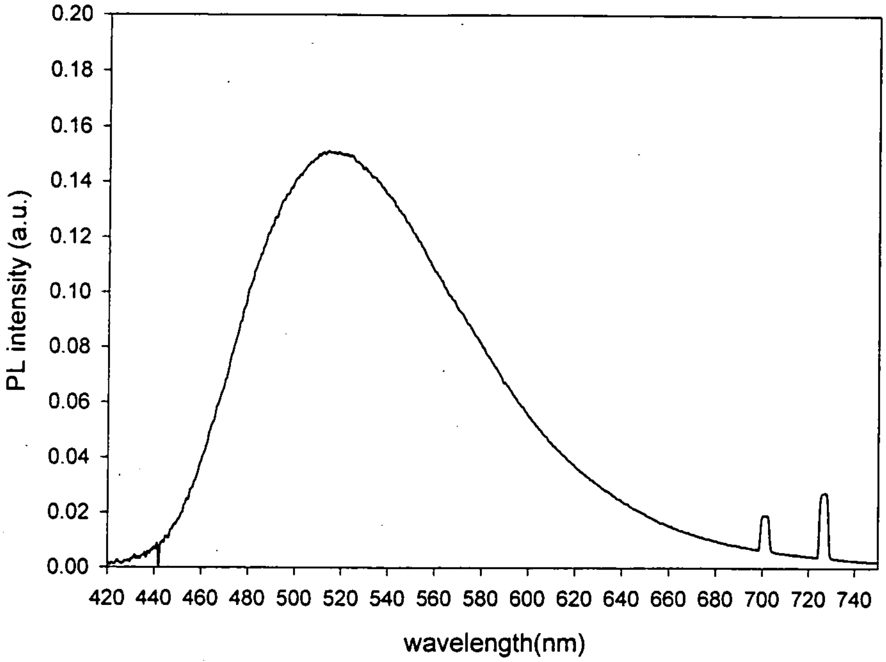
Appendix 4.2.1 PL spectrum of PDPV (McMurry, M_n=5740)



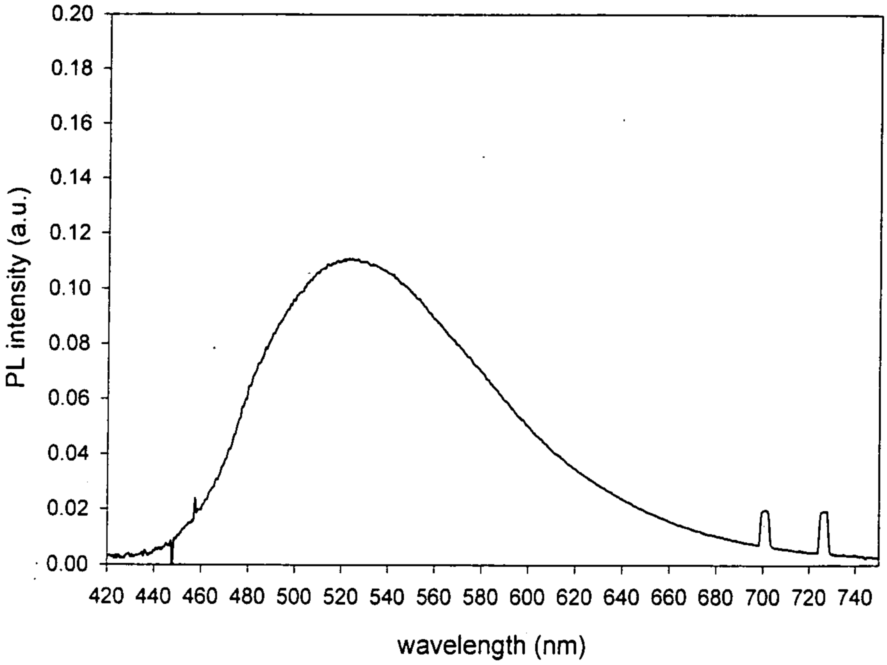
Appendix 4.2.2 PL spectrum of PDPV (McMurry, M_n=42900)



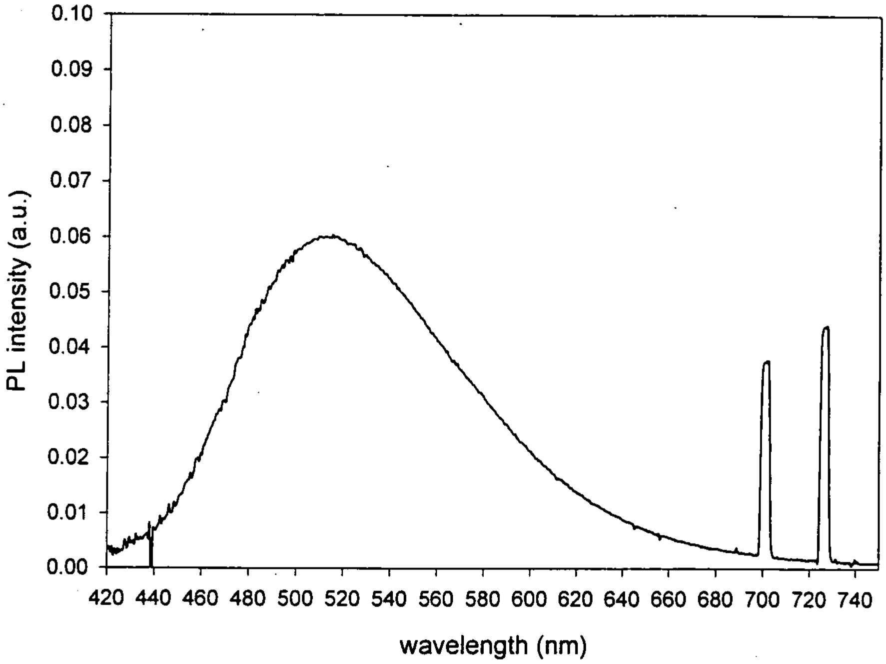
Appendix 4.2.3 PL spectrum of PDPV (Yamamoto, 59% *cis*, M_n=1200)



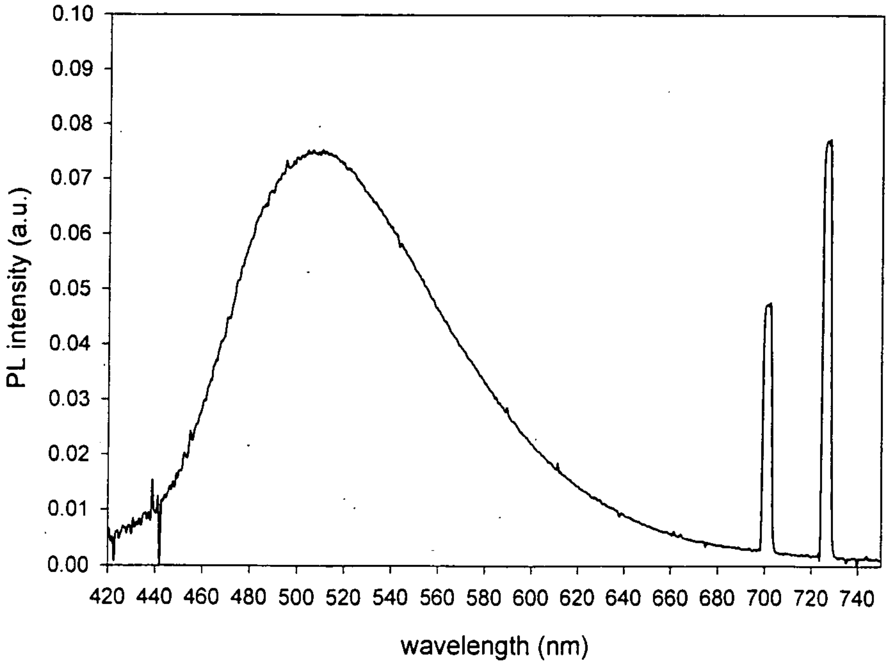
Appendix 4.2.4 PL spectrum of PDPV (Yamamoto, 48% *cis*, M_n=1900)



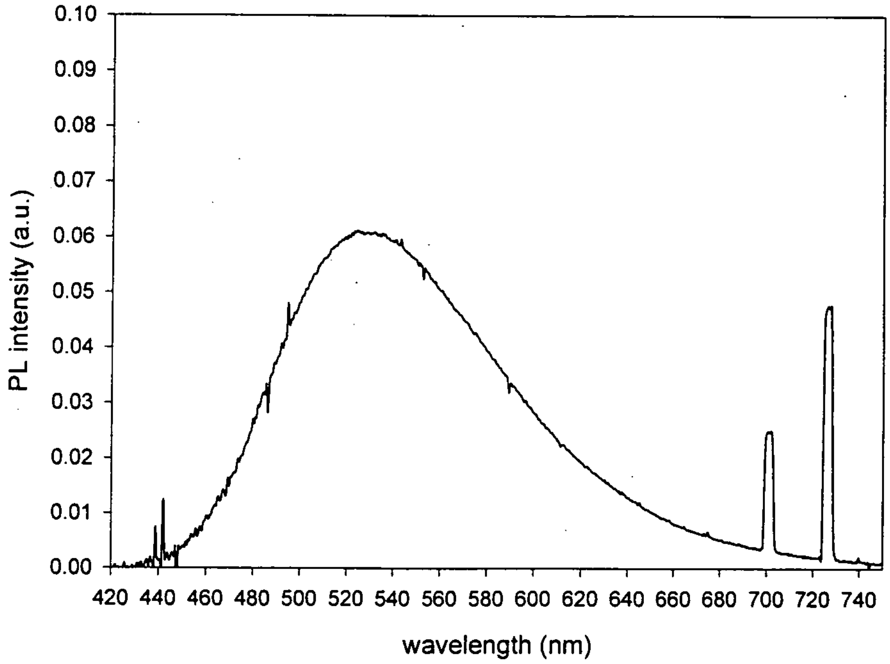
Appendix 4.2.5 PL spectrum of PDPV (Yamamoto, 37% *cis*, M_n=2900)



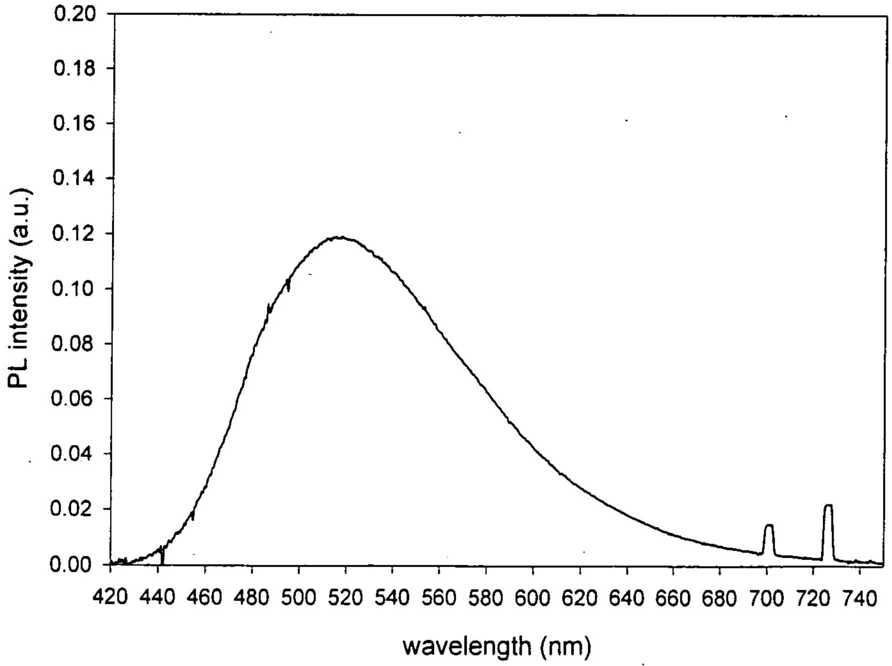
Appendix 4.2.6 PL spectrum of P3PV-DP (48% *cis*, M_n=1500)



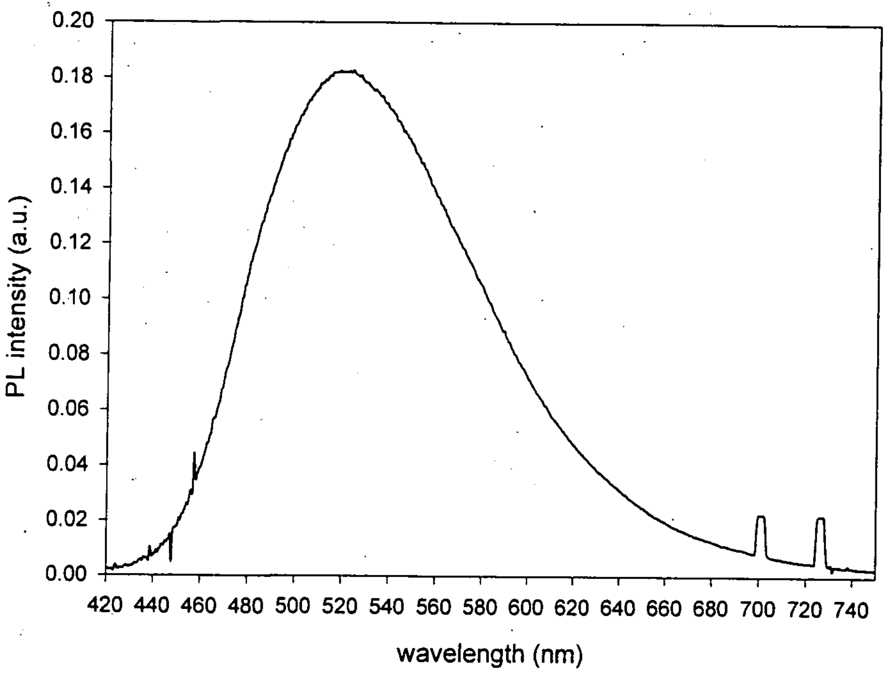
Appendix 4.2.7 PL spectrum of P4PV-DP (2% *cis*, M_n=1800)



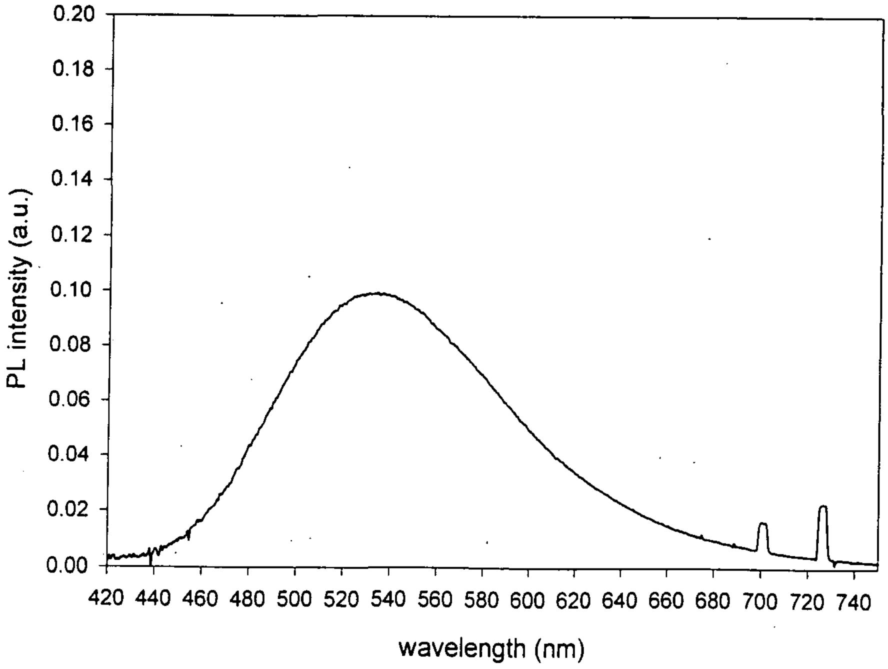
Appendix 4.2.8 PL spectrum of P4PV-DP (32% *cis*, M_n=16300)



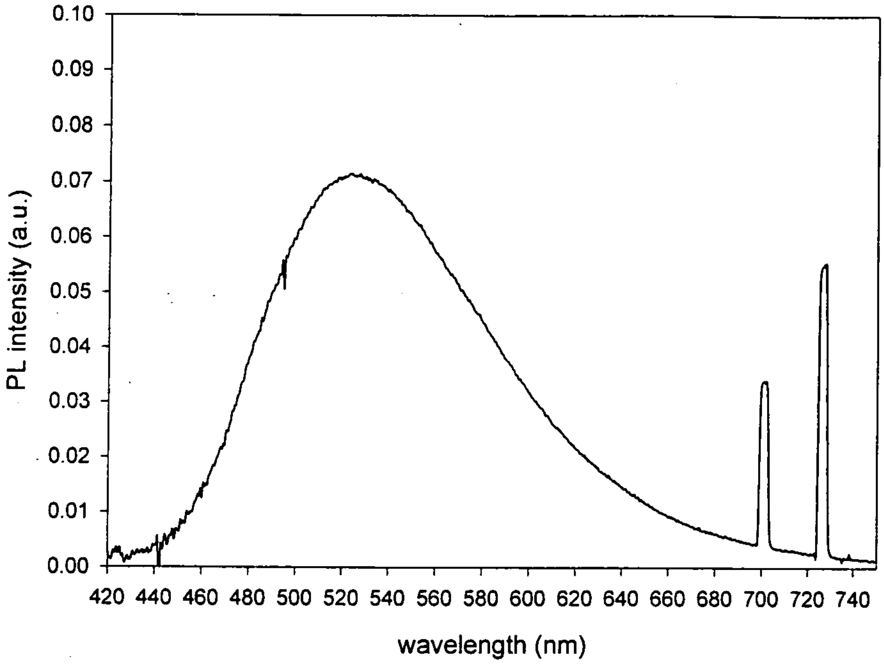
Appendix 4.2.9 PL spectrum of P4PV-DP (32% *cis*, M_n=2800)



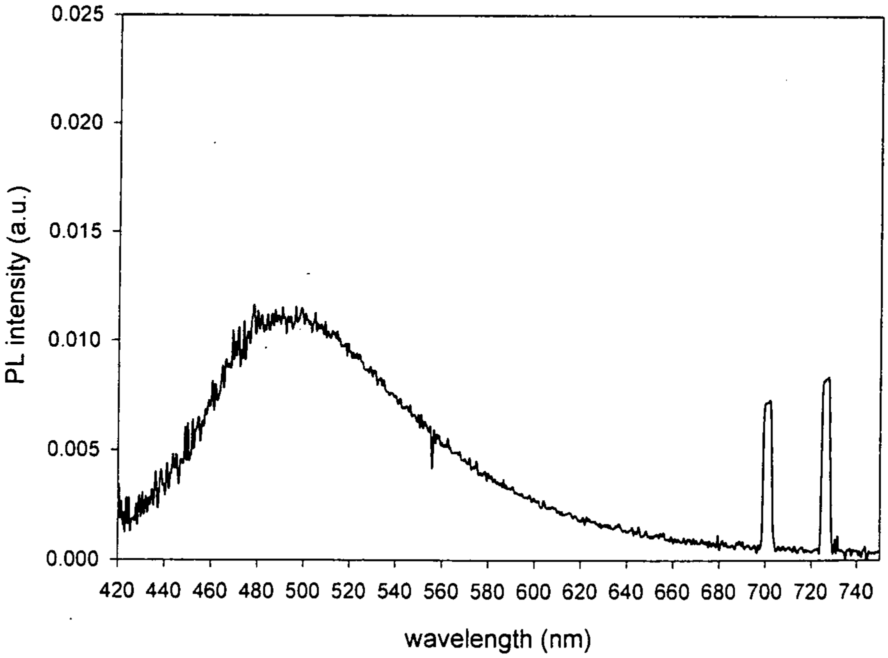
Appendix 4.2.10 PL spectrum of P4PV-DP (48% *cis*, M_n=4200)



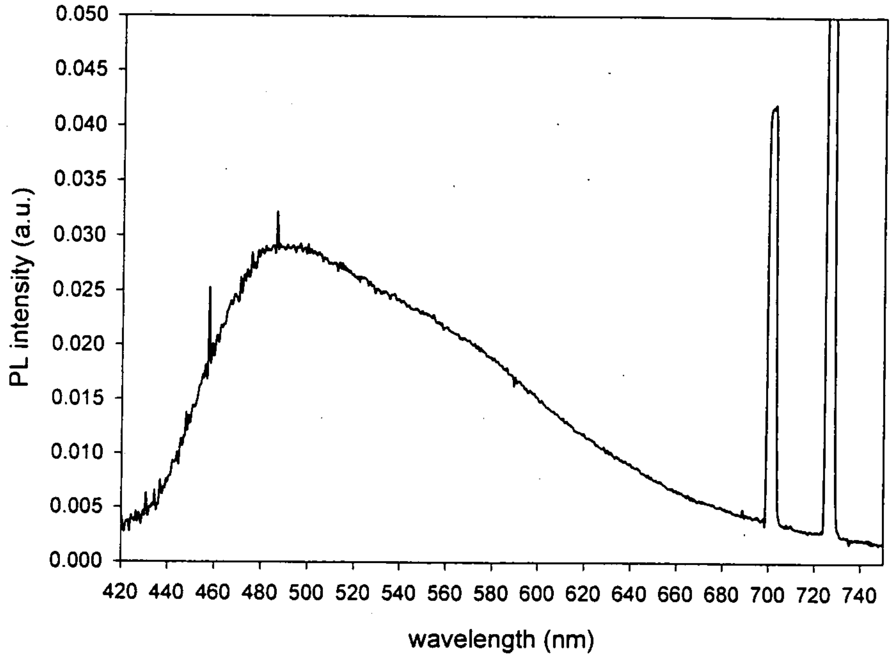
Appendix 4.2.11 PL spectrum of P4PV-DP (62% *cis*, M_n=5000)



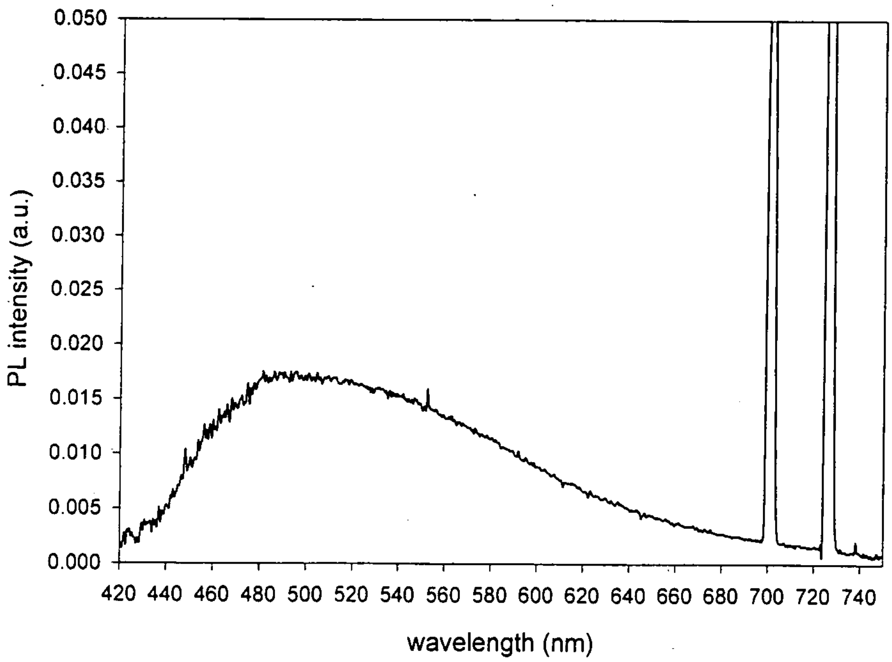
Appendix 4.2.12 PL spectrum of P4PV-DP (97% *cis*, M_n=2900)



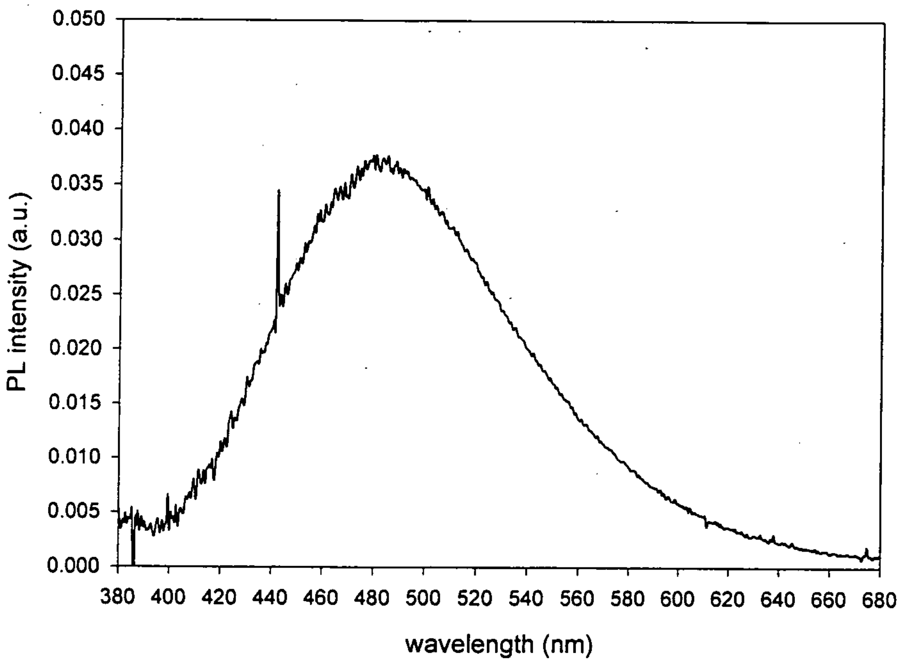
Appendix 4.2.13 PL spectrum of m-PPV-DM (M_n=1000)



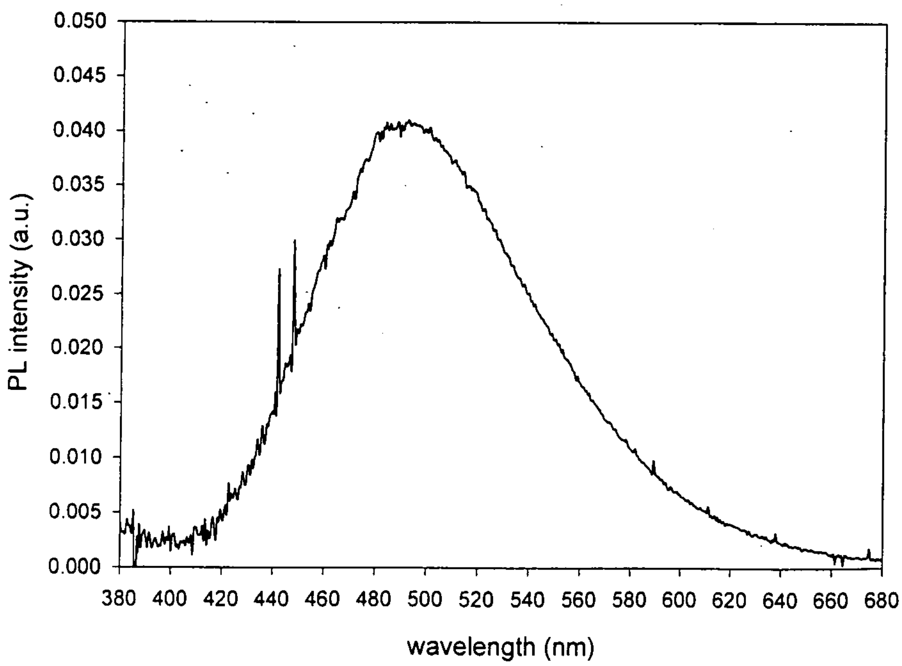
Appendix 4.2.14 PL spectrum of PDPV-DF (M_n=5500)



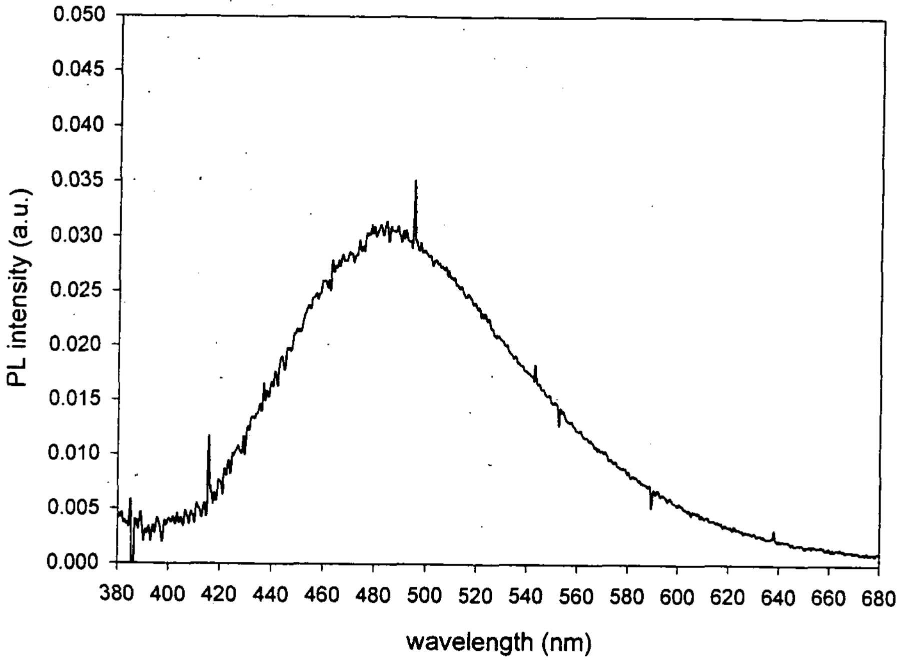
Appendix 4.2.15 PL spectrum of PDPV-DF (M_n=3000)



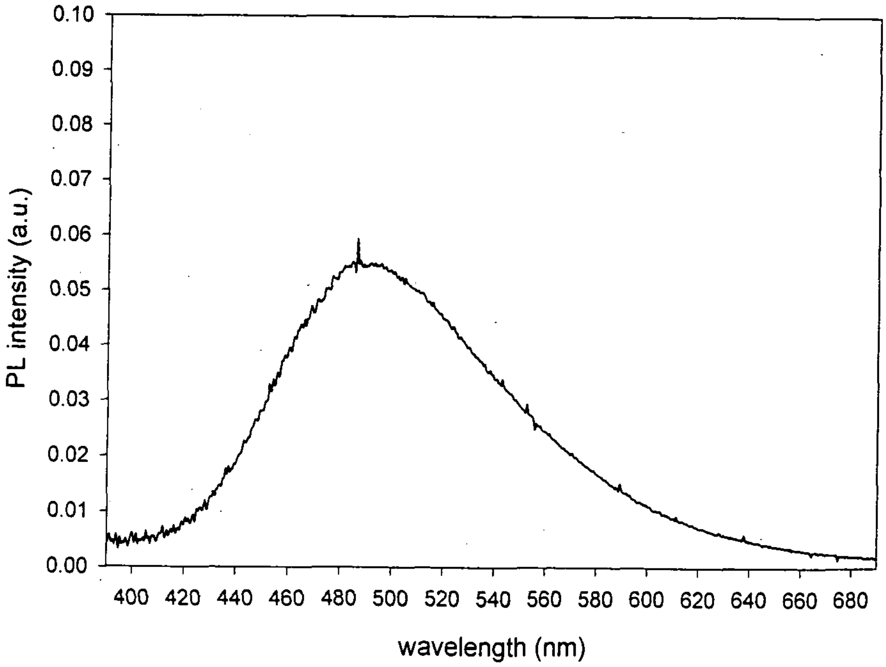
Appendix 4.2.16 PL spectrum of P3PV-DMe (80% *cis*, M_n=1900)



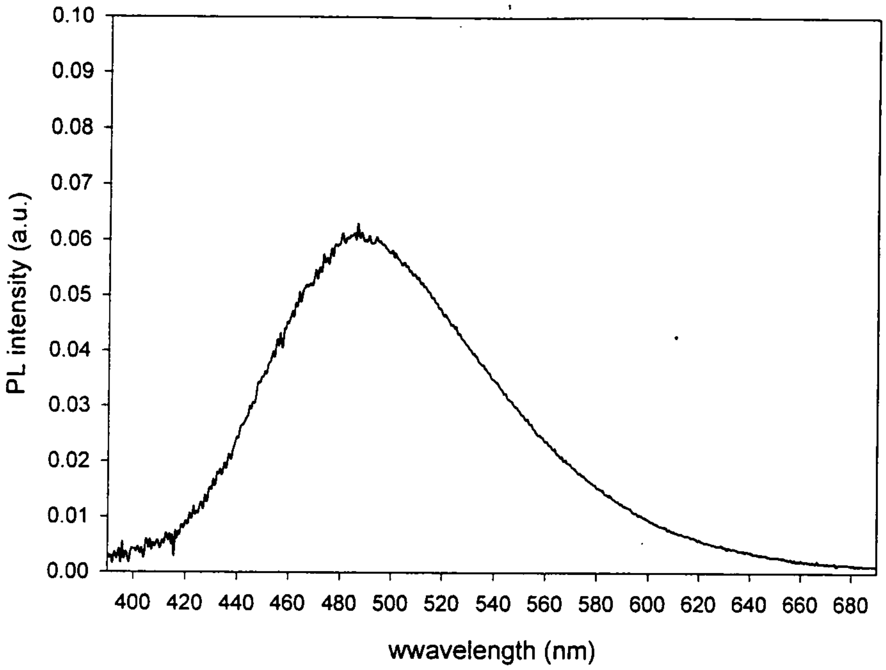
Appendix 4.2.17 PL spectrum of P3PV-DMe (98% *cis*, M_n=1600)



Appendix 4.2.18 PL spectrum of PDMeV (98% *cis*, M_n=2650)



Appendix 4.2.19 PL spectrum of m-PPV-DP (M_n=19000)



Appendix 4.2.20 PL spectrum of m-PPV-DP (M_n=1400)

Appendix 4.3 Experimental methods for photoluminescence and photoluminescence efficiency

4.3.1 Photoluminescence

To measure photoluminescent properties, samples were photoexcited with a *Coherent Innova 300 series* Argon-ion laser which lases in the UV region of the electromagnetic spectrum. The UV output of two dominating lines at 351.4 and 363.8 nm is obtained in a 'multi-line' mode. The output power typically ranges between 1 and 500 mW. Power attenuation is achieved by neutral density filters.

Photoluminescence spectra have been recorded with the *ORIEL Instaspec IV* system consisting of a spectrograph coupled to a Peltier-cooled CCD array. Luminescence is captured by a collector lens and transmitted through a fibre bundle onto the entrance slit of the spectrograph. The CCD array is read out by a PC system. The *ORIEL* system is spectrally calibrated with a calibrated tungsten lamp to correct for the spectral response of the fibre, spectrograph and CCD array. The overall spectral resolution is < 5nm. The detection threshold for the CCD-array is < 3.8 fJcm^{-2}. Schematically, *Figure A4.3.1.1* shows the set-up for PL measurements.

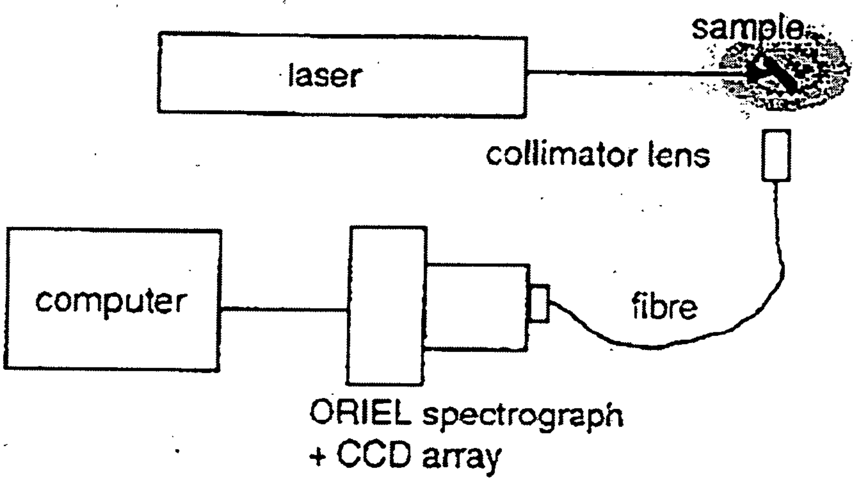


Figure A4.3.1.1 Schematic set-up for PL measurement.

4.3.2 Photoluminescence efficiency

The external quantum efficiency of solid state polymer films was measured with the *ORIEL* system described earlier in conjunction with an integrating sphere. This method allows the measurement of the PL efficiency with anisotropic emission characteristics and is not influenced by strong scattering or small Stokes' shifts. In practice, three spectra are taken:

1) The first one is of the laser hitting the sample mounted in the centre of the sphere. The PL as well as the non-absorbed laser light are diffused by the reflective coating inside the sphere and collected by the collimator lens of the *ORIEL* system. The lens is protected by a baffle valve to avoid direct illumination.
2) The non-absorbed laser light is reflected inside the sphere and causes a further PL contribution which distorts the efficiency measurement. This is corrected by taking a second spectrum with the laser missing the sample.
3) Finally, the spectrum of the laser hitting the empty sphere is recorded to determine the incident light intensity.

The PL efficiency is given by

$$\eta = \frac{\text{no. of photons emitted}}{\text{no. of photons absorbed}} = \frac{S_{HIT} - (1 - A)S_{OFF}}{L_0 A}$$

S_{HIT} = spectrally integrated signal of laser and PL when laser hits sample

S_{OFF} = spectrally integrated signal of laser and PL when laser misses sample

A = light absorbed in sample

L_0 = incident light

The estimated error of this quantum efficiency is ±3%.

Colloquia, Lectures and Seminars Attended

1994

October 5	Prof. N. L. Owen, Brigham Young University, Utah, USA Determining Molecular Structure - the INADEQUATE NMR way
October 19	Prof. N. Bartlett, University of California Some Aspects of Ag(II) and Ag(III) Chemistry
November 2	Dr P. G. Edwards, University of Wales, Cardiff The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands
November 3	Prof. B. F. G. Johnson, Edinburgh University Arene-metal Clusters
November 9	Dr G. Hogarth, University College, London New Vistas in Metal-imido Chemistry
November 10	Dr M. Block, Zeneca Pharmaceuticals, Macclesfield Large-scale Manufacture of ZD 1542, a Thromboxane Antagonist Synthase Inhibitor
November 16	Prof. M. Page, University of Huddersfield Four-membered Rings and β-Lactamase
November 23	Dr J. M. J. Williams, University of Loughborough New Approaches to Asymmetric Catalysis
December 7	Prof. D. Briggs, ICI and University of Durham Surface Mass Spectrometry

1995

January 18	Dr G. Rumbles, Imperial College, London Real or Imaginary Third Order Non-linear Optical Materials
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

November 8	Dr. D. Craig, Imperial College, London New Stategies for the Assembly of Heterocyclic Systems
November 17	Prof. David Bergbreiter, Texas A&M, USA Design of Smart Catalysts, Substrates and Surfaces from Simple Polymers
November 22	Prof. I Soutar, Lancaster University A Water of Glass? Luminescence Studies of Water-Soluble Polymers.
November 29	Prof. Dennis Tuck, University of Windsor, Ontario, Canada New Indium Coordination Chemistry
December 8	Professor M.T. Reetz, Max Planck Institut, Mulheim Perkin Regional Meeting

1996

January 17	Prof. J. W. Emsley , Southampton University Liquid Crystals: More than Meets the Eye
February 21	Dr C R Pulham , Univ. Edinburgh Heavy Metal Hydrides - an exploration of the chemistry of stannanes and plumbanes
March 13	Prof. Dave Garner, Manchester University Mushrooming in Chemistry
October 9	Professor G. Bowmaker, University Aukland, NZ Coordination and Materials Chemistry of the Group 11 and Group 12 Metals : Some Recent Vibrational and Solid State NMR Studies
October 16	Professor Ojima, Guggenheim Fellow, State University of New York at Stony Brook Silylformylation and Silylcarbocyclisations in Organic Synthesis
October 22	Professor Lutz Gade, Univ. Wurzburg, Germany Organic transformations with Early-Late Heterobimetallics: Synergism and Selectivity
October 23	Professor H. Ringsdorf (Perkin Centenary Lecture), Johannes Gutenberg-Universitat, Mainz, Germany Function Based on Organisation

October 30	Dr Phillip Mountford, Nottingham University Recent Developments in Group IV Imido Chemistry
November 6	Dr Melinda Duer, Chemistry Department, Cambridge Solid-state NMR Studies of Organic Solid to Liquid-crystalline Phase Transitions
November 12	Professor R. J. Young, Manchester Materials Centre, UMIST New Materials - Fact or Fantasy? Joint Lecture with Zeneca & RSC
November 13	Dr G. Resnati, Milan Perfluorinated Oxaziridines: Mild Yet Powerful Oxidising Agents
November 18	Professor G. A. Olah, University of Southern California, USA Crossing Conventional Lines in my Chemistry of the Elements

1997

January 16	Dr Sally Brooker, University of Otago, NZ Macrocycles: Exciting yet Controlled Thiolate Coordination Chemistry
January 21	Mr D. Rudge, Zeneca Pharmaceuticals High Speed Automation of Chemical Reactions
January 29	Dr Julian Clarke, UMIST What can we learn about polymers and biopolymers from computer-generated nanosecond movie-clips?
February 4	Dr A. J. Banister, University of Durham From Runways to Non-metallic Metals - A New Chemistry Based on Sulphur
March 19	Dr Katharine Reid, University of Nottingham Probing Dynamical Processes with Photoelectrons
May 7	Prof. M. Harrington, Caltech, Pasadena, USA Polymers both Enable from Gene Regulation to Mad Cow Disease
May 20	Prof. J. Jin, President, Korean Chemical Society Poly PPV and its Derivatives - Synthesis, Structure and Properties

Conferences and Courses Attended

1995

January 10	IRC Polymer Physics Introduction Course, University of Leeds
January 12	IRC Polymer Engineering Introduction Course, University of Bradford
July 10-14	International Symposium on Olefin Metathesis (ISOM 11), Durham
Sept. 27-28	IRC Industrial Club Seminar, Durham

1996

April 10-12	Aspects of Contemporary Polymer Science, MACRO Group UK Family meeting, Manchester
June 3	The Melville Lectureship, Department of Chemistry, University of Cambridge

1997

April 2-4	MACRO Group UK Spring Meeting for Young Researchers, Leeds
May 11-16	SELOA Spring School on Conjugated Polymers, Sala Sant Ansano, Siena, Italy