

SYNTHESIS AND PROPERTIES OF LIQUID CRYSTALLINE CONDUCTING POLYMERS

BY

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A Thesis Submitted In Partial Fulfilment Of The Requirements Of Kingston University For The Degree Of Doctor Of Philosophy.

MAY 1996

KINGSTON UNIVERSITY School of Applied Chemistry



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TO VINCENT ...

ABSTRACT

Novel conducting polyanilines which are thermoplastic and have mesogenic sidechains have been synthesised and investigated in order to study the use of liquid crystal alignment to produce higher conductivity. The backbone was based on *ortho*-substituted aniline polymers.

A large variety of suitable *ortho*-substituted nitrobenzene precursors with liquid crystalline properties were synthesised and investigated by microscopy and differential scanning calorimetry. A study of the 4-methoxyphenyl 4-[x-(2-nitrophenoxy)alkoxy] benzoate series (x = 2-10) showed that only the molecules with even spacer lengths were liquid crystalline whereas the ones with odd spacer lengths were not. All the even molecules were nematic in character. Some substituted biphenyl nitrobenzenes were also synthesised and 4-cyano 4'-[6-(2-nitrophenoxy)hexoxy]biphenyl exhibited a monotropic nematic phase. A large variety of *ortho*-substituted nitrobenzenes with transition temperatures above 100°C were also synthesised. Depending on their structure, nematic as well as smectic phases were characterised.

The *ortho*-substituted nitrobenzene molecules were subsequently reduced to the required anilines. Their liquid crystal properties were similar to their respective nitro-compounds.

These liquid crystalline aniline monomers were chemically polymerised by use of an emulsion system. The polymers obtained were fully characterised by spectroscopic analysis, and were a head-to-tail emeraldine type substituted polyaniline.

The physical properties of these potentially liquid crystalline conducting polymers were fully investigated. They were found to be soluble in DMF, DMSO, THF and CHCl₃. UV/visible study revealed an average band gap of 3.4 eV. Gel permeation chromatography analysis showed the presence of oligomers and higher polymers in smaller proportion for each samples. These polymers were also structurally stable up to 300° C.

Polarising hot-stage microscopy and differential scanning calorimetry showed the existence of liquid crystal properties for two of these polymers namely : poly[2-(hexoxy)-6-(4-biphenyloxy-4'-carboxylic acid)]aniline and poly{2-[4-cyanophenyl-4-carboxylate 6-(4'-

i

oxybiphenyl)hexoxy]aniline}. In fact, a nematic phase was exhibited for the carboxylic acid polymer between 225 and 261°C and between 120 and 175°C for the ester polymer.

Study of their electrical conductivities showed some semi-conducting characteristics with values as high as 1.2×10^{-3} S cm⁻¹ for the H₂SO₄ vapour doped carboxylic acid polymer and equal to 8×10^{-6} S cm⁻¹ for the HCl doped ester polymer. An increase in conductivity values was also observed as the temperature reaches the nematic liquid crystal transitions, demonstrating the effect of the mesogenic groups on the ordering of the polymer backbone. Laser alignment of these two liquid crystal semi-conducting polymers was also carried out. A conductivity anisotropy was observed along the laser written samples. This technique could also be of great potential interest as a method of localised conductivity enhancement.

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ACKNOWLEDGMENTS

I would like to express my gratitude and thanks to my supervisors, Dr Peter Foot and Dr John Brown for their guidance and help during the three years of my study at Kingston University.

Thanks to Dr Richie Simon from Greenwich University for allowing me to use his laser equipment and for helping me to use his camera in order to take photographs of my liquid crystals.

Thanks to Dr John Bunning from Sheffield Hallam University for doing X-ray diffractometry of my monomers in order to identify the smectic phases of my liquid crystals.

I wish to thank the PCFC for sponsoring my studies as well as Prof Geoffrey Pritchard and Prof Cliff Wells for the provision of research facilities.

The research presented in this thesis would not have been possible without the assistance of the technical staff Mrs J. Falla and Mr P. Stovell for running my NMR and mass spectrometry respectively, Mr F. Quentin for helping me to set the HPLC, Dr S.J. DeMars for taking care of the thermoanalysis equipment, Mr Steve Pike for dealing with all the broken bits of the autoclave, Mr A. Bunby (Bert) for preparing all the glassware needed for my experiments, Mr D. Higgs for allowing me to use the physics laboratory and for taking the pictures of my liquid crytals.

Many thanks to all my friends inside or outside the lab for giving me the joy, happiness and mainly for their great patience throughout this period. I would like to extend my thanks particularly to Dr P. Ibison (Paul), for putting up with me and keeping my spirit high during the last two years.

My sincere gratitude goes to my family for their constant encouragement and emotional support all the way throughout these years.

My biggest thanks are going to my fiancé Vincent Teissier for his love, support, encouragements, and above all exceptional patience since the beginning of this adventure.

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LIST OF ABBREVIATIONS

b.p.	boiling point
BuLi	butyllithium
CB	conduction band
conc.	concentrated
CSA	camphorsulphonic acid
DBSA	dodecylbenzenesulphonic acid
DSC	differential scanning calorimetry
DMF	N,N-dimethylformamide
DMSO	dimethylsulphoxide
EA	elemental analysis
E.C.	electrochemical
Et	ethyl
FET	field-effect transistor
FTIR	Fourier transform infra-red
GPC	gel permeation chromatography
h	hours
HPLC	high performance liquid chromatography
I	isotropic
IMS	industrial methylated spirits
LC	liquid crystal
LCD	liquid crystal display
LCP	liquid crystalline polymer
MCLCP	main-chain liquid crystalline polymer
m.p	melting point
Me	methyl
min	minutes
MS	mass spectrometry
m.u.	monomer units
MW	molecular weight
N	nematic
NMP	1-methyl-2-pyrrolidinone

х

NMR	nuclear magnetic resonance
OMe	methoxy
PA	polyacetylene
PADPA	<i>p</i> -aminodiphenylamine
PANI	polyaniline
PAnthra	polyanthracene
PAz	polyazulene
P.C.	photochemical
PCbz	polycarbazole
PdiA	polydiacetylene
PF	polyfuran
Ph	phenyl
PITN	polyisothianaphthalene
PNaphta	polynaphthalene
PPhena	polyphenylene
PPO	poly(<i>p</i> -phenylene oxide)
PPP	poly(<i>p</i> -phenylene)
PPS	poly(p-phenylene sulphide)
PPy	polypyrrole
PPz	polypyridazine
PSSAH	poly(styrenesulphonic acid)
PT	polythiophene
PTV	polythiophenevinyl or poly(2,5-thienylene vinylene)
S	smectic
SCLCP	side-chain liquid crystalline polymer
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
ГGA	Thermo-gravimetry analysis
THF	tetrahydrofuran
TLC	thin-layer chromatography
ГМА	thermo-mechanical analysis
UV	ultra-violet
VB	valence band
wt	weight

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GENERAL INTRODUCTION



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GENERAL INTRODUCTION

This chapter is intended to introduce the reader to several areas of the chemistry and physical sciences in which there have been almost unparalleled levels of research for a long time.

The first part of this chapter is concerned with **liquid crystals**. A brief historical background and the physical nature of liquid crystals is presented. Most of the liquid crystalline structures, classes and categories have been described and also a wide description of the structural requirements necessary for a rod-like molecule to exhibit liquid crystal behaviour.

Polymer science has witnessed extensive developments, with a move towards more systematic preparations of polymers with specific properties for specific applications. Therefore this chapter presents a brief introduction to diverse aspects of polymer science, in particular liquid crystal polymers and conducting polymers.

The second part deals with **liquid crystal polymers** which is an area of intensive research in modern times. Both factors (i.e. liquid crystal formation and polymeric nature) have a drastic effect on the overall properties of the material obtained and can be combined to give materials with different electrical, optical or mechanical properties. The main overall characteristics and influences of the attachment of liquid crystals on polymers have been described.

The third part reviews the history of **conducting polymers** followed by a basic description of the processes that permit certain organic materials to become electrically conducting. A brief review of the most known conjugated polymers is given, with an emphasis on the most commercially used.

This thesis is particularly concerned with the conducting polymer **polyaniline** so its development, preparation and typical properties will be reviewed with more details in the fourth part of this chapter.

Finally, as the central aim of this thesis is to prepare conducting polymers that possess liquid crystalline behaviour and characterise these materials, a survey of the latest developments and publications in this area is described in the fifth part.

A final section will be dealing with the aims and objectives of this thesis in order to explain the diverse decisions taken during the course of the practical work.

2

I.1 : LIQUID CRYSTALS

I.1.1. Historical Background

The first recorded observation of liquid crystallinity was over 100 years ago in 1888, when Reinitzer¹, an Austrian botanist, observed that cholesteryl benzoate (I) (Fig. I.1) exhibited an unusual melting behaviour. The original white crystalline ester was observed to melt at 145.5°C to a cloudy, viscous state, which persisted until 178.5°C before becoming a clear liquid (the isotropic melt). This behaviour was observed even after numerous crystallisations, with the transition temperatures being reproducible. Also, the reverse phenomena was observed upon cooling from the liquid state. The cooling cycle was also characterised by the appearance of a deep blue colour at the transitions. Later investigations revealed that the colour behaviour Reinitzer observed was characteristic of many compounds containing the cholesterol moiety.

In 1889 and 1890, Lehmann reported similar melting properties for silver iodide², ammonium oleate³, and p-azoxyphenetole (II)³ (Fig. I.1). It was Lehmann who first used the terms "flowing crystal" and "fluid crystal" for this phase intermediate between crystal and liquid states. Indeed, the combination of characteristics -flow properties like a liquid and optical properties like a solid- finally led Lehmann to label these substances Liquid Crystals.

This terminology was not accepted by all the scientific community and in 1922, Friedel⁴ argued that although this state of matter exhibited some properties of both liquids and crystals, it was neither a true crystal nor a true liquid, so the term liquid crystal was misleading. Friedel proposed the more accurate term, **mesophase** (meaning intermediate state or phase). Today, mesophase and liquid crystal are both used, and a single liquid crystal material can show several mesophases.

In 1935, an important group of compounds exhibiting mesomorphic behaviour but differing from liquid crystals was recognised by Timmermanns⁵. These compounds were called plastic or cubic crystals. In the plastic crystals, the freedom for the molecules to rotate exists in the crystal lattice, because the molecules are globular in shape and the

coherence of the crystal is broken only at a higher temperature, the melting point.



Figure I.1 : The first identified liquid crystalline molecules : (I) cholesteryl benzoate, (II) p-azoxyphenetole

The 1930's was a time of intensive research ; many novel liquid crystalline compounds were synthesised and theoretical aspects investigated. After this period there was something of a decline as the field was presumed to be of academic interest only. Since the early 1960's, with the recognition of the important applications of liquid crystals in the electronics/display industry, and the development of suitable materials, interest has dramatically increased. Many more applications have been found and we have now reached a stage such that products resulting from research and development work in liquid crystals are in everyday use.

I.1.2. Definitions of Liquid Crystallinity

It is generally accepted that the higher the temperature, the more the molecules are moving and vibrating in a random way, and so the ability of the attractive intermolecular forces to keep the molecule ordered in any way must decrease as the temperature increases. A solid phase possesses positional order and orientational order whilst a liquid does not. When a solid melts to a liquid crystal, the positional order may be lost although some of the orientational order may remain. The molecules in the liquid crystal phase are free to move about in much the same way as in a liquid, but as they do so they tend to remain oriented in a certain direction. However, the orientational order is not nearly as perfect as in a solid⁶.

A measure of the degree of orientational order (alignment) in the liquid crystal is given by the order parameter $S^{7,8}$:

$$S = 1/2 < 3 \cos^2 \theta - 1 >$$

where θ is the angle between the long axis of a representative molecule and some preferred direction which is denoted as the director (n).

The order parameter of the liquid crystal is this function, averaged over all the molecules.



Figure I.2 : Picture of the molecules in the liquid crystal phase.

This order parameter decreases as the temperature increases. Indeed, in a crystalline solid, S would be equal to 1.0, meaning perfect order, but for a completely random distribution, as is found in a normal isotropic liquid, S would be equal to 0. The order parameter for liquid crystals falls somewhere between these limits and decreases somewhat with increasing temperature (Fig. I.3). For a liquid crystal, the average values for the order parameter S would be between 0.3 to 0.9^9 .



Figure I.3 : Order parameter variation with temperature in the liquid crystal phase.

I.1.3. Categories, Classes, Structures and Optical Textures

Since the original work done by Reinitzer¹ and Lehmann^{2,3}, the field of liquid crystals has grown, especially during the last 25 years, with the development of successful applications such as electrooptical displays. With this growth has come a development of terminology. For a better understanding, we should define the different categories, classes and structures of the various liquid crystal systems.

I.1.3.1. Categories

Liquid crystals may be divided into two broad categories¹⁰ :

- Lyotropic liquid crystals

- Thermotropic liquid crystals

* <u>Lyotropic</u> liquid crystals result from the action of a solvent and, hence, are multicomponent mixtures. They are formed from compounds with amphiphilic properties and solvents (commonly water).

*<u>Thermotropic</u> liquid crystals result from the melting of mesogenic solids and, hence, are thermally activated mesophases. They are formed from compounds (predominantly organic but also organometallic) whose molecules are mainly either rod-shaped or disc-shaped, either by heating the crystalline solid or cooling the isotropic liquid.

I.1.3.2. Classes And Structures

For this project, we will be dealing only with thermotropic systems. Therefore, within the thermotropic category, three distinctive structural classes of liquid crystals have been identified¹¹:

- the NEMATIC structure
- the SMECTIC structure
- the CHOLESTERIC structure

These structures are related to the dimensionality and packing aspects of the residual molecular order.

(i) NEMATIC : (N)

The nematic mesophase is the least ordered of the various types of mesophases. As such, it is more liquid-like in nature. The long axes of molecules remain substantially parallel in the nematic structure (Fig. I.4), and the positions of the centres of gravity are more disorganised than in smectic liquid crystals. The nematic mesophase is unique because of its low viscosity, since the molecules are oriented along the long axis, flow of the molecules along this direction is easier than flow in the isotropic melt.

Common textures observed in a nematic phase under polarising microscope^{12,13} are the Schlieren and the threaded textures. In addition to these textures, others less common may be observed¹² : homogeneous and homeotropic.



Figure I.4 : The nematic liquid-crystal structure

(ii) CHOLESTERIC : (Ch)

The second type of liquid crystal modification, the cholesteric structure, is so named because many compounds that form this mesophase are derivatives of cholesterol¹⁴. Generally, however, the classification has to do with the unusual optical properties of the structure.

The essential requirement for this structure is a **chiral centre**, and the cholesteric mesophase is closely related to the nematic phase but differs significantly in that the director is not constant in space, but undergoes a helical distortion. The structure may be envisaged as composed of layers of nematic liquid crystal as shown earlier. Indeed, the director of an individual layer is rotated through a small angle with respect to the director in adjacent layers. As a succession of layers is passed through, the director turns through 360° and this thickness represents the pitch length for the helix (Fig. I.5). The main chemical feature which distinguishes a Ch material from a N material is that its molecular structure is chiral and therefore not superimposable on its mirror image.



The director (arrow) traces out a helical path

The 'blue phase' :

The blue phase has been observed for several cholesteric substances in a small temperature

Figure I.5 : The cholesteric liquid-crystal structure

region immediately below the clearing point^{15,16}. They have been extensively studied in the mid 80's and it appears that there are at least three phases^{17,18,19,20} : blue phase I (BPI) is body-centred cubic, BPII is primitive cubic and BPIII is known as "blue fog" and no structural symmetry has been observed. The phases usually exhibit an optically bluish isotropic texture²¹.

(iii) SMECTIC

Smectic liquid crystals are not only distinguished by a parallelism of molecular, long axes but by a layering of the molecular centres of gravity in 2-dimensional planes or sheets (Fig. I.6).



Figure I.6 : The smectic liquid-crystal structure

In the smectic phase, not only is the small amount of orientational order of liquid crystals present, but there is also a small amount of positional order. The molecules are free to move around quite randomly, but they also tend to point along the director and arrange themselves in layers.

The smectic mesophase is the most solid-like of the liquid crystal modifications, and smectic liquid crystals retain a good deal of 2-D solid order ; the order parameter may be as high as 0.9.

As the smectic phases are arranged in layers, the molecules can be oriented in an angular or perpendicular manner with respect to the plane of the layers. These possible orientations combined with the degree of order of the molecules within and between the layers give rise to a large number of smectic phases. There are at least 11 smectic phases reported in the literature²². These mesophases are designated by the alphabet letters A through K^{23} . These smectic mesophases differ in the orientation of molecules within a given layer, in intralayer spacings and the molecular layers are generally able to slip past each other.

Between these 11 smectic phases, there are two slightly different groups : In the first group, the director is perpendicular to the layer planes, while in the second the director makes an angle other than 90° to the planes.

In the first group, we find the following phases : S_A , S_B , E

In the second group, we have the phases : S_C, S_F, G, H, S_I, J, K

(NB : the D is not completely defined but is believed to be cubic in structure).

There is also a difference between both S_A and S_C , which behave like true 2-D liquids and the other smectic phases. Indeed, in both S_A and S_C phases, the molecules randomly diffuse within each plane. No positional order exists within each plane. However, other smectic liquid crystal phases do have their molecules ordered within each plane.

As the structural details of the various smectic phases have been fully established during the last decade, some of the phases, namely E, G, H, J and K have been renamed crystal phases as they possess three dimensional correlations of molecular positions and consequently are structurally crystalline²⁴ (Fig. I.7).



Figure I.7 : Degree of order in the various mesophases.

Optical studies of smectic phases using the hot-stage cross-polarised optical microscope can produce two types of phase texture, natural or paramorphotic. Natural optical textures are those formed on cooling directly from the nematic or isotropic phase. Paramorphotic textures are those inherited on cooling from a higher temperature smectic phase. For example, the smectic B phase will exhibit the focal-conic fan texture when it is formed by cooling a smectic A or C phase which was already exhibiting that texture. This property can often make microscopic phase identification complex and difficult.

(a) 1st GROUP : Molecular director perpendicular to the layer planes

Smectic A) The smectic A phase is the smectic polymorphic modification which possesses least order and the most common. In any phase sequence which includes S_A , this phase precedes all other smectic phases upon cooling either the isotropic liquid or the nematic phase. In the S_A phase, the molecules are arranged perpendicular to the layer plane. The centres of gravity are ordered with random spacing between a molecule and its neighbour (Fig. I.8).



Figure I.8 : Representation of a smectic A structure

The smectic A phase can be identified by two natural textures formed, the homeotropic and the focal conic (fan shaped or polygonal)^{25,26}. The homeotropic texture is optically isotropic and appears dark under the microscope, in fact this texture is the result of director alignment parallel to the incident light beam. The focal conic fan texture is characterised by the development of batonnets or needle shaped regions which merge to form a complete structure. The back of the fans are crossed with faint lines.

In the two other phases of this group smectic B and crystal E, the tilt disposition is also orthogonal but the molecular packing is no longer random, there is more order in the hexagonal S_B and the orthorhombic E phases than in the S_A phase.

Smectic B) There are two forms of the smectic B phase, the hexatic B and the crystal B. The structure of the hexatic B phase is similar to that of the smectic A phase except that the molecules are arranged in a layers in a hexagonal close packed manner with the molecular long axes orthogonal to the planes of the structured layers (Fig. I.9). Within the hexatic B there are no positional correlations between layers, but three dimensional long range bond orientational order is present. The crystal B phase shows long range layer correlations and long range positional ordering within the layers. The phase is truly crystalline but shows considerable thermal disorder, such as rapid rotation about the molecular long axes.

The S_B phase exhibits two natural textures the homeotropic²⁷ and the mosaic²⁸ and a single paramorphotic focal conic fan texture²⁹. The mosaic texture consists of interlocking platelets and is characterised by the presence of H-shaped platelets. The paramorphotic focal conic fan texture is formed from the similar texture of S_A , but has smoother fan backs.



Figure 1.9 : The smectic B phase where the molecules are orthogonal to the layers (side view) and packed in a hexagonal array (top view)

Crystal E) The crystal E or, as it is often still known, the smectic E has a long range ordering of both the molecular positions within the layers and interlayer correlations. An orthorhombic array of the molecules within the layers characterises the E phase. The molecules are arranged in a long range 2-dimensional order within a layer. The E phase is a highly ordered smectic state. The difference between a S_B and a E phase is a contraction of the hexagonal net in one of the three possible directions separated by angles of 60°, this contraction resulting in a orthorhombic arrangement (Fig. I.10).

There are very few examples of direct isotropic to crystal E transitions so it is difficult to

determine the characteristics of the natural crystal E textures³⁰. However, the three paramorphotic textures formed, the focal-conic fan, the platelet, and the mosaic have been characterised. The focal conic fan texture³¹ shows very clear arcs across the backs of the fans which remain throughout the temperature range of the phase. The platelets formed on cooling the homeotropic texture of the S_A or S_B phase appear grey-blue to yellow and ghost-like³². The mosaic texture consists of interlocking well-defined platelets crossed with parallel lines.



Figure I.10 : The crystal E phase and the orthorhombic arrangement b>a (top view)

(b) 2nd GROUP : Director with an angle other than 90°

Smectic C) The smectic C phase is closely related structurally to the S_A phase. Molecules are arranged in layers, but unlike the S_A phase they are tilted with respect to the layer planes. The molecules are also randomly spaced about the molecular centres of gravity within a given layer (Fig. I.11).



Figure I.11 : Smectic C structure

The S_c phase exhibits two natural textures, the schlieren and the focal-conic fan. The schlieren texture can be distinguished from that of the nematic phase by the fact that it is less mobile, only consists of four brushes point singularity and does not flash when subjected to mechanical stress³³. The focal conic fan texture is generally formed paramorphotically from the smectic A and is typically very broken and sanded resulting in an ill-defined appearance³⁴. The natural focal conic fan texture is rarely formed but when seen is less broken than that of the paramorphotic one.

For the other smectic phases of this group, the tilt disposition can have various values, such as the molecular packing which can be hexagonal (smectics F and I, crystals G and J) or monoclinic (crystals H and K). Furthermore, this second group can also be chiral.

Smectic F) The S_F phase consist of layers of hexagonally packed molecules in which the director is tilted with respect to the layer normal (like in the S_C phase). The hexagonal net in each layer is not correlated between the layers, so within the layers there is no long range positional ordering of the molecular centres of mass and no long range interlayer correlations exist. The tilt angle of the hexagonal net is to the side of the hexagon (Fig. I.12).

The smectic F phase exhibits two natural textures, the mosaic and a texture which may be of the cylindrical, spherulitic, or fan type, as well as a large number of paramorphotic textures. The mosaic texture is not a true mosaic, but shows mosaic platelets separated by very fine lines. The platelets have a tendency to contain schlieren-like brushes, therefore it is also called mosaic-*schlieren* because of this similarity³⁵.



Figure I.12 : Tilt to side of the hexagonal net in S_F

Smectic I) The structure of the S_I phase is similar to that of the S_F phase but the tilt angle of the hexagonal net is to the apex of the hexagonal net (Fig. I.13).

The S_I phase exhibits very similar textures to the S_F , and when observed are very difficult to distinguish one from the other.



Figure I.13 : Tilt to apex of the hexagonal net of S_I

Crystal G) The G phase was originally classified as smectic but in recent years it has been known as a crystal phase, as a result of the three dimensional long range order it possesses. It has been shown that the molecules in the G phase are packed in layers and pseudo-hexagonally close packed. The molecules within the layers have their long axes tilted with respect to the normal to the layer planes (average tilt angle in the range 25-30°), so the G phase is the tilted analogue of the crystal B phase and the crystal analogue of the S_F. Indeed, the tilt direction is to the side of the hexagonal net (Fig. I.14).

The crystal G phase exhibits numerous microscopic textures because it is formed from a large variety of precursor phases on cooling³⁶.



Figure I.14 : The correlated three-dimensional structure of the G phase. Tilt direction towards a side of the pseudo-hexagonal net.

Crystal J) It is also called G', because it possesses the same hexagonal packing, except for the tilt direction which is tilted to the apex of the hexagonal net.

Crystal H) Most of the X-ray diffraction studies performed on the H phase indicate that it has a structure equivalent to that of the crystal E phase, except that the molecules have their long axes tilted with respect to the normal to the layer planes. It is assumed that the molecules adopt an orthorhombic close-packing in a plane at right angles to the molecular long axes. However, because of the tilt, the pseudo-hexagonal net becomes even more distorted, and the phase really has a monoclinic structure (Fig. I.15).

The H phase has not yet been obtained directly on cooling the isotropic liquid or the nematic phase, and therefore has not exhibited its natural texture. The phase does however show a number of paramorphotic textures based on the textures of the phases preceding it on cooling. Commonly, these are the paramorphotic fan³⁷ and mosaic³⁸ textures.



Figure I.15 : The layer structure of crystal H phase.

Crystal K) It is also called H', because it has a similar structure to crystal H but the tilt direction is different. In fact, K and H differ as to the side (a or b) of the monoclinic cell towards which the molecules are tilted (see Fig. I.10).

The tilted modification of the S_A is S_C , for the S_B the tilted modifications are S_F and S_I (respectively tilted to side and apex), for the crystal B the tilted modifications are G and J (respectively tilted to side and apex) and for E the tilted modifications are H and K.

(c) The D phase

The D phase is a rarely observed phase, so the structure of the D mesophase is not completely defined but it is believed to be based on a cubic unit cell and having three dimensional periodicity, with the molecules associated in micellar groups. In contrast with other smectics, the D phase is optically isotropic (not homeotropic) and then can be mistaken for an isotropic liquid, except that it is highly viscous. Since the D phase is optically isotropic, it has no texture in the real sense. A uniform film of D presents an optically extinct (black) field of view. The phase is distinguished from the isotropic liquid or the homeotropic phases by the fact that the black, isotropic D phase develops in the S_c phase distinctive shapes : rectangles, squares, rhombs, and hexagons^{39,40}.

I.1.3.3. Discotic Liquid Crystals

So far the introduction has been devoted to the liquid crystals phases formed by rodlike molecules. The reason is, these phases are the most common and therefore the most well known. However, in 1977 researchers⁴¹ in India discovered that disc-like molecules also form liquid crystal phases in which the axis perpendicular to the plane of the molecule tends to orient along a specific direction. These phases and the molecules that form them are called **discotic** liquid crystals (Fig. I.16).

The most simple discotic phase is also called the **nematic** (N_D) phase, because there is orientational order but no positional order. In addition to the orientational order, positional order is possible and occurs when the molecules tend to position themselves in columns to give rise to the **columnar** or smectic discotic phase. The columns can also be arranged in a hexagonal lattice like the rodlike molecules. Chiral nematic discotic liquid crystal phases can also exist.



Figure I.16 : Molecular Structure of a typical Discotic Liquid Crystal.

The studies of this thesis is based on rod-like thermotropic liquid crystalline molecules, so only these type of liquid crystals will be considered further.

I.1.4. Requirements For Liquid Crystallinity

It is not yet possible to predict completely all the properties of new liquid crystal compounds. However, it has been established that certain rules exist that can be used to predict the occurrence of liquid crystallinity⁴².

The general, common feature is an elongated, narrow molecular framework⁴³, but mesomorphism is also connected with the strength and position of polar groups within the molecule, the molecule's overall polarisability, and the presence of chiral centres (for cholesteric)^{44,45}. Molecular interactions that lead to attraction are dipole-dipole interactions, dipole-induced dipole interactions, dispersion forces and hydrogen bonding. In order for dipole-dipole and dipole-induced dipole interactions to be effective, the molecule must contain polar groups and/or be highly polarisable. So, ease of electronic distortion is favoured by the presence of aromatic groups and double or triple bonds. Also, the thermal stability of a smectic mesophase is determined mainly by the lateral intermolecular attractions (i.e. attractions operating between the sides and planes of molecules) whereas the thermal stability of a nematic phase is determined by residual terminal and lateral attractions between molecules which maintain their parallel arrangement.

The most common nematogenic and smectogenic molecules^{46,47,48,49,50} are of the following type:



WHERE :

- * a and b have small integral values.
- * \mathbf{R}_1 and \mathbf{R}_2 represent a range of terminal substituents such as alkyl, alkoxy and cyano.
- * A—B represent a linking unit in the core structure.

Some general features have been reported relating liquid crystalline behaviour with molecular structure :

I.1.4.1. Terminal substituents

A nematic terminal group efficiency order has been reported⁵¹ :

 $Ph > NHCOCH_3 > CN > OCH_3 > NO_2 > Cl > Br > N(CH_3)_2 > CH_3 > F > H$ This means that when H is replaced in a terminal position by any of the above substituents, the nematic thermal stability is enhanced, the effect being greatest for groups that are compact, polar and polarisable.

For smectic systems, the following orders have been found⁵² :

 $NHCOCH_3 > Ph > Br > Cl > F > N(CH_3)_2 > CH_3 > H > NO_2 > OCH_3 > CN > H$

The orders are generally different between the nematic and the smectic, with the exception of the highly polarisable Ph and NHCOCH₃ substituents. This would be expected due to the difference in the nature of the properties needed to stabilise the two types of mesophase. For example, the cyano- and nitro- groups are quite inefficient in promoting smectic behaviour as they possess large dipoles lying in the direction of the long molecular axis. This gives rise to repulsive forces between molecules lying parallel to one another and does not favour layer formation. The methoxy group has a dipole moment which acts across the long axis of the molecule and this could be expected to enhance smectic thermal stability. It is, however, found⁵³ that the methoxy group does not enhance smectic phase stability and this is mainly due to possible rotation of the oxygen-ring bond which can align the dipole statistically closer to the long molecular axis than would be initially predicted.

I.1.4.2. The role of the central linking group

It has been established that the central linking group governs the mesophase thermal stability rather than the type of mesophase exhibited⁵⁴. The nematic to isotropic transition temperatures are raised if the central linking group permits conjugation to occur between the rings. This can increase the anisotropy of molecular polarisability. Thus linking units containing multiple bonds that maintain the rigidity and linearity of the molecule are the most satisfactory in preserving high transition temperature from nematic to isotropic phase. Again, a reported central group nematic efficiency order is⁵⁵ :

CH=CH trans > N=N > CH=N > C=C > N=N > CH=N > C-O > none

$$\downarrow \qquad \downarrow \qquad \parallel$$

O O O O

Groups such as -CH=CH- are rigid and can interact with the π -electrons of the ring, whereas ester groups do not permit conjugation between the rings, and saturated groups such as -CH₂-CH₂- and -CH₂-O- are too flexible and contain no π -electrons.

I.1.4.3. The influence of lateral substituents

These can have three effects :

(i) Molecular broadening

Any lateral substituent in a given system will increase the breadth of that system and the general effects on a mesogen is found to be^{56} :

- to decrease the N-I transition temperature, the larger the substituent the greater effect.

$$H < F < CH_3 < Cl < Br < I \simeq NO_2$$

- to decrease the S-N or S-I transition temperatures again the larger the substituent the greater the effect.

$$H < F < Cl < Br \simeq NO_2 < CH_3 < I$$

However, the dependence on molecular size is sometimes countered by the dipole moment of the substituent.

(ii) Steric effects

Even though lateral substitution can broaden the molecule, it can impose a steric effect on the system (which increases in proportion to the size of the substituent) by causing a twist about one of the bonds, so that parts of the molecule are rotated out of the plane of the remainder of the molecule. This is not only increasing intermolecular separation but also the thickness of the molecules leading to a decrease in the anisotropy of molecular polarisability, so this causes the mesophase thermal stability to decrease at a faster rate than expected from a consideration of molecular broadening alone.

(iii) Branching of terminal alkyl chains

This results in lowering of the thermal stabilities of both nematic and smectic mesophase⁵⁷. The effect is most pronounced if the branching occurs at the 1-position (i.e. at the carbon atom nearest to the molecular centre) and becomes less pronounced as the point of branching progresses towards the end of the chain. The extent of the lowering of thermal stability also depends on whether or not the alkyl chain is attached directly to the ring or via oxygen atoms (e.g. in ether or esters).

I.1.4.4. Other structural factors

In accordance with the general requirement of elongated and fairly rigid molecular structure, the following points are also established :

* Any increase in a and/or b rapidly elevates the $T_{\text{N-I}}$ or $T_{\text{S-I}}$

* In the case of carboxylic acids, hydrogen bonding can induce mesomorphic behaviour by lengthening the molecular unit through dimerization as illustrated in Fig. I.17:



Figure I.17 : Hydrogen bonding of carboxylic acids.

There are a lot of other factors which can influence the mesomorphism but the main ones have been discussed above.

We need to emphasise that a liquid crystal compound can take on more than one type of mesomorphic structure as the conditions of temperature or solvent are changed, to give rise to **polymorphism** as illustrated by the following example⁵⁸ in Fig. I.18 :



Figure I.18 : Transition Temperatures[§] (°C) of 4-n-Decyloxyphenyl 4-n-decylbenzoate.

[§] The temperatures in bracket are monotropic liquid crystal phases (exhibited liquid crystalline properties only on cooling)
I.2 : POLYMER LIQUID CRYSTALS

I.2.1. Introduction

Whilst the majority of early research into liquid crystals was concerned with the synthesis and characterisation of low molecular weight compounds, it soon became clear to scientists like Onsager⁵⁹ and Flory⁶⁰ that liquid crystal polymers (LCP) should also exist. The first systematic experimental verification of this prediction came in 1950⁶¹ from work on concentrated solutions of poly(τ -methyl glutamate) and poly(τ -benzyl glutamate). It was later shown in the mid-70's that anisotropic solutions were formed by some rigid aromatic polyamides and cellulose derivatives. These lyotropic nematic solutions could be treated to form fibres containing highly orientated polymeric chains. The additional ordering leading to very high strength fibres, known as aramid fibres (poly(*m*-phenylene isophthalamide) trade name Nomex, poly(*p*-benzamide) also called Fibre B and poly(*p*-phenylene terephthalamide) trade name Kevlar are the best known), which are stronger than steel but much less dense, making them very attractive and successful alternatives^{62,63}.

For these reasons, the development during the last few decades, of polymers exhibiting a liquid crystalline state has become of increasing theoretical and technological interest because of their properties, which are a combination of polymer specific properties (e.g. their ease of processing) and the anisotropic behaviour of liquid crystals to enhance particularly electrical and optical properties.

Ringsdorf and Finkelmann^{64,65,66} in Mainz, Shibaev and Plate^{67,68} in Moscow and Blumstein⁶⁹ were the pioneers to design and synthesise in the late 70s new comb-like polymers in which the tail of the mesogenic unit was attached to the polymer backbone. An excellent review on the subject up to 1984 was prepared by Finkelmann and Rehage⁷⁰, and this can be combined with some later comprehensive reviews^{71,72,73} on the subject.

I.2.2. Definitions and Classification of Liquid Crystalline Polymers

As previously discussed a possible condition for the appearance of the liquid crystal state is a rigid, anisotropic molecular shape^{74,75}. This concept is directly applicable to polymers, the monomer units (m.u.) of the polymer backbone containing the mesogenic

moieties.

:

The liquid crystal state can be directly related to the chemical constitution of the molecules, two classes of monomers causing liquid crystallinity in the polymer can be distinguished

- Thermotropic liquid crystal.
- Lyotropic liquid crystal.

In **Thermotropic** systems, the liquid crystalline phase only exists within a particular temperature range. It lies between the crystal melting point, T_m (or in cases where crystallinity is absent, the glass transition temperature, T_g), and the so-called upper transition temperature where the liquid crystal phase reverts to an isotropic liquid.

Lyotropic liquid crystalline phases contain non-mesogenic solvent molecules in addition to the mesogenic ones. Lyotropic systems are particularly significant in liquid crystalline polymers, as the addition of the solvent is an important means of reducing crystalline melting points to manageable levels.

The monomers can be attached together in two different ways to realise a macromolecule with mesogenic reactive monomeric liquid crystals :

- the mesogenic moieties are connected head to tail forming main chain polymers.
- the mesogenic moieties are attached as side chains to the monomer units of the

polymer backbone. They are called liquid crystal side chain polymers.

Furthermore, the polymer may contain mixtures of both main-chain and side-chain mesogenic units.

In either case, the attachment of the liquid crystal group to the polymer chain can be via either a short or long spacer chain. This spacer is called rigid when the mesogenic groups are connected directly to the polymer chain or flexible when the mesogenic groups are connected via a flexible spacer assuming a sufficient spacer length, giving more freedom of motion.

These concepts give rise to the different types of liquid crystal polymers^{76,77,78} which are illustrated in Figure I.19 :

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Figure I.19 : Some model representations of liquid crystalline polymers.

In addition to these terminally attached polymers, a series of laterally attached ones can be designed (Fig. I.20).



Figure I.20 : Examples of laterally attached liquid crystalline polymers.

A complete classification of all the different types of liquid crystal polymers has been proposed in the article by Brostow⁷⁹. As for conventional polymers, the polymer main chain

may be linear, branched or crosslinked. Thus, a vast number of potentially mesogenic polymers of diverse structure may be produced.

In addition to the synthesis of homopolymers, which have only one type of monomer unit, a variety of copolymers have been prepared^{80,81}.

A polymer liquid crystal may also possess one or more liquid crystal phases (smectic, nematic, cholesteric), which can give rise to polymorphism^{82,83}.

This thesis is concerned with perhaps the biggest area of interest, namely thermotropic mesogenic side-chain polymers. The attractiveness of these polymers lies in their physical arrangement. This particular system can then be applied to the preparation of liquid crystalline conducting polymers, in which the liquid crystal unit is attached to the conducting polymer backbone by a flexible spacer-chain, without affecting the conjugated nature of the backbone.

I.2.3. Thermotropic Liquid Crystal Side Chain Polymers

In their chemical constitution these polymers consist of two elements :

- One is the **polymer backbone**, which can be widely varied in chemical and physical properties.

- The other is the **mesogenic side chain**, for which a large number of chemical constitutions are also conceivable.

One principal aspect of these polymers is whether polymer-specific properties are influenced by the anisotropic state of the mesogenic side-chains and vice-versa.

First, we need to emphasise that polymers can exist in more than one phase, as is true of all substances. The solid phase of polymers can be either crystalline or amorphous. In the crystal phase, the polymer molecules occupy positions in a specific arrangement. In the amorphous phase, the polymers are arranged quite randomly but are not free to move to other positions. The amorphous solid phase of polymers is also called the **glassy** phase. These two phases can often coexist over a significant temperature range. A solid polymer, whether crystalline or glassy, will melt when heated. If it melts to a liquid crystal phase of some sort, it is called a polymer liquid crystal.

It could therefore seem easy to prepare polymers with mesogenic side chains. Indeed, compared with low molecular weight liquid crystals, in principle the only change of the mesogenic moiety is the restriction of translational and rotational motions due to the

linkage to the backbone. These restrictions should be more or less influenced by the physical properties of the main chain and in which way the rigid mesogenic moiety is linked to the backbone.

I.2.3.1. Influence of the Flexible Spacer Group

Several experiments have demonstrated⁸⁴ that a direct linkage of rigid mesogenic groups to a polymer backbone is generally not sufficient to obtain mesogenic polymers. Indeed, polymers without spacer groups are not liquid crystalline on heating. In most cases, only isotropic polymer melts are observed or solid polymers with a liquid crystalline structure. (This latter structure disappears irreversibly if the polymer is heated above the glass transition temperature, T_g . When these polymers are subsequently cooled below T_g , isotropic glasses are obtained). This structure does exhibit some "frozen in" order from the monomer phase order during polymerisation. The development of this "frozen in" order has been attributed to the interaction between side groups and the limited motion of the main chain^{85,86}.

Thus, direct linkage of mesogenic groups to the polymer main chain results in a different system than the low molecular weight liquid crystal. In fact, because of the covalent linkage to the main chain, motion of the mesogenic groups is drastically reduced. Translational diffusion is no longer independent of the neighbouring molecules. As space filling models show, large mesogenic groups are prevented from attaining parallel alignment because of strong steric hindrance. This also causes a stiffening of the polymer chain, which is often indicated by an increase of T_{e} .

These problems can be overcome by the separation of the liquid crystalline moiety from the polymer backbone with a **flexible spacer group** such as alkyl or alkyloxy chain. The flexible spacer allows, to an extent, the decoupling of the motion of the backbone of the polymer from the mesogenic side group motion.

Although above the glass transition temperature the polymer main-chain tends to adopt a statistical chain conformation, the flexible spacer enables the mesogenic side chains to order anisotropically. Under these conditions, the mesogenic side chains can be anisotropically ordered in the liquid state even though the polymer main chain tends to adopt a statistical chain conformation. Consequently, variation of the spacer length should clearly influence the liquid crystal order of the side chain. As illustrated in Figure I.21, if the spacer-chain is too short or non-existent, then the effect of the polymer backbone on

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the mesogenic units is extreme and prevents anisotropic alignment. If the spacer-chain is too long, then the mesogenic units have enough freedom to adopt a more ordered structure, with the result that smectic phases only are obtained.



Nematic mesophase



Smectic phases or Glasses



Direct attachment, no mesophase formation

Figure I.21 : Model considerations of liquid crystalline side chain polymers

I.2.3.2. Phase Behaviour of Polymer Liquid Crystals

Because the polymer backbone and the mesogenic groups are free to move, thermotropic liquid crystalline polymers can be produced. These types of polymers have been shown to exhibit nematic, smectic, and cholesteric mesophases.

The phase behaviour is related to the molecular structure. Indeed, if we compare the phase behaviour of the mesogenic monomer with that of the corresponding polymer, two important changes in property are observed :

- the increased tendency towards formation of smectic phases

- the increased liquid crystal phase transformation temperatures with increasing the degree of polymerisation (DP).

The tendency towards formation of the higher ordered smectic phases for the polymers can be explained by the reduced mobility of the mesogenic side chains connected via the polymer backbone⁸⁷. Rotational as well as translational motions are restricted, favouring the formation of the smectic state. Thus, for the production of nematic polymers, higher mobility of the mesogenic side chain is necessary through a flexible spacer or a sufficient flexibility of the chain segments. In practice, to obtained nematic polymers, it was found that the use of non- (but potentially) mesomorphic monomers, or monotropic nematic monomers, resulted in the formation of nematic polymers (normally incorporating a spacer chain containing around 6 methylene or oxy- groups). If the monomer was already nematic, in most cases smectic polymers resulted⁸⁸.

The increase of the LC phase transition temperature by polymerisation can be almost quantitatively explained by the reduction of the specific volume in going from the monomer to the polymer^{89,90}. A strong decrease in specific volume is observed for a degree of polymerisation (DP) DP<10 and levels off for DP>100. Similarly, the phase transformation temperatures increase with DP. Interestingly, the S-N or S-I transformation temperatures do not increase with DP as strongly as the N-I transformation temperatures :

ΔT_{N-I}	١	ΔT_{s-i}		$\Delta T_{\text{S-N}}$
****	/		~	
Δ DP		Δ DP		Δ DP

A third important aspect of the majority of liquid crystal side chain polymers is their glass transition at low temperatures^{89,90}. While the monomer and dimer crystallise, for DP>3 a crystallisation is no longer observed at low temperatures but there is instead a transition into the glassy state. In the case of non-crystallisable polymers⁹¹, the low temperature limit for the existence of the LC state is the T_g (and not the melting temperature as for crystallisable polymers). As a rule this temperature is lower than the clearing temperature (T_c) and in a T_g-T_c interval the polymer either in the form of elastomer or in the form of viscous melt is in a liquid crystal state. On cooling, a low molecular weight LC will normally crystallise at or just below the melting temperature (T_m) whereas LC SC polymers undergo a glass transition. A liquid crystalline structure characteristic of the mesophase is then preserved in a glassy state. Below the T_g the LC structure may thus be frozen and a glassy polymer having liquid crystalline structure obtained. This constitutes one of the most interesting properties of SC LC polymers.

The properties of SC LC polymers enables materials to be prepared in which it is possible to freeze a liquid crystal texture into the glassy state by supercooling. It is also possible to produce thin films of these materials which respond to electric and magnetic fields above the T_g . These properties are of great interest for display purposes and above T_g , an electric or magnetic field can be used to put in information that can be durably stored at lower temperatures in the glassy state of the material.

I.3 : CONDUCTING ORGANIC MATERIALS

I.3.1. Introduction

Organic materials have traditionally been regarded as exceptional electrical insulators, ie. they do not sustain the flow of an electrical current. For example, polyethylene is a widely used insulator for electrical cables. Whilst there was evidence from as early as 1954^{92} that organic materials could be made to exhibit electrical conductivity, the level of research into such materials only became truly significant in the 1970's, with the advent of two important discoveries. In 1973, Ferraris et al⁹³ found that the organic complex between tetrathiafulvalene and 7,7,8,8,-tetracyano-p-quinodimethane (also known as TTF-TCNQ, see Figure I.22), was metallic in behaviour with room temperature conductivity $\sigma \approx 500$ S cm⁻¹, whilst in 1977, Shirakawa et al⁹⁴ found that suitably prepared polyacetylene exhibited metallic-like conductivity with room temperature conductivities ($\sigma = 1000$ S cm⁻¹). Nowadays, conjugated polymers can exist with extrinsic conductivities ranging from that of glass to that of copper^{95,96} (Fig. I.23).



Figure I.22 : TTF-TCNQ



Figure I.23 : Conductivities of various elements, compounds and polymers

I.3.2. Structural Requirements for Electrical Conduction in Organic Materials

Conducting organic compounds have been categorised⁹⁷ as belonging to one of the three types of organic materials :

- * Charge-transfer complexes and ion radical salts, eg. TTF-TCNQ.
- * Organometallic species, eg. Nickel dithiolate salts.
- * Conjugated polymers, eg. polyacetylene.

All these materials have at least one structural feature in common : they all possess high levels of **conjugation**, i.e. an extended sequence of strictly alternating single and double bonds. π -electrons are an inherent feature in conjugated molecules and are contained in p_z -orbitals orthogonal to the plane containing the associated nuclei and σ -bonds. They are less tightly held to the nuclei than their σ -bonded counterparts since they occupy the space above and below the internuclear axis. Consequently, removal of π -electrons does not

provoke severe nuclear repulsions, and the electrons may be regarded as belonging to a delocalised orbital. If this orbital is spread over a large number of atoms, then the π -electrons may be considered to occupy a delocalised energy band, according to the simple principles of **Band Theory**⁹⁸. It is these π -electrons which are available for conduction processes, along with the lone pairs of electrons which occupy similar, orthogonally situated p-orbitals and play an additional part in some heteroatom-containing materials. Any organic species therefore, which possesses π -electrons or lone pairs which can be delocalised over a large number of atoms, is a potential electrical donor.

I.3.3. Electrical Conductivity : Band Theory

Electrical conductivity reflects the net charge motion brought about by an electric field E, that is :

$$\sigma = J / E$$
 where J is the current density.

The ability of materials to conduct electricity can be explained simply using band models to describe the energy levels of a material's electrons. The energy difference between the valence band (which contains valence electrons) and the conduction band (of higher energy) determines whether a material is a conductor, a semi-conductor or an insulator⁹⁹ as illustrated in Figure I.24 :



Figure I.24 : Band-gap Diagram for Solid Materials

For conductors, the highest level of the valence band and the lowest energy of the conduction band are similar, therefore there is little or no gap and electrons can move easily into the conduction band. For insulators, the separation between the two bands is large (ΔE >3eV) and promotion of an electron to the conduction band is not possible. In semi-conductors the energy gap is much smaller, usually a few times kT, and there is then some chance for promotion to occur.

Electrical conduction, in organic materials, may occur through the movement of either electrons or ions. For each of these, the conductivity σ is equal to the product of the carrier mobility, μ , its charge, q, and the number of carriers per m³ or the concentration n, as in :

 $\sigma \text{ in } Sm^{-1}$ $\mu \text{ in } m^2 s^{-1} V^{-1}$ q in C $n \text{ in } m^{-3}$

All variables are dependent upon the environment in question and therefore a number of conduction mechanisms are possible.

I.3.4. Conjugated Polymers

The conductivity of these materials arises from electrons in the conjugated π -orbitals distributed along the polymer backbone. They are desirable materials because they combine the necessary properties of a polymer with the electrical properties of a conventional semiconductor. Conjugated polymers are therefore expected to become prime constituents in electronics based on organic materials⁹⁷. There are already some established applications and there is a considerable volume of research in progress in order to commercialise most of these materials¹¹⁰. The properties of these polymers could be the basis of a variety of practical applications such as information storage and optical signal processing, substitute materials for batteries and devices for solar energy conversion, while electroluminescence from poly(p-phenylene vinylene) based devices is a rapidly expanding field of interest. Furthermore, larger-scale electronics using conjugated polymers as semi-conductors in for example field-effect transistors (FET) or as control elements for liquid crystal displays (LCD) is feasible due to the improved performance of these organic materials. However, the development of all these possible applications has to some degree been limited by the low stability towards oxidation and lack of processibility often characteristic of these polyconjugated systems. As a result, a considerable research effort has been directed towards the preparation of well-defined conjugated oligomers and polymers with improved processibility and/or stability, and this activity has provided materials with significantly improved properties. Several classes of polyconjugated materials have been synthesised, studied and applied. Polyacetylenes, polydiacetylenes, polyphenylenes and the alternating copolymers of acetylene and phenylenes (the poly(phenylene vinylene)s), are the most important classes of hydrocarbon polymers with extended π -conjugation. Another important class of polyconjugated materials consists of heterocyclic polymers, such as polythiophenes and polypyrroles, and other polymers with heteroatoms in the main chain, like polyaniline. Moreover a variety of heterocyclic structures have been introduced to decrease the band gap of the conjugated polymers, while many copolymers have been prepared and studied. Polypyrrole and polyaniline appear to be the front-runners as stable conducting polymers and are directly synthesised in their doped states.

I.3.4.1. Polyacetylene

Polyacetylene is the simplest polyconjugated polymer and the first reports on these long polyene polymers date back to the last century¹⁰⁰. Despite the work of Natta in 1958, it was not until 1974 that Shirakawa and coworkers^{101,102} developed a simple method of preparing films which on treatment with oxidising agents such as AsF₅, exhibited significant electrical conductivity. A variety of experimental details of this Ziegler-Natta polymerisation have been optimised during the years following this discovery, finally leading to the Naarmann-route using the so-called reducing agent method¹⁰³, further optimised by Tsukamoto¹⁰⁴. The all-*trans*-polyacetylene samples thus obtained were stretchable and on iodine doping yielded conductivity values of more than 10⁵ S cm⁻¹. Unfortunately, the conductive form was stable under inert atmosphere conditions only, limiting the applicability of the polymer.

Polyacetylene has both *cis* and *trans* forms (Fig. I.25) and the polymer's conjugated chain consists of a carbon backbone of σ -bonded carbon atoms with a set of carbon p_z wavefunctions forming π -orbitals. The overlap of the π -orbitals (C(p_z)) of one monomer unit with those of its neighbours forms valence and conduction band orbitals that extend over the entire molecule. These give rise to high electron mobilities along the polymer chain.



TRANS

CIS

Figure I.25 : Polyacetylene cis and trans Isomers

In the undoped state these isomers are wide-band-gap semi-conductors and are in the main insulating. However, if charge transfer agents (dopants) are added to the polymer they can oxidise or reduce it, dramatically changing the backbone geometry and electronic structure. The partially oxidised polymer backbone (with associated counterions) is deficient in, or has an excess of electrons on the chain, producing defect states in the gap and possibly a metal-like partially filled band and a high conductivity.

By chemically or electrochemically doping polyacetylene films, their electrical conductivities can be varied from those of an insulator through semiconductor to metallic conductor. A common technique employed to synthesise some of these conducting polymers is electrochemical polymerisation. It permits the use of simple monomers and electrolytes, and the production of good quality polymer films. The technique also allows the incorporation of dopant into the polymer at the same time as synthesis, since the dopant molecules can be used as part of the supporting electrolyte. Dopants used may be either electron attracting (p-type dopants such as AsF_5 , Br_2 , I_2 or $HClO_4$) or electron donating (n-type dopants such as an alkali metal naphthalide). Chemical doping is typically achieved by exposing *cis* or *trans* films to vapour of the dopant. The doping of *cis* films has been more extensively studied than *trans* films because their doped conductivities are two or three times greater than those of the *trans* analogues.

While the addition of a donor or acceptor molecule to the polymer is called "doping", the reaction which take place is actually a redox reaction¹⁰⁵ and is unlike the doping of Si or Ge in semiconductor technology where there is substitution of an atom in the lattice.

Therefore, we need to remember in all this thesis that doping of conducting polymers involves the formation of a polymer salt. The reactions can be represented (Figure I.26) in the generalised case for oxidation where P_n represents a section of polymer chain. the first step is the formation of a cation (or anion) radical, which is called a **soliton** or a **polaron** (these terms will be explained later). This step may then be followed by a second electron transfer with the formation of a dication (or dianion) known as a **bipolaron**. Alternatively, after the first redox reaction, charge transfer complexes (Figure I.26) may form between charged and neutral segments of the polymer when possible.

$$P_{n} \xrightarrow{Ox/A^{-}}_{Red} \left[P_{n}^{\dagger} A^{-}\right] \xrightarrow{Ox/A^{-}}_{Red} \left[P^{2+} 2 A^{-}\right]$$
$$\left[P_{n}^{\dagger} A^{-}\right] + P_{m} \xrightarrow{} \left[(P_{n} P_{m})^{\dagger} A^{-}\right]$$

Figure I.26 : Doping of a Conducting Polymer involves Redox Reaction

I.3.4.2. Mechanism of Conduction of Polyacetylene

Polyacetylene is unique in having a degenerate ground state with single and double bonds which can be interchanged without changing the energy, as depicted in Figure I.27.



Figure I.27 : Degenerate ground state in trans-Polyacetylene

This leads to stable defects in the polymer chain (free radicals) which are termed neutral **solitons** (Fig. I.28). The location of each defect is not restricted to one carbon atom as illustrated, and in fact they are delocalised over about 15-20 CH groups¹⁰⁶. The presence of solitons introduces degenerate energy levels (or bands) within the band gap which permits the excitation of electrons between the Fermi level and these empty or partly empty

conduction bands, giving *trans*-polyacetylene its intrinsic conductivity of 10⁻⁷ to 10⁻⁸ S cm⁻¹ corresponding to semi-conductor status¹⁰⁷.

Mechanisms have been proposed to explain the conductivity change as a function of dopant concentration for polyacetylene. For levels of oxidation or reduction where there are electrical charges but no electron spin, the **soliton** model has often been used as a description. However, when the processes of redox reaction break π -bonds to form both spins and charge together, bound spin-charge pairs, known as **polarons**, are used to describe the transport mechanism. Polyacetylene is able to support both the solitonic and polaronic modes of electrical conduction.

A given chain is composed of domains where the double bonds alternatively belong to one form of a configuration or another. The frontier between the domains is a carbon atom with a non-bonded electron called a soliton :





Figure I.28 : Neutral Soliton formation



The free radical located on the non-bonding orbital introduces a localised state exactly in the middle of the gap between the valence and the conduction bands. Electron acceptors (or oxidising agents), preferentially react with that electron, forming a positive soliton, whilst electron donors (or reducing agents), add an electron to the mid-gap state, which becomes doubly occupied forming a negative soliton (Figure I.29).

I.3.4.3. Other Conjugated Polymers

Numerous other conjugated polymers are conducting as illustrated in Table I.1. Poly-p-phenylene, polyaniline, polypyrrole and polythiophene (respectively illustrated in Figure I.30) are the best known and will be briefly reviewed :



Figure I.30 : Most common Conjugated Polymers

Unlike polyacetylene, these cyclic systems do not possess a degenerate ground state, so the soliton defects are not stable. In fact, the majority contain aromatic benzenoid rings, which if disrupted by bond alternation, give rise to quinonoid structures of much higher overall energy than the benzenoid rings (Figure I.31). Soliton defects cannot be sustained since they separate regions of high and low energy and would become unstable with respect to pairing up to give the all-benzenoid structure of the neutral, insulating polymer.



Figure I.31 : Benzenoid-Quinonoid Structures

Consequently, for these systems there is an additional contribution to the semiconductor

energy gap, which is increased relative to polyacetylene (3.5eV for poly-p-phenylene, 3.0eV for polypyrrole, 2.2eV for polythiophene and 1.5eV for polyacetylene)¹⁰⁸.

Polymer [§]	Method [§] of	Dopant	Typical	Ref.
	Preparation		σ /S cm ⁻¹	
PA Straight	a) Chemical	I ₃ -	10 ³	109
	b) Chemical (orientated)	I ₃ -	105	110
PdiA $+=-$	Thermally or by Irradiation	Not possible	Unknown	111
	a) Chemical	AsF5	50	112
n n	b) E.C.	AsF ₆	100	113 114
	a) Chemical	H⁺, Cl⁻	5	115
PANI	b) Chemical	H⁺ SO4 ²⁻	100	116
	b) E.C.	ditto	5	117
pps	E.C.	AsF ₆ -	200	118 119

[§] Notes : Abbreviations are listed in pages x - xi

[§] Notes : E.C. -Electrochemical ; P.C. -Photochemical

PTV [S]n	Chemical	I ₂	62	120
	a) E.C.	BF ₄ -	100	121
PPy [N] H	b) E.C.	Tos	500	122
	c) Chemical	FeCl ₃	328	123 124
	a) E.C.	BF ₄ -	100	125
PT (s),	b) E.C.	BF4-	106	126
	c) E.C.	PF ₆ -	200	127
PF $\left[\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	E.C.	BF4-	80	125
PPz	E.C.	ClO ₄ -	10	128
PNaphta	E.C.	AsF ₆ -	10-3	129

PAnthra - [O]	E.C.	AsF ₆ -	10-3	130
PPhena [] n	E.C.	ClO₄-	10 ⁻¹ - 1.0	131
PCbz - [O] n H	E.C.	ClO ₄ -	10 ⁻⁴ -10 ⁻³	131
	a) Chemical	Br ₂	5.10 ⁻³	132
	b) E.C.	ClO ₄ -	10 ⁻² -10 ⁻¹	125
	c) E.C.	BF4-	10 ⁻² - 1	131
	a) Chemical	ClO4-	50	133
PITN IS n	b) P.C.	Br ⁻	3.10 ⁻⁴	134
			,	

Table I.1 : Representative Conducting Organic Polymers

So, for these polymers, with non-degenerate ground states, the charge carriers produced by doping are termed **polarons** and **bipolarons**. A polaron is an isolated added charge carrier,

whereas a bipolaron is a pair of like charges. A bipolaron is often, but not always, favoured energetically over isolated polaron states. In chemical terminology, radicals, radical ions and di-ions are analogous to solitons, polarons and bipolarons respectively.

(i) Poly(p-phenylene) : (PPP)

Poly(p-phenylene) was originally synthesised by Kovacic and Kyriakis¹³⁵ in 1962 by oxidative coupling of benzene via treatment with a Lewis acid catalyst/oxidant system (AlCl₃/CuCl₂). Subsequent adaptations of this procedure by Shacklette et al^{136,137} in 1979 and 1980, gave compressed polymer pellets which exhibited conductivities up to 50 S cm⁻¹, on doping with AsF₅. Further studies by the same workers showed that the polymer could be either *p*-doped or *n*-doped, by strong electron acceptors or donors respectively, giving materials suitable for use as rechargeable battery electrodes¹³⁸. More recent years have seen a number of attempts to prepare PPP electrochemically^{139,140}, despite the high oxidation potential (2.4V vs Ag/AgCl) of benzene. The first highly conducting films of PPP prepared electrochemically were reported by Satoh et al¹⁴¹ and later Ohsawa et al¹⁴², giving films with a conductivity of 100 S cm⁻¹. PPP is now regarded as one of the best examples of a conducting polymer with a non-degenerate ground state which can be *n*- or *p*-doped.

(ii) Polythiophene : (PT)

The first polythiophene synthesis was described in 1883^{143} , where the purification of benzene with sulphuric acid yielded a black insoluble material. Since that time, regioregular PT has been prepared chemically by Yamamoto et al¹⁴⁴ in 1980, and by Koβmehl and co-workers¹⁴⁵ in 1981, yielding respectively I₂-doped and AsF₅-doped powders. The electrochemical preparation was reported by Tourillon and Garnier¹⁴⁶ in 1982, and Kaneto et al¹⁴⁷ in 1983. The oxidised polymer was obtained as a flexible, metallic-blue, free-standing film with an electrical conductivity of 100 S cm⁻¹. The films exhibited electrochromic properties and could be cycled repeatedly between the metallic-blue doped state and a red-coloured neutral state. However, oxidised films of PT have been found to be unstable in moist air or protic solvents¹⁴⁸. Despite its oxidative lability, PT remains an important conductivities obtained (200 S cm⁻¹ in 1985 by Sato et al¹⁴⁹). These values have also been improved by using 3-substituted^{150,151,152} and 3,4-disubstituted¹⁵³ derivatives, allowing at the same time better solubility and tractability.

(iii) Polypyrrole : (PPy)

The electrochemical polymerisation of pyrrole to give "pyrrole black" was first performed by Dall'Olio et al¹⁵⁴ in 1968. Pyrrole was polymerised using an electrolytic solution of aqueous sulphuric acid, giving a powdery, insoluble precipitate at the anode. The material was found to have an electrical conductivity of 8 S cm⁻¹. In 1979, Diaz and co-workers¹⁵⁵ electropolymerised pyrrole by use of an organic solvent (acetonitrile) and Et₄NBF₄ as the electrolyte giving shiny black-blue films. These films, unlike the powders produced by Dall'Olio, could be peeled off the electrode as thick, free-standing films with electrical conductivities as high as 100 S cm⁻¹. Whilst oxidation of the monomer is irreversible, the polymer films can be placed in a solution of clean electrolyte and repeatedly driven electrochemically between a reduced, yellow insulating form and an oxidised, blue-black conducting form, with no apparent change in the material (if an inert atmosphere is employed)¹⁵⁶. The redox reaction is fast and the resultant colour change can form the basis of an electrochromic device. One of the principal advantages of PPy over other doped polymers is the excellent thermal stability in air of its oxidised conducting form. It is thermally stable up to 250°C, showing little degradation of its conducting properties below this temperature. Above 250°C, the polymer loses weight, at a rate which rapidly increases over 600°C¹⁵⁷. Although chemical analysis of PPy varies with preparative conditions, elemental analyses have indicated that the pyrrole rings remain intact, with each unit being connected by its α carbons. The pyrrole units carry a partial positive charge which is balanced by one BF_4 ion to every four pyrrole rings¹⁵⁸. PPy has also been produced with ClO_4 and $CH_3C_6H_4SO_3$ as the counter ions in place of BF_4 . Conductivities as high as 500 S cm⁻¹ have been reported for PPy prepared electrochemically from aqueous solution, employing sodium *p*-toluenesulphonate as the electrolyte¹⁵⁹.

Pyrrole can also be polymerised using a vast number of chemical oxidants and was in fact first prepared as "pyrrole black" in 1916, when Italian chemists Angeli and Alessandri employed H_2O_2 as the oxidising agent¹⁶⁰. Other chemical oxidants have included 2M $H_2SO_4^{161}$, FeCl₃¹⁶², Fe(ClO₄)₃¹⁶³, Cu(ClO₄)₂¹⁶⁴, Fe(BF₄)₃¹⁶⁵, Fe(arylsulphonate)₃¹⁶⁶, I₂ and Br₂¹⁶⁷. The conductivities of the prepared polymers were generally not as high as those obtained for electrochemically prepared PPy, but may be improved by further doping with oxidant vapour, for example, I₂. However, by chemically varying the oxidation potential

of FeCl_3 in an optimally chosen, binary medium of methanol and acetonitrile, Miyata et al^{168,169} have prepared PPy with conductivities as high as 328 S cm⁻¹, comparable with the highest values obtained electrochemically.

(iv) Poly(p-phenylene sulphide) (PPS) and Poly(p-phenylene oxide) (PPO)

Most aromatic conducting polymers are highly intractable, ie. they tend to be completely insoluble in most solvents and are infusible on heating, but PPS and PPO are exceptions to this. Indeed, PPS is a commercially available melt-processable thermoplastic, which becomes conducting on suitable doping^{170,171}. It is sold by Philips Petroleum as an engineering thermoplastic known as RytonTM and is finding use as a moulding compound for the encapsulation of electronic components. Unfilled, it is a white polymer with a melting point of 288°C and is intrinsically insulating having a conductivity of less than 10^{-16} S cm⁻¹. Doping with AsF₅ leads to an increase in conductivity to around 1-10 S cm⁻¹ although there is a deterioration in mechanical properties and a colour change to dark blue. Solutions of AsF₅ doped PPS in AsF₃ have been produced and films with good mechanical properties and conductivities up to 200 S cm⁻¹ can be cast¹⁷².

In the case of PPO, this can be doped with AsF_5 to yield a conductivity as high as 10^{-3} S cm⁻¹ ¹⁷³.

Phenol is interesting to investigate as a monomer with a similar structure to aniline, in particular to study the influence of the oxygen atom on the polymerisation process. However, there isn't a lot of work published on conducting poly(*p*-phenylene oxide) because during the last 15 years, research has focused on the electrochemical growth of non-conducting polymer films of phenol. In fact, there are many industrial applications of these in the area of polymer coating. The few OH-containing aromatic compounds (e.g. phenol and 2,6-dimethylphenol) electropolymerised have generally been reported to lead to electroinactive polymeric films and in some cases electroactive dimeric compounds, depending on the electrolysis conditions¹⁷⁴. But in 1987, Oyama and co-workers¹⁷⁵ found that the electro-oxidative polymerisation of phenol in acetonitrile solutions with graphite electrodes gave electroactive, conducting polymer films with electrical conductivities of ca. 10⁻⁸ to 10⁻¹ S cm⁻¹, depending on the nature of the supporting electrolyte (NaClO₄ and Bu₄NPF₆ respectively). However, the characterisation of these materials revealed a mixture of irregularly substituted polymers. A mechanism for electropolymerisation of phenol by one-electron oxidation to give free radicals which then undergo C-O coupling has been



Figure I.32 : Formation of poly(p-phenylene oxide) from phenol

I.4 : POLYANILINE

Polyaniline (PANI) is one of the oldest known synthetic organic polymers, having first been reported in 1862 by Letherby¹⁷⁷ as a "blue substance" and has been described in many papers during the past 100 years. However, it is only recently in the 1980's that great interest has been shown in the polymeric product and its structure finally defined^{178,179,180}. Therefore, electroactive films of PANI have been studied by many groups, who have used a variety of routes to synthesise the polymer such as oxidative chemical or electrochemical polymerisation as reviewed by Genies et al.¹⁸¹.

I.4.1. Basicity and Reactivity of Aniline

Aniline is a very weak base, having a $pK_b = 9.38$. Like ammonia, amines are converted into their salts by aqueous mineral acids and are liberated from their salts by aqueous hydroxides. Like ammonia, therefore, amines are more basic than water and less basic than hydroxide ion :

ArNH ₂	+	H ₃ O ⁺ >	ArNH ₃ +	+	H ₂ O
stronger					weaker
base					base
ArNH ₃ +	+	OH ⁻ >	ArNH ₂	+	H ₂ O
		stronger	weaker		
		base	base		

Aniline is a weaker base than ammonia because the lone pair of electrons is partly shared with the ring and is thus less available for sharing with a hydrogen ion. In fact, in aniline the nitrogen atom is bonded to an sp² hybridised carbon atom but, more significantly, the unshared electron pair on N can interact with the delocalised π -orbitals of the nucleus as illustrated in Figure I.33.

It is also well known that the $-NH_2$ group (electron donating) acts as a powerful activator and *ortho*, *para* director in electrophilic aromatic attack.



Figure I.33 : Delocalisation of the electron pair along the ring

I.4.2. Structure of Polyaniline

In the 1980s MacDiarmid et al.^{178,182} and Genies et al.^{183,184,185} discovered the real structure of polyaniline after many years of uncertainty and controversy. Indeed, PANI exhibits a much greater complexity of properties and structures than most other electroactive polymers. In fact, polyaniline shows various colours because it can take various forms such as reduced form, oxidized form, or salt form, base form. For these reasons polyaniline should be thought of as a family of three polymers depending on oxidation state.

* The fully reduced form, known as **Leucoemeraldine**, has the simplest polymer backbone: It is a simple polyaromatic, which has an unconjugated backbone and hence is colourless and insulating.



Leucoemeraldine

* In the fully oxidised **Pernigraniline** state, all nitrogens are present in quinonediimine form. This is the most optically intriguing material because the system is fully conjugated and even more strongly coloured. However, the polymer is an insulator because of the impossibility of delocalisation of any charge on nitrogen atom amongst other resonance structures.



Pernigraniline

* If the polymer is 50% oxidised, so that half the nitrogens are expected to be doublebonded to quinoid rings in what is formally a benzenamine-quinonediimine polymer, then we obtained the electrically most interesting state which is **Emeraldine** :



Amine nitrogen

Imine nitrogen

Emeraldine

Therefore, PANI can be pictured to have four benzene rings repeat units as illustrated in Fig.I.34.



Figure I.34 : Polyaniline repeat unit

Furthermore, polyaniline is almost unique among conducting polymers in that electronic properties are governed by two parameters^{186,187}: the **oxidation level** as seen above and also the protonation level. Indeed, this material can be varied from an insulating state to a conducting one through oxidation (in its protonated state) and through protonation (in its oxidised state).

So, all the previous forms may be partly or completely protonated with a protonic acid to give the corresponding 'salt' repeat units¹⁷⁸ (Fig.I.35).



Fully reduced Pani Monoprotonated salt







Fully oxidised Pani Diprotonated salt

Figure I.35 : Degree of protonation of Polyaniline

In both cases, either one or both nitrogen atoms in a repeat unit may be protonated, depending on the pH of the solution to which the polymer has been exposed. Therefore, depending on the oxidation and the protonation states, a series of compounds can be formed. The approximate composition corresponding to a given colour and their classical names are listed in Table I.2¹⁸⁸.

X [§]	Name	Base form	Protonated form
1	Leucoemeraldine	pale yellow	pale yellow
0.75	Protoemeraldine	blue	light green
0.5	Emeraldine	dark blue	green
0.25	Nigraniline	blue-black	blue
0	Pernigraniline	violet	violet

Table I.2 : Possible composition of polyaniline

If the emeraldine base, which is a combination of 50% of fully reduced repeat unit and 50% of fully oxidised repeat unit, is treated with a protonic acid which of the nitrogen atom in repeat units will be protonated : the **amine** or the **imine** ?

Mac Diarmid¹⁸⁶, believed that the imine nitrogen atoms are preferentially protonated to give

[§] Notes : X = Fraction of benzenoid rings or amine nitrogens

the emeraldine salt, at a pH of ~0.



In this case, the emeraldine salt form is very greatly stabilised by resonance effects (as illustrated in Fig.I.36) because all the N atoms, all C-N bonds and all C_6H_4 rings would be identical. Each nitrogen atom would bear a +0.5 charge and all N atoms would be intermediate between an imine and an amine nitrogen. Similarly, all C-N bonds would be intermediate between a single and a double bond and all C_6H_4 rings would be intermediate between a single and a double bond and all C_6H_4 rings would be intermediate between benzenoid and quinoid. The resulting highly conjugated π system would permit the high conductivities observed.

This theory was confirmed by diverse studies which show that maximum conductivity occurs when polyaniline is half oxidised and in acid solution¹⁸⁹.

So, emeraldine is a good electronic conductor because of the possibility of the combination of charge and of its delocalisation amongst the possible resonance forms of its structure. This conjugation leads to strong visible absorptions and a green colour.



Figure I.36 : Resonance forms for the emeraldine salt polymer

We need to emphasise that A⁻ is the counterion which can be Cl⁻, ClO_4^- , SO_4^{2-} , $BF_4^$ and many others. The electroactivity of the polymer is dependent of the size and concentration of this doping anions as described by Koziel and Lapkowski¹⁹⁰.

I.4.3. Mechanism of polymerisation

Since the discovery of "Aniline Black", a wide variety of methods have been employed for the preparation of PANI leading to the formation of products whose nature and properties differ greatly. As a result of the many studies carried out on PANI and its derivatives, a multitude of polymerisation mechanisms have been proposed by different authors.

According to most authors, the first step in the oxidation of aniline is the formation of a **radical cation** (Fig.I.37), which is the governing criterion for the polymerisation reaction.



Figure I.37 : Formation of the radical cation in aniline

This radical cation is resonance stabilised and can be represented by the following canonical forms as illustrated in Figure I.38.



Figure I.38 : Resonance of the radical cation

Mohilner¹⁹¹ was the first in 1962 to ascertain that in sulphuric acid medium, the oxidation of aniline mainly resulted in *para*-coupled chains. However, *para* coupling is not exclusive; radical cation coupling at the *ortho* position (Fig.I.39) may lead to low yields of other products¹⁹².

An intermediate product of the oxidation of aniline has been identified by FT-IR spectroscopy, this being *p*-aminodiphenylamine (PADPA). Its formation mechanism is as followed in Figure I.40.







Figure I.40 : Formation of p-aminodiphenylamine

Once the dimer is formed, it is oxidised via a single two-electron step to quinoidal diimine form. The radical dication is therefore coupled with another *para*-radical forming later PANI. Therefore, according to Genies et al.¹⁹³ and Wei et al.¹⁹⁴ the most reasonable mechanism for the chemical and electrochemical polymerisation of aniline in acidic media appears to be the one illustrated in Figure I.41.



Figure I.41 : Mechanism of polymerisation of aniline

I.4.4. Methods of Synthesis

Polyaniline is generally prepared by direct oxidation of aniline using an appropriate chemical oxidant or by electrochemical oxidation on different electrode materials. The majority of authors admit that the characteristics of the polymer depend on the mode of synthesis. The two most common modes are classical chemical synthesis and electrochemical synthesis.

I.4.4.1. Classical Chemical Synthesis

Various chemical oxidising agents have been used by different authors : potassium dichromate $(K_2Cr_2O_7)^{192,185,195}$, ammonium persulfate or peroxodisulfate $((NH_4)_2S_2O_8)^{178,182,185,194,196,197}$, hydrogen peroxide (H_2O_2) , ceric nitrate $(Ce(NO_3)_4)$ and ceric sulfate $(Ce(SO_4)_2)^{198,199}$. Recently, chromyl chloride (CrO_2Cl_2) and trimethylsilyl chlorochromate $(ClCrO_3Si(CH_3)_3)$ have been use to chemically oxidise 2-chloro and 2-

fluoroaniline²⁰⁰.

Hand and Nelson^{197,198} used a quantity of the chemical oxidant which is in excess of the corresponding stoichiometric quantity. MacDiarmid et al.^{178,182} used a stoichiometric equivalent of the oxidant, whereas Genies et al. preferred a quantity that was less than the stoichiometric equivalent. In fact, a degradation of the polymer can be observed if too high a quantity of oxidant is used^{192,185}.

The reaction is mainly carried out in acid medium, in particular sulphuric acid, at pH between 0 and 2. MacDiarmid et al. used hydrochloric acid at pH 1.

In most cases, aniline is mixed with the chemical oxidant in a reaction vessel at a temperature close to zero Celsius and left under stirring for a certain period of time (depending on the temperature and the concentration of active species). The solution gradually becomes coloured and a black precipitate of PANI appears.

I.4.4.2. Electrochemical Synthesis

Anodic oxidation of aniline on an inert metallic electrode is the most common current method for the synthesis of PANI. In fact, this method presents some advantages as the resulting product is cleaner (does not need to be extracted from the initial monomer/oxidant/solvent mixture) and there is some possibility of coupling with physical spectroscopic techniques.

The anodic oxidation of aniline is generally effected on an inert electrode material which is usually platinum^{201,202,203,204,205}. However, several studies have been carried out with other electrode materials such as : iron^{206,207,208,209}, copper²¹⁰, zinc, chrome-gold²¹¹, lead, palladium²¹² and different types of carbon^{213,214,215,216}, or on semiconductors²¹⁷. Depositions of PANI have also been effected on optically transparent electrodes generally based on glass or from polymer films, which are rendered conducting by deposits of platinum, gold or indium or tin oxides²¹⁸.

The two electrochemical modes mainly employed are galvanostatic or potentiostatic. In the latter case, the potential is fixed or cycled, with the value of the applied potential being in the order of 0.7 to 1.2 V (versus saturated calomel electrode (SCE)). The sweep rates most commonly used are between 10 and 100 mV s⁻¹. Figure I.42 shows a typical cyclic voltammogram²¹⁹ of chemically synthesised emeraldine hydrochloride powder in HCl 1M with schematic representations of the change in potential of the peaks as a function of the pH of the electrolyte. Approximate colours of the polyaniline observed at different stages

55

of oxidation are also shown.



Figure I.42 : Cyclic voltammogram (50mVs⁻¹) of emeraldine powder

I.4.5. Physical and Chemical Properties

Diaz²²⁰, Kobayashi²²¹, McManus²²², Watanabe²²³, Genies²²⁴ and Foot²²⁵ have observed a wide range of colours from pale yellow to blue for both thin and thick films on various substrates. This is due to the different possible forms of polyaniline depending on the degree of oxidation and reduction as well as the degree of protonation (Table 2). So the various colours are observed as a result of the numerous possible structures seen previously.

More important than the electrochromic properties of PANI, are the electronic properties. In fact, the conductivity values quoted²²⁶ range from 10⁻¹³ to 10 S cm⁻¹, depending on the mode of synthesis. We have seen before that only the emeraldine salt shows high conductivity values due to its highly conjugated backbone. Jozefowicz et al.²²⁷ obtained a material having a conductivity as high as 100 S cm⁻¹ by using a well-defined method which simply involved the oxidation of aniline by ammonium persulfate in sulphuric acid at pH 1.

It is generally accepted that PANI is insoluble in most common organic and aqueous solvents, irrespective of the method of synthesis. Only solvents such as dimethylformamide, dimethyl sulfoxide, 1-methyl-2-pyrrolidinone, 80% acetic acid and formic acid can partially

solubilise PANI. This is a major problem in efforts to further process these materials. Some recent improvements have been made in this area, and several organic solvent-soluble, and water-soluble polyaniline derivatives have been prepared. These have included PANI, covalently bonded at the ring or at the heteroatom, with alkylsulphonic acid salts, giving water-soluble PANI. Emeraldine ionically protonated with long-chain diesters of phosphoric acid, has been found to be soluble in a variety of common organic solvents ; thermal processing gave free-standing films with conductivities exceeding 10 S cm⁻¹.

Shannon and Fernandez²²⁸ have reported some water-soluble poly(styrene sulphonic acid)doped (PSSAH) polyaniline prepared by both chemical persulfate oxidative coupling and anodic oxidation, whereas Bergeron et al.²²⁹ have obtained water-soluble conducting poly(aniline propanesulphonic acid) and its sodium salt. This N-substituted polyaniline was synthesised by derivatisation of the leucoemeraldine form of PANI.

The processibility of conducting PANI was also improved by Cao²³⁰ in 1992 by introduction of specific counter-ion such as functionalised protonic acid (H⁺(M-R)), where M⁻ is SO₃ and R the functional group is chosen to be compatible with nonpolar or weakly polar organic liquids such as dodecylbenzenesulphonic acid (DBSA). In fact, the long alkyl chains of the dodecylbenzene functional group lead to solubility in common solvents, such as toluene, xylenes, decalin, chloroform and many others. Following this paper on solvent-soluble PANI, more work has been published in this area where soluble conducting PANI has been prepared via protonation with suitable sulphonic acids^{231,232} (DBSA and camphor-sulfonic acid) or phosphoric acid esters^{233,234} (bis(2-methylpropyl))hydrogen phosphate, bis(2-ethylhexyl)hydrogen phosphate and bis(n-octyl)hydrogen phosphate). However, PANI doped with low-molecular mass compounds might deprotonate in basic media. This could inevitably lead to a decrease of conductivity, therefore one possible approach developed to overcome this is the use of polymeric-type protonating agents. Kulszewicz-Bajer et al.²³⁵ prepared some poly(alkylene phosphates)-doped polyaniline which were soluble in the protonated state.

Furthermore, Osterholm et al.²³⁶ directly polymerised aniline using an emulsion comprising water and a non-polar or weakly polar organic solvent in the presence of the functionalised protonic acid DBSA. The resulting PANI-DBSA complexes exhibited high solubility in non-polar organic solvents. Cast films exhibited conductivities in the range 100-400 S cm⁻¹. Moreover, Gan et al.²³⁷ synthesised PANI in an inverse microemulsion using the surfactant Empilan NP5 (poly(oxyethylene)₅₋₉ nonyl phenol ether), HCl 2-3M, petroleum ether (60-80°C) and potassium persulfate. Pressed pellet conductivity values were around 8 S cm⁻¹.

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The thermal stability of PANI has been studied and PANI prepared by either electrochemical or chemical methods is known to be a stable material^{238,239}. In fact, thermal analysis of the salt and base forms of PANI has revealed that no backbone structural decomposition occurs up to $400^{\circ}C^{240}$. In the case of the doped PANI, the thermal stability is dependent on the counter ion²⁴¹; for HCl the loss of acid dopant occurs above 140°C, whereas *p*-toluenesulphonic acid was lost above $200^{\circ}C^{242}$. The doped form of polyaniline sold under the trade name VersiconTM, is used for its good thermal stability and dispersibility with thermoplastics such as PVC, PETG and nylon 12²⁴³.

I.4.6. Substituted Polyanilines

For many applications, conductive materials must be air-stable and solution-or meltprocessable. Unfortunately, we have seen that like many other conjugated polymers, polyaniline is only soluble in special or aggressive solvents (e.g. 1-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and 80% acetic acid) due to the rigid nature of its backbone. In contrast, it has been shown that introduction of alkyl-substituents on a polythiophene chain can improve its solubility. The same study has been performed with various substituents in different positions on PANI.

In 1973, Prater²⁴⁴ studied the influence of ring substitution on electrode filming by polyanilines. He found two categories of substituents on the basis of cyclic voltammograms :

1st category : * electron-donating groups, ortho to the amine (NH₂, OH, OCH₃, Cl).

* electron-withdrawing groups, *ortho* and *meta* to the amine group (NO₂). 2^{nd} category : * electron-donating groups, *meta* to the amine (NH₂, OH, OCH₃, Cl). The first categories showed similar behaviour to aniline, whereas the second category formed some "electrode filming" (nonconducting insoluble material). The difference between these two groups of compounds was explained by the fact that electron-donating groups (including NH₂) activate the ring to electrophilic attack at the *ortho* and *para* positions. Therefore, a compound having 2 electron donating groups (the amine of the aniline and the added group) *meta* to one another will have 3 ring positions which are doubly activated and then can give rise to highly crosslinked polymer, whereas if the 2 electron donating groups are *ortho* to one another, there are no doubly activated positions. Furthermore, the presence of electron withdrawing group anywhere on the ring would be expected to decrease the susceptibility toward electrophilic attack and then favour head-to-
head polymerisation.

In 1986, Shenglong et. al.²⁴⁵ studied the chemical polymerisation of *m*-toluidine, *o*-chloroaniline and nitro-aniline. He found that *m*-toluidine and *o*-chloroaniline can be polymerised with conductivity values as high as 1.7×10^{-1} S cm⁻¹ and 2.2×10^{-4} S cm⁻¹ respectively, while for nitroaniline no polymer was isolated. He also found that the conductivity of *m*-toluidine decreases when treated with aqueous NaOH to 6.4×10^{-4} S cm⁻¹ in agreement with MacDiarmid's work on polyaniline. The solubility was similar to that of polyaniline.

In 1988, Cattarin et.al.²⁴⁶ studied in more detail the influence of electron-donor (CH₃, OCH₃ and SCH₃) and electron-acceptor (Cl, Br, I, NO₂, COCH₃ and SO₃H) substituents in the 2- and 3-positions on the electropolymerisation of substituted anilines. They found that electropolymerisation appears to be favoured by electron-donor substituents and in particular by σ -donors (CH₃) in either the *ortho* or *meta*-position but by π -donors (OCH₃, Cl) in the *ortho*-position only. Polytoluidines and polyanisidine were reversibly oxidised in two steps like polyaniline, displaying a conductivity of 10⁻³ and 2.10⁻³ S cm⁻¹ respectively, whereas polychloroaniline was oxidised in a single one-electron process displaying a conductivity of 2.10⁻⁴ S cm⁻¹. Furthermore, polymerisation with Br and I substituents was revealed to be very difficult and even impossible with the methylmercaptan group due to lower π -conjugation on the substituent atom and some steric factors.

At the same time, Macinnes et.al.²⁴⁷ studied more precisely *ortho*-methoxyaniline which they found to be soluble in trifluoroacetic acid, acetic acid and sulphuric acid and partially soluble in acetonitrile, chloroform and dichloromethane. Electropolymerisation results of the monomers were in agreement with Cattarin and they apparently claimed some conductivity values as high as "3 S", but the units used were ambiguous.

Again in 1988, Leclerc et. al.²⁴⁸ investigated the effect of a methyl group in the *ortho*, *meta* and *para* positions on the mechanism of electropolymerisation and the electrochromic properties of the polymers formed. Electropolymerisation of *ortho*- and *meta*-toluidine in aqueous sulphuric acid gave uniform polymer films while only low molecular weight species were obtained with *para*-toluidine. As observed for polyaniline, both poly(*ortho* and *meta*-toluidine) exhibited multiple colour changes in correlation with oxidation processes.

In 1989, Leclerc's group²⁴⁹ and Wei's group²⁵⁰ synthesised poly(alkylanilines) both chemically and electrochemically. Leclerc et.al. found that the 2-substituted anilines always

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give better polymerisation yields and more regular head-to-tail structures than the 3substituted ones. But on the other hand, no electroactive polymer was synthesised with a substituent having more than two carbon atoms (ethyl group). This was explained by the presence of too bulky substituents which hinder the formation of head-to-tail couplings. The conductivity values were ranging from 1 to 0.3 S cm⁻¹ for the acid doped polymers and were about 10⁻⁹ S cm⁻¹ for the insulating base-treated polymers. All the base-treated poly(alkylanilines) were also completely soluble in common organic solvents (e.g. THF and chloroform). Wei et al. studied poly(ortho and meta-methylaniline and poly(orthoethylaniline); they found the polymer-bases soluble in dichloromethane and chloroform, amongst other solvents. The conductivity values increased dramatically from the base-form (ca. 10⁻⁸ S cm⁻¹) to the acid-form (ca. 10⁻¹ for polytoluidines and ca. 10⁻³ for poly(oethylaniline). These relatively low values compared to polyaniline (5.6 S cm⁻¹) were explained by steric effects. In fact, the substituent on the phenyl ring can increase the torsional angle between adjacent rings to relieve steric strain. A systematic influence of the alkyl substituents on polyaniline backbone relative to the steric and electronic effects was noted. The steric effects were suggested to be mainly responsible for :

- (1) the decrease in the conductivities
- (2) the hypsochromic shifts of the π - π * transition band in the UV spectra
- (3) the decrease in the basicity of the amine nitrogen
- (4) the lower ΔE_{44} values of the alkyl ring-substituted polyanilines.

The electronic effects were suggested to be mainly responsible for the increase in the basicity of the imine species in the alkyl-substituted polymers.

At the same period, Foot and $Simon^{251}$ studied the electrochromic behaviour of substituted polyanilines. In the case of 2,6-dimethylaniline, no film could be grown despite evidence that the monomer was electroactive. Poly(3-methoxyaniline) gave a brown film with no electrochromism and little electroactivity, whereas 2-methoxy and 2-ethoxy derivatives produced good electrochromic films. Conductivity values were as high as 40 S cm⁻¹ for poly(2-ethoxyaniline).

More recently, in 1993 D'Aprano and Leclerc²⁵² studied the steric and electronic effects in mono- and di-substituted methyl and methoxy polyanilines. They also found that with the introduction of an electron-donating substituent, the monomer is more easily oxidised. From UV-visible absorption and electrochemical measurements, it was revealed that methyl substituted anilines give polymers which are less planar than the methoxy derivatives due to the more pronounced steric effects induced by the methyl group. This

effect was even greater in the case of disubstitution (poly 2,5-dimethoxyaniline $\sigma = 0.22$ S cm⁻¹, poly 2,5-dimethylaniline $\sigma = 3.10^{-6}$ S cm⁻¹).

Furthermore, since 1992, a lot of work has been done on poly(o-alkylanilines) by Bodalia²⁵³ and Conklin²⁵⁴, on poly(o-methoxyaniline) by Gupta²⁵⁵ and Mattoso et. al.^{256,257,258,259,260}, on poly(2,5-dimethoxyaniline) by Zotti²⁶¹ and Storrier²⁶², and on generally *ortho*-substituted polyaniline by Gruger et. al.²⁶³, in order to characterise fully these polymers and improve their properties.

I.5 : Side Chain Liquid Crystalline Conducting Polymers

We have seen in the last two sections on conducting organic materials that conjugated polymers can exhibit near metallic conductivities with values as high as 10⁵ S cm⁻¹ when strongly doped. However, most of these materials are amorphous and are not easily processible. In order to improve these properties, the most common and most successful approach to this objective is to attach pendant side groups to the aromatic system. 3-Substituted polythiophenes²⁶⁴ have been successfully synthesised and shown to be soluble. In order to combine better processibility with better ordering it is possible to introduce side-chain groups with mesogenic properties and several research programmes on this theme have recently begun in England, France, USA and Japan.

In 1988, Tsibouklis et al.²⁶⁵ were the first to report the synthesis and polymerisation of unsymmetrical diacetylenes showing liquid crystal behaviour. More work was done in 1989 by Le Moigne et al.²⁶⁶ who synthesised and polymerised some acetylenic and diacetylenic liquid-crystalline monomers. No values of conductivity were reported for these potentially conducting polymers, but they were probably very low, as is usual for substituted polydiacetylenes.

A short communication in 1991 by $Bryce^{267}$ described the electropolymerisation of 3-(4-methoxy-4'-cyanobiphenyl)thiophene with an electronic conductivity of 1.5×10^{-2} S cm⁻¹ (film). Differential scanning calorimetry revealed a reversible peak at 58°C but no optical microscopy results were listed for confirmation. Also, no details regarding the molecular weight or spectroscopic analysis of the polymer were given.

At the start of this project, the Bryce publication was the only one available on side chain liquid crystal conducting polymers, and all the current work quoted below has appeared during the course of this project or at the time of writing.

In 1991, Jin et al.²⁶⁸ investigated polyheptadiyne with long side-chain liquid crystalline groups. Poly{4-methoxy-4'-(hexoxyloxy)biphenyl dipropargylacetate] (Figure

I.43 when X = H) was cyclopolymerised by transition-metal catalysts, with MoCl₅ having greater catalytic activity than that of WCl₆. Use of $(n-Bu)_4$ Sn as a cocatalyst for the polymerisation of this monomer was shown to improve the yield (95%) as well as the number-average molecular weight (10.5 x 10⁴) of the polymer. The polymer was found to exhibit a smectic phase at 92°C which melted to an isotropic at 105°C. Room temperature conductivities of the polymers undoped and doped with I₂ were found to be 6.3 x 10⁻¹¹ and 10⁻² S cm⁻¹, respectively.



Figure I.43 : Polyheptadiyne derivatives

In 1995, the same group with Yoshino et al.²⁶⁹ studied polyheptadiyne derivatives with two long side chains. The polymer poly (bis(4-methoxy-4'-hexyloxy biphenyl)-dipropargyl malonate) PMHBDPM, as illustrated in Fig. I.43, was found to exhibit a smectic phase at the temperature range around 85-115°C. They also claimed that the electrical conductivity of PMHBDPM increases with increasing temperature and two inflection points were observed at the phase transitions between the smectic phase and the other phases, but no absolute value of conductivity has been recorded.

Another conjugated polymer, polypyrrole, with pendant mesogenic groups was first studied in 1993 by Langley et al.²⁷⁰. 3-[6-(4'-cyanobiphenyl-4-oxy)hexyl]pyrrole was polymerised chemically but the polymer obtained exhibited no mesophase.

Following these two papers, Awaji et al. have claimed in recent Japanese patents to have synthesised a large variety of "highly conducting" mesogenic oligomers and polymers based on polythiophene^{271,272} and polypyrrole²⁷³. 3-[10-(4'-cyanobiphenyl-4-oxy)decyl]thiophene was polymerised and doped with FeCl₃, and a film of this polymer showed a smectic-isotropic phase transition temperature at 98°C and a response time of 0.7s ($2x10^6$ Vm⁻¹, 50°C). The monomer (X) (Fig. I.44) was also polymerised and doped with FeCl₃ and a film of this polymer showed a nematic-isotropic phase transition at 90°C and

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an electrooptical response speed equal to 0.5s. The pyrrole monomer (Y) (Fig. I.44) was polymerised as well and doped with FeCl₃ and a film of the oligomer (M_n 3580) formed was cast on a glass slide showing a smectic-isotropic phase transition at 93°C.



Figure I.44 : Monomers (X) and (Y) synthesised by Awaji

In 1994, Koide²⁷⁴ published another patent on polythiophene. 3-substituted thiophenes were polymerised to form some oligomers showing liquid crystalline (smectic) and electrochromic properties. But in all these patents, no systematic study of the electrical conductivity of the synthesised polymers has been described.

In 1993, K.S. Ho and K. Levon²⁷⁵ in an international patent claimed that 3dodecylthiophene polymerised chemically exhibited a crystal to liquid crystal transition temperature at about 70°C, and a liquid crystal to isotropic transition temperature at about 140°C. The polymer, frozen in its liquid crystal state, doped with FeCl₃ or I₂ exhibited an electrical conductivity of 1S cm⁻¹.

In the meantime, a French team was working on acetylenic, diacetylenic²⁷⁶ and pyrrole-based^{277,278} liquid crystalline polymers. They at first studied the following acetylenic series A_3C_m (Fig. I.45). These monomers were then polymerised.



Figure I.45 : Acetylenic series (A_3C_m) synthesised by Vicentini

They found the polymers to be liquid crystalline, showing a smectic phase for m equal to 1,4 and 8. In the case of the diacetylenic polymers, no mesomorphic behaviour was detected by optical observation in the polarizing microscope. The electronic conductivity of the polymer of A_3C_8 was studied under different conditions. The DC conductivity was found to be equal to 10^{-11} S cm⁻¹ for the undoped sample. After doping by iodine vapour the value increase to 5×10^{-8} S cm⁻¹. The undoped polymer was also oriented in a magnetic field of 5T and heated into the isotropic state, then after freezing in the liquid crystalline state a conductivity of 10^{-9} S cm⁻¹ was achieved. These preliminary results did show that orientation of a side-chain conjugated polymer can enhance its conductivity. Following this work, the French group studied pyrrole derivatives including the molecule pictured in Fig. I.46.



Figure I.46 : Molecule synthesised by Mauzac et al.

Chemical polymerisation gave soluble and fusible polymers with fairly low molecular weights (6000-8000 g mol⁻¹ versus polystyrene standards) and with a smectic A mesophase (S_A 160°C I). The conductivities of the mesomorphic polypyrroles did show higher values than those of the homologous polyacetylenes. The conductivities, determined by a four probe technique, reached 10⁻² S cm⁻¹ on pressed samples realised with ferric chloride/ naphthalenesulfonate oxidising agent and are about 10⁻³ S cm⁻¹ for polymers synthesised with I_2 . They also studied in the oriented polymers, the conductivity in both the parallel and perpendicular direction with regard to the orientation of the mesogens. The values were equal to 10⁻³ S cm⁻¹ in the mesogens' direction and 10⁻² S cm⁻¹ in the perpendicular direction parallel to the smectic layers, in agreement with the expectation of unidirectional conductivity.

Recently, more work has been published in the area of conducting liquid-crystalline polymers. Polythiophenes²⁷⁹ and polypyrroles^{280,281} are the focus of these new developments. Thobie-Gautier²⁷⁹ reported a new PT derivative which was obtained by electropolymerisation of a thiophene monomer in which a *p*-cyanobiphenyl mesogenic

group has been attached at the 3-position of the thiophene ring via a flexible octyl spacer. Indeed, under appropriate conditions, electropolymerisation of 4-cyano-4'-[8-(3-thienyl)oxy]biphenyl can lead to a polymer with electrochemical, optical and electrical properties close to those of the corresponding poly(3-alkylthiophenes). Two-probe conductivity measurements of thin films gave values in the range of 10^{-2} - 10^{-1} S cm⁻¹, but no mesomorphic properties have been reported on the conductive material.

D. Melamed et al.²⁸⁰ synthesised the N-substituted pyrrole : 4-pentyl-4'-biphenylpyrrole in order to electropolymerise this monomer, but the monomer failed to show any polymer growth upon repeated anodic cycling. On the other hand, Ibison et al.²⁸¹ synthesised 1-(N-pyrrolo)-6-(4-cyano-4'-biphenyloxy)-hexane and succesfully polymerised this N-substituted pyrrole to form a thin brown film on the electrode surface. The electrochemically produced polymer was found to be infusible and insoluble. However, when chemically produced, the polymer exhibited a monotropic liquid crystalline phase and was soluble in chloroform.

Finally, at the time of writing a new paper just has been published on polyacetylene derivatives by Akagi et al.²⁸². They investigated the side-chain liquid crystalline polymers of the structures illustrated in Figure I.47. The monomers were polymerised by using Ziegler-Natta (Fe(acac)₃-AlEt₃) and metathesis (MoCl₅-Ph₄Sn) catalysts. The first technique gave higher molecular weight polymers as well as the cyclohexylphenoxy-derivatives. The polymers did show monotropic schlieren nematic phases and fan-shaped texture of a smectic phases.



Figure I.47 : Side-chain Liquid Crystalline Polyacetylenes

The electrical conductivity values were low even after iodine doping $(10^{-7} - 10^{-8} \text{ S cm}^{-1}$ depending on polymers) but alignment of the polymer chain using an external magnetic

field of 0.7 T enhanced these values to 10^{-6} S cm⁻¹ and gave rise to a notable electrical anisotropy.

We have seen that during the last 5 years a lot of preliminary work has been carried out in the area of thermotropic conducting side chain liquid-crystalline polymers. Polyacetylene, polydiacetylene, polyheptadiyne, polypyrrole and polythiophene have been studied by diverse groups whereas no research has so far been published on polyaniline. Liquid-crystalline properties of polyaniline have only been investigated in solution by Cao and Smith²⁸³. Indeed, PANI fully protonated with camphorsulphonic acid (Fig. I.48) was found to form liquid-crystalline solutions in *m*-cresol above a critical concentration. Such liquid crystalline solutions are potentially useful for the preparation of highly oriented fibres and films with enhanced electrical and mechanical properties, unfortunately the properties of such oriented systems derived from lyotropic solutions of PANI have not been published so far.



Figure I.48 : Camphorsulphonic acid

I.6 : Aim and Objectives of the Project

This chapter has tried to present the reader with an overview of several areas of intensive and current scientific research. Conducting organic polymers have enormous potential as viable alternatives to traditional metals in a wide variety of applications, since they can be fabricated from simple, cheap and widely available materials. However, these materials must be made processible to be used on a practical and commercial scale. At present, most of these conducting polymers are intractable and infusible. The use of soluble precursor polymers has been employed successfully to surmount some of these problems, especially for polyacetylene^{284,285}, though electrical properties tend to suffer slightly.

An alternative pathway for solubilisation has also been demonstrated, which is to introduce alkyl or alkoxy chains to polythiophenes, polypyrroles and polyanilines. However, electrical conductivities and morphologies usually suffer with increasing chain length and solubility. This has been attributed to the increased disorder of the polymer backbones due to disruption by the flexible side-chains ; the electrical properties are, of course, heavily dependent on the conformational regularity of the polymer backbones. Clearly, improvements in this conformational regularity whilst maintaining good solubility levels would potentially lead to processible and highly conducting polymers. One way in which these criteria may be met would be to prepare liquid crystalline derivatives of conducting polymers. The use of liquid crystal technology in preparing highly orientated polymers, for example Kevlar, has been mentioned previously in this chapter. Therefore, the aim of this project was to combine the properties of aligned liquid crystals with those of conducting polymer via a flexible spacer, to form a conducting side-chain liquid crystal polymer which would have the potential for electrically and magnetically controllable conductivity.

This thesis was concerned with the preparation of polyaniline derivatives which have liquid crystal units chemically bonded to them. Careful evaluation of spacer length, and of the range and type of liquid crystal phase transitions was carried out in order to understand the factors which could produce a polymer with the correct properties. The use of such systems offers several potential advantages :

(i) the flexible side-chains and mesogenic units should still permit solution processibility, as for long chain alkylpyrroles and alkylthiophenes.

- (ii) the formation of polymeric mesophases should of course assist thermal processing.
- (iii) the ability of the polymer to exhibit a liquid crystalline mesophase or structure should improve the conformational regularity of the polymer backbones, and hence possibly improve levels of intrinsic electrical conductivity.

The first part of Chapter 2 of this thesis describes some synthetic routes to 2-substituted anilines bearing mesogenic groups. The second part deals with the polymerisation of these monomers, using chemical or electrochemical techniques and the study of the resultant polymers' spectroscopic data.

Chapter 3 describes firstly the phase behaviour of the mesogenic intermediates and monomers, whereas the second part deals with an investigation of the polymers and their physical properties using available techniques.

The results from Chapter 3 are summarised briefly in Chapter 4 and some general conclusions are drawn about the research presented in this thesis and its possible developments.



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II.1 : INTRODUCTION

This chapter is concerned with the preparation of anilines substituted at the 2position with mesogenic substituents and their subsequent polymerisation. The first objective of the project was to synthesise the monomers, make an assessment of their liquid crystal properties and investigate their potential as precursors to processable conducting polymers. Aniline polymerises head-to-tail and only the *ortho* and *meta* positions are available for the substitution with liquid crystalline groups. It has been established in Chapter I that the 2-substituted anilines always give higher polymerisation yields and more regular head-to-tail structures than the 3-substituted ones²⁸⁶. Furthermore, the aniline molecule is not very stable. Indeed, oxidation of the amine group occurs easily in air at room temperature. It was thus decided to work on suitable substituted nitrobenzenes and once the mesogenic groups had been attached in the *ortho*-position, these were hydrogenated to yield 2-substituted anilines which were then polymerised.

In Chapter I, we have discussed the requirements for liquid crystallinity of low molecular weight compounds, and also the influence of the flexible spacer group between the potential monomer backbone and the mesogenic moiety. It was therefore obvious that we had to introduce a flexible spacer group between the nitrobenzene molecule and the rigid mesogenic group. For ease of synthesis and following an investigation of previous work done on side-chain liquid crystalline polymers, it was decided to use an alkyloxy chain as a flexible spacer. We also found in the literature^{287,288} that the length of the flexible spacer can influence the liquid crystal order of the side-chain. Indeed, the minimum length of the flexible spacer to allow sufficient decoupling between the mesogenic moiety and the polymer backbone is generally equal to three (but this could depend on the nature of the two moieties). It was then decided to use a spacer length of average size and to synthesise in parallel a molecule with an even and another with an odd spacer group. In addition, a full series of one type of monomer was prepared in order to assess the influence of the spacer group length on the liquid crystal properties of the molecular systems we have been using.

The choice of the mesogenic group and the phase transition temperatures were not very clear at the beginning of the project because the glass transition temperature of the polymer was not known. Thus, it was not possible to predict the influence of a large *ortho*substituent on the backbone T_g of polyaniline. Therefore, monomers substituted with alkoxy groups (Scheme 1) were first synthesised and polymerised in order to assess the behaviour of the glass transition with increasing chain length. Monomers with low liquid crystal transition temperatures were then synthesised (Schemes 2 and 3), then we moved to monomers with higher mesogenic transition temperatures (Schemes 4, 5, 6 and 7) to ensure that the liquid crystal transition temperatures were higher than the backbone T_g . A general discussion of the synthetic strategies adopted is given at the end of the monomers experimental section.

Once the syntheses of the *ortho*-substituted nitrobenzene molecules and *ortho* sidechain aniline molecules were achieved and found to possess liquid crystalline properties, the following stage was to polymerise these monomers. It has been seen in the Chapter I on conducting polymers that polyaniline is a semiconductor in its emeraldine salt form and polymerises head to tail at pH \approx 1; therefore we had to polymerise our monomers in acidic conditions. Because of the size of the side-chain groups, our monomers were fairly insoluble in aqueous acidic media, therefore modified polymerisation conditions such as emulsion polymerisation were used. It was then possible to synthesise side chain liquid crystalline polymers and investigate their properties.

II.2 : GENERAL PROCEDURES AND INSTRUMENTATION

II.2.1. Chemicals and Solvents

All chemicals used during the course of this research were purchased from Aldrich, Avocado, BDH, TCI or Alfa, and were used as supplied, unless stated otherwise. All solvents used during reactions, work-ups and purification procedures were used as supplied (different grades were used as required), unless otherwise stated.

II.2.2. Chromatography Techniques

Analytical Thin-Layer Chromatography was carried out on silica gel of pore diameter 60 Å on plastic sheet with fluorescent indicator. The TLC plate was then visualised by short (254 nm) and long (365 nm) wave ultraviolet irradiation and immersion in iodine vapour or permanganate solution.

Flash Column Chromatography was performed on silica gel using 230-400 mesh (0.040-0.063 mm) ASTM silica.

II.2.3. Spectroscopy Techniques

Infra-red spectra were recorded using a Perkin-Elmer (1600 and Paragon 1000 series) Fourier transform infra-red spectrophotometer, with the sample and potassium bromide forming a pressed disc and liquids forming thin films. Absorption bands are quoted in wave-numbers (cm⁻¹) relative to a polystyrene standard.

Proton nuclear magnetic resonance (¹H N.M.R.) spectra were measured at 300 MHz and ¹³C N.M.R. spectra were recorded at 75.75 MHz, both on a Bruker AC-300 Fourier transform nuclear magnetic resonance spectrometer.

Mass spectra were determined using a V.G. TRIO-2 mass spectrometer. Unless otherwise stated, the mass spectra were recorded under electron impact (E.I.) conditions with a source temperature of 180°C and an electron energy of 70 eV.

Ultra-violet/visible Spectra were recorded using a Kontron Uvikon 940 UV/VIS Spectrophotometer.

II.2.4. Purity of Compounds Synthesised

Purity of the compounds synthesized was assessed either by elemental analysis (EA) or high performance liquid chromatography (HPLC).

Elemental analyses were performed by Butterworth Laboratories Ltd, Analytical and Consulting Chemists (Middlesex). Results within $\pm 0.4\%$ of the expected values were accepted as representative of a pure sample.

The purity of novel liquid crystals and other monomers was established by HPLC analysis and found to be greater than 99.5%. HPLC was run using a Spherisorb column 5 ODS 1. The liquid chromatography pump used was a Perkin Elmer Series 410 set with a flow of 1 cm³/min of 80% aqueous acetonitrile as mobile phase. The detector was a diode array Perkin Elmer LC-235 with UV wavelength set at 255 nm and 280 nm. The results were analysed with the Apex Chromatography Workstation Model M625-4 software Version 2.02 by Autochrom Inc.

Liquids were purified by small scale distillation using a Kügelrohr apparatus.

II.2.5. Determination of Transition Temperatures

Liquid crystal and glass transition temperatures were measured by differential scanning calorimetry (DSC) using a Mettler DSC 20 and DSC 25 with a thermal-analysis processor Mettler TC 10A based on a TA 3000 system for the measurements and evaluations. The software used for the graphics was Graphware TA 72. A static nitrogen atmosphere was used in the furnace, and the reference material was an empty aluminium pan.

The transition temperatures were accurately measured using a Nikon polarising microscope (Optiphot-2) fitted with a Linkam THMS-600 heating stage, a JVC TK-1085E colour video camera and a TM-1500PS colour video monitor, using a Linkam control unit including a TMS 91 display and keyboard, a VTO 232 video text overlay and a CS 196 cooling system. The liquid crystal phases were identified by their characteristic textures when observed under the polarizing microscope.

II.2.6. Molecular Weight Measurements

The molecular weight distributions of the polymers were determined by gel permeation chromatography performed by RAPRA Technology Ltd (Shropshire). The chromatographic conditions were : Columns 2 x PLgel mixed bed-B, 10 microns, 30 cm ; solvent dimethylformamide with lithium bromide ; flow-rate 1.0 cm³/min ;

temperature 80°C; refractive index detector. The system was calibrated with monodisperse samples of polyethylene oxide and polyethylene glycol.

The number average molar mass was measured by a Knauer vapour pressure osmometer. Benzil (molecular weight 210.23) was used as the standard.

The viscosity average molecular weight was measured by an Ubbelohde suspended level dilution model viscometer at a constant temperature of 30°C with DMF as solvent.

II.2.7. Others techniques

II.2.7.1. Cyclic Voltammetry

The equipment used was the BioAnalytical Systems (BAS) 100B/W Electrochemical Workstation, and all measurements were made with respect to a silver/silver chloride reference electrode.

II.2.7.2. Thermoanalysis

Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 thermobalance coupled with a Perkin-Elmer thermal analysis controller TAC 7/DX. The samples were analysed under an inert atmosphere of nitrogen.

Thermomechanical analysis was performed with a Mettler TMA40 measuring cell.

II.2.7.3. Conductivity measurements

Electrical conductivities of the polymers produced were measured using a Keithley 617 programmable electrometer and a Keithley 224 programmable current source. These measurements were manually or computer controlled depending on the techniques used (4-probes, 2-probes, interdigitated cells).

Van der Pauw's four probe method²⁸⁹ was used for monitoring the electrical conductivities of the classical polymers produced. The current was passed through one pair of electrodes and the voltage recorded between another pair of electrodes as illustrated in Figure II.1. The contacts were made with metallic screws covered with silver dag (conducting paint). In this case, the measurements were computer controlled and the resistivity (independent of electrode separation) was equal to the following equation :

$$\rho = \frac{t R \pi}{\ln 2}$$

$$\rho = resistivity (\Omega cm)$$

$$t = thickness (cm)$$

$$R = resistance (\Omega)$$



Figure II.1 : Four-probes technique for Conductivity measurements

The conductivity (S cm⁻¹) is equal to the inverse of the resistivity : $\sigma = 1 / \rho$

In the case of 2-probe measurements the equation will depend on the shape of the samples and the distance between the two electrodes and will be equal to :

$$\rho = \frac{R A}{l}$$

$$A = cross-sectional area (cm2)$$

$$l = length of the specimen between the electrodes
(5 x 10-3 cm)$$

In the third case (conductivity as a function of the temperature), a ceramic platinum cell was used, containing an interdigitated array with 4 pairs of lines as illustrated in Figure II.2. The value of the resistivity was calculated with the same equation as in the case of the 2-probes but with 1 equal to the electrode gap.



Figure II.2 : Interdigitated cell for conductivity measurements

II.2.7.4. Laser Alignment

A He-Ne red laser (Ealing Electro-Optics) providing 20 mW at 632.8 nm was focused down, by means of a plano-convex lens, to a spot size of ca. 5 nm. The samples were moved perpendicular to this laser beam by means of the X-Y translation stage. Polymeric films about 150 μ m thick were produced by solvent casting onto microscope cover slips.

II.2.7.5. Molecular Modelling

Simple molecular modelling was carried out using the Oxford University Press package DTMM version 2.0 in order to predict the energy-minimised structures of selected monomers.

II.2.7.6. Hydrogenator

Hydrogenation under pressure was performed on a Chas. W. Cook & Sons Ltd apparatus designed for use at temperatures up to 300°C and at working pressures up to 500 psi[§] using stainless steel reaction bottles with a glass liner. The aluminium carrier, where the bottle fits, is pivoted in a support frame to allow controlled rocking by a motor. A photograph²⁹⁰ of the equipment is shown in Figure II.3.



Figure II.3 : Pressure Hydrogenator

[§] Notes : Pound per square inch (psi). 14 psi is equal to 1 bar.

II.3 : SYNTHESES OF MONOMERS

II.3.1. SCHEME 1 : Preparation of *ortho* **substituted nitrobenzenes**



For Compound (1)

(a to c) $R = n - C_3 H_7$ to $n - C_5 H_{11}$

For Compound (2)

(a to i) x = 2 - 10

[i] n-RBr / Cyclohexanone / K₂CO₃

[ii] $Br(CH_2)_xBr / Cyclohexanone / K_2CO_3$

II.3.1.1. 2-n-Alkoxynitrobenzenes ; Compounds (1a to 1c)

A mixture of 2-nitrophenol (10.04 g, 72 mmol), anhydrous potassium carbonate (48.0 g, 350 mmol) and the appropriate n-bromoalkane (168 mmol) was heated under reflux in cyclohexanone (100 cm³) with constant stirring during 3h. On cooling, the precipitated salts were filtered off and washed with cyclohexanone (50 cm³). The solvent was removed from the combined filtrate and washings under reduced pressure and the product was purified by vacuum distillation (Kügelrohr) to yield 2-n-alkoxynitrobenzenes as yellow liquids.

n-alkane R	b.p.°C/mm Hg	Yield %	Compound number	
C ₃ H ₇ -	94-98/0.25	83	(1a) ,	
C ₄ H ₉ -	114-125/0.2	99	(1b)	
C ₅ H ₁₁ -	150-155/0.35	73	(1c)	

<u>Spectral results</u>: All products showed the expected spectroscopic data, and typical results are given for compound (1b) :

m/z 195 (M⁺) ; υ_{max} (thin film) 3079 (CH aromatic), 2960, 2874 (CH alkane), 1600, 1489 (C=C aromatic), 1526, 1354 (N-O), 1281, 1256, 1165 (CO ether), 745 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl₃) 7.77 (1H, d, ArH), 7.49 (1H, t, ArH), 7.05 (1H, d, ArH), 6.97 (1H, t, ArH), 4.08 (2H, t, CH₂O), 1.79 (2H, m, CH₂), 1.50 (2H, m, CH₂-CH₃), 0.95 (3H, t, CH₃) ; ¹³C (CDCl₃) 152 (C=C-O), 140, 134, 125, 120, 114 (C=C aromatic), 69 (OCH₂), 31 (CH₂), 19 (<u>C</u>H₂-CH₃), 14 (CH₃).

<u>II.3.1.2. 2-(x-Bromoalkoxy)nitrobenzenes {or α-bromo-ω-(2-nitrophenoxy)alkanes}</u>; <u>Compounds (2a to 2i)</u>

The reaction of 2-nitrophenol (15.02 g, 108 mmol) with the appropriate ndibromoalkyl (378 mmol) in cyclohexanone (150 cm³) and anhydrous potassium carbonate (71.59 g, 518 mmol) was carried out as described previously in page 78 for compounds (1a-1c) with constant stirring during 4h. The product was purified by vacuum distillation (Kügelrohr) to yield 2-(x-bromoalkoxy)nitrobenzenes as orange liquids.

n-alkyl (x)	b.p.°C/mm Hg	Yield %	Compound number
$C_{2}H_{4}-$	145-150/0.3	56	(2a)
$C_{3}H_{6}$ -	104-109/0.05	57	(2b)
C_4H_8 -	152-157/0.2	66	(2c)
C ₅ H ₁₀ -	155-165/0.25	76	(2d)
C ₆ H ₁₂ -	152-155/0.10	86	(2e)
C ₇ H ₁₄ -	180-185/0.35	69	(2f)
C ₈ H ₁₆ -	195-205/0.3	77	(2g)
C ₉ H ₁₈ -	180-187/0.15	71	(2h)
$C_{10}H_{20}$ -	202-206/0.2	69	(2i)

Spectral results :

Spectroscopic characteristics of the series are broadly similar and the following data for the pentoxy and hexoxy homologues are typical of the series.

Compound (2d) : 2-(5-bromopentoxy)nitrobenzene

m/z 287-289 (M⁺) ; υ_{max} (thin film) 2943, 2868 (CH alkane), 1608, 1488 (C=C aromatic), 1525, 1353 (N-O), 1281, 1043 (CO ether), 852 (C-N), 745 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl₃) 7.76 (1H, d, ArH), 7.48 (1H, t, ArH), 7.04 (1H, d, ArH), 6.97 (1H, t, ArH), 4.07 (2H, t, CH₂O), 3.40 (2H, t, CH₂-Br), 1.86-1.61 (6H, m, CH₂ alkyl). ¹³C (CDCl₃) 152 (C=<u>C</u>-O), 140, 134, 125, 120, 114 (C=C aromatic), 69 (OCH₂), 34, 32, 28, 25 (CH₂).

Compound (2e) : 2-(6-bromohexoxy)nitrobenzene

m/z 301-303 (M⁺) ; υ_{max} (thin film) 2939, 2860 (CH alkane), 1608, 1488 (C=C aromatic), 1525, 1353 (N-O), 1281, 1044 (CO ether), 856 (C-N), 745 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl₃) 7.70 (1H, d, ArH), 7.44 (1H, t, ArH), 7.01 (1H, d, ArH), 6.92 (1H, t, ArH), 4.02 (2H, t, CH₂O), 3.34 (2H, t, CH₂-Br), 1.77-1.42 (8H, m, CH₂ alkyl). ¹³C (CDCl₃) 152 (C=<u>C</u>-O), 140, 134, 125, 120, 114 (C=C aromatic), 69 (OCH₂), 34, 33, 29, 28, 25 (CH₂).

II.3.2. SCHEME 2 : Synthesis of 4-methoxyphenyl 4-[x-(2-nitrophenoxy)

alkoxy]benzoates



For Compounds (2) to (5)

(a to i) x = 2 - 10



- [ii] KOH/EtOH (aq) ; then conc HCl
- [iii] (CF₃CO)₂O/CH₂Cl₂/ но-О-осн_в

<u>II.3.2.1. Ethyl 4-[x-(2-nitrophenoxy)alkoxy]benzoates {or α-(4-ethylbenzoate-oxy)-ω-(2-nitrophenoxy)alkanes}</u>; Compounds (3a to 3i)

A mixture of ethyl-4-hydroxybenzoate (2.74 g, 16.5 mmol), anhydrous potassium carbonate (10.95 g, 79.2 mmol) and the appropriate 2-(x-bromoalkoxy)nitrobenzene (2a-2i) (16.5 mmol) was heated under reflux in cyclohexanone (80 cm³) with constant stirring

under an atmosphere of nitrogen for 3.5h. On cooling, the precipitated salts were filtered off and washed with cyclohexanone. The solvent was removed from the combined filtrate and washings by rotary evaporation and the brown solid obtained was purified by recrystallisation in methylated spirit to yield ethyl 4-[x-(2-nitrophenoxy)alkoxy]benzoates as white crystalline solids.

n-alkoxy	m.p.°C	Yield %	Compound number
C ₂ H ₄ O-	100.5-102.5	69	(3a)
C ₃ H ₆ O-	81.8-82.1	76	(3b)
C₄H ₈ O-	78.9-80.1	89	(3c)
C ₅ H ₁₀ O-	62.5-63.7	63	(3d)
C ₆ H ₁₂ O-	90.0-91.0	88	(3e)
C ₇ H ₁₄ O-	64.1-64.6	81	(3f)
C ₈ H ₁₆ O-	56.4-56.5	83	(3g)
C ₉ H ₁₈ O-	49.5-50.7	60	(3h)
C ₁₀ H ₂₀ O-	44.7-46.0	77	(3i)

Spectroscopic characteristics of the series are broadly similar and the following data for the hexoxy homologue (compound (3e)) are typical of the series.

m/z 387 (M⁺) ; υ_{max} (KBr) 3086 (CH aromatic), 2948 (CH alkane), 1703 (C=O aryl ester), 1603, 1472 (C=C aromatic), 1523, 1355 (N-O), 1283, 1106, 1009 (CO aryl alkyl ether), 1252, 1171 (CO aromatic ester), 857, 775 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl₃) 8.12 (2H, d, ArH), 7.95 (1H, d, ArH), 7.64 (1H, t, ArH), 7.16 (2H, m, ArH), 7.03 (2H, d, ArH), 4.48 (2H, q, CH₂ ester), 4.25 (2H, t, CH₂O), 4.16 (2H, t, CH₂O), 1.99-1.70 (8H, m, CH₂ alkyl), 1.52 (3H, t, CH₃ ester) ; ¹³C (CDCl₃) 166 (C=O), 163, 152, 140, 134, 132, 126, 123, 120, 114, 114 (C=C aromatic), 69, 68 (OCH₂), 61 (CH₂ ester), 29, 29, 26, 26 (CH₂), 14 (CH₃).

II.3.2.2. 4-[x-(2-Nitrophenoxy)alkoxy]benzoic acids {or α-(4-benzoic acid-oxy-)-ω-(2nitrophenoxy)alkanes} ; Compounds (4a to 4i)

The appropriate ester (3a-3i) (12.9 mmol) was added to potassium hydroxide (2.19 g, 39 mmol) in 80% aqueous ethanol (100 cm³) and the mixture was heated under

reflux for 3h. The reaction mixture was cooled, diluted with water (100 cm^3), and acidified with concentrated hydrochloric acid. The precipitate was filtered off and washed with dil. HCl (50 cm^3) followed by cold methylated spirits (20 cm^3). The acids were then recrystallised from methylated spirits to give 4-[x-(2-nitrophenoxy)alkoxy]benzoic acids as white solids.

n-alkoxy	m.p.°C	Yield %	Compound number
C ₂ H ₄ O-	206.0-208.0	89	(4a)
C ₃ H ₆ O-	178.7-179.9	93	(4b)
C ₄ H ₈ O-	180.2-182.4	93	(4c)
C ₅ H ₁₀ O-	150.0-152.0	84	(4d)
C ₆ H ₁₂ O-	165.0-167.0	95	(4e)
C ₇ H ₁₄ O-	111.1-112.5	90	(4f)
C ₈ H ₁₆ O-	148.0-149.0	93	(4g)
C ₉ H ₁₈ O-	106.0-108.0	91	(4h)
C ₁₀ H ₂₀ O-	129.0-131.0	90	(4i)

Spectroscopic characteristics of the series are broadly similar and the following data for the hexoxy homologue (compound (4e)) are typical of the series.

m/z 359 (M⁺) ; v_{max} (KBr) 2950, 2875 (CH alkane), 2660, 2539 (OH acid), 1674 (C=O aryl acid), 1605, 1428 (C=C aromatic), 1526, 1355 (N-O), 1281, 1256, 1168, 1006 (CO ether), 849, 775 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl₃) 8.17 (2H, d, ArH), 7.96 (1H, d, ArH), 7.65 (1H, t, ArH), 7.18 (2H, m, ArH), 7.07 (2H, d, ArH), 4.26 (2H, t, CH₂O), 4.19 (2H, t, CH₂O), 2.01-1.73 (8H, m, CH₂ alkyl), no obvious OH peak. $\delta_{\rm H}$ (DMSO) 12.62 (1H, s, OH D₂O exchanged), 7.86 (3H, m, ArH), 7.64 (1H, t, ArH), 7.35 (1H, d, ArH), 7.10 (1H, t, ArH), 6.99 (2H, d, ArH), 4.16 (2H, t, CH₂O), 4.04 (2H, t, CH₂O), 1.75-1.48 (8H, m, CH₂ alkyl).

<u>II.3.2.3. 4-Methoxyphenyl 4-[x-(2-nitrophenoxy)alkoxy]benzoates {or α-(4-methoxy phenyl-4-oxybenzoate)-ω-(2-nitrophenoxy)alkanes}</u>; Compounds (5a-5i)

4-Methoxyphenol (1.38 g, 11.1 mmol) was added to a stirred mixture of the appropriate acid (4a-4i) (11.1 mmol) and trifluoroacetic anhydride (2.73 g, 13 mmol) in dry

dichloromethane (120 cm³) contained in a flask fitted with a $CaCl_2$ guard tube. The mixture was stirred for 3 days at room temperature. The solvent was removed by rotary evaporation, and the residue purified by column chromatography on silica gel, eluting with a mixture of toluene : ethyl acetate (3:1). The esters were then recrystallised from methylated spirit to yield 4-methoxyphenyl 4-[x-(2-nitrophenoxy)alkoxy]benzoates as white crystalline solids.

The purity was checked by HPLC analysis and was found to be equal to or greater than 99.5%.

Yield %	Compound number
88	(5a)
87	(5b)
80	(5c)
86	(5d)
94	(5e)
90	(5f)
87	(5g)
87	(5h)
96	(5i)
	Yield % 88 87 80 86 94 90 87 87 87 96

The melting points, mesomorphic transition temperatures and other data for the esters are presented in the Results and Discussion chapter, pages 138-144.

The spectroscopic characteristics of the esters are broadly similar and the following data for the hexoxy homologue (compound (5e)) are typical of the series.

m/z 466 (M⁺) ; ν_{max} (KBr) 2941, 2860 (CH alkane), 1720 (C=O ester), 1607, 1465 (C=C aromatic), 1515, 1350 (N-O), 1257, 1168, 1075, 988 (CO aryl ether and ester), 848, 766 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl₃) 8.26 (2H, d, ArH), 7.95 (1H, d, ArH), 7.65 (1H, t, ArH), 7.05-7.28 (8H, m, ArH), 4.26 (2H, t, CH₂O), 4.20 (2H, t, CH₂O), 3.96 (3H, s, OCH₃), 2.01-1.72 (8H, m, CH₂ alkyl) ; ¹³C (CDCl₃) 166 (C=O ester), 163, 157, 152, 150, 145, 134, 132, 126, 123, 122, 120, 114, 114, 114 (C=C aromatic), 69, 68 (OCH₂), 56 (OCH₃), 29, 29, 26, 26 (CH₂).

II.3.3. SCHEME 3 : Synthesis of 4-[6-(2-Nitrophenoxy)hexoxy]biphenyl and other

biphenyl substituted nitrobenzenes



II.3.3.1 4-[6-(2-Nitrophenoxy)hexoxy]biphenyl {or α-(4-oxybiphenyl)-ω-(2-nitro phenoxy)hexane ; Compound (6)

A mixture of 4-phenylphenol (0.57 g, 3.3 mmol), anhydrous potassium carbonate (2.2 g, 15.9 mmol) and 2-(6-bromohexoxy)nitrobenzene (2e) (1 g, 3.3 mmol) was heated under reflux in cyclohexanone (10 cm³) with constant stirring during 4h. On cooling, the precipitated salts were filtered off and washed with cyclohexanone (10 cm³). The solvent was removed from the combined filtrate and washings by rotary evaporation and the dark brown solid obtained was purified by recrystallisation from methylated spirit. The product was further purified by column chromatography on silica gel eluting with 4:1 petroleum

ether 60-80°C/ethyl acetate to yield 4-[6-(2-nitrophenoxy)hexoxy]biphenyl as a white solid 0.65 g (50%), purity 97.7% ; m/z 391 (M⁺) ; υ_{max} (KBr) 2939, 2859 (CH alkane), 1607, 1488 (C=C aromatic), 1521, 1356 (N-O), 1284, 1250, 1005 (CO ether), 830 (C-N), 840, 764 (CH bend) cm⁻¹. $\delta_{\rm H}$ (CDCl₃) 7.96 (1H, d, ArH), 7.66 (5H, m, ArH), 7.56 (2H, t, ArH), 7.45 (1H, m, ArH), 7.22-7.05 (4H, m, ArH), 4.26 (2H, t, CH₂O), 4.17 (2H, t, CH₂O), 2.01-1.72 (8H, m, CH₂ alkyl).

The melting points, mesomorphic transition temperatures and other data for compound (6) are presented in the Results and Discussion chapter, pages 145-147.

<u>II.3.3.2. 4-Cyano 4'-[x-(2-nitrophenoxy)alkoxy]biphenyls {or α-(4-cyanobiphenyl-4'-</u> oxy)-ω-(2-nitrophenoxy)alkanes} ; Compounds (7a and 7b)

4-Cyano 4'-[x-(2-nitrophenoxy)alkoxy]biphenyls were prepared by the procedure described for compound (6), using 4-cyano-4'-hydroxybiphenyl (3.01 g, 15.4 mmol), anhydrous potassium carbonate (10.21 g, 73.9 mmol), the appropriate 2-(x-bromoalkoxy) nitrobenzene (2d and 2e) (15.4 mmol) and cyclohexanone (90 cm³) with constant stirring under an atmosphere of nitrogen during 4h. The crude products were crystallised from methylated spirit and the solids obtained were purified by column chromatography on silica gel, eluting with a mixture of toluene : ethyl acetate (3:1), and then recrystallised from methylated spirit to yield 4-cyano 4'-[x-(2-nitrophenoxy)alkoxy]biphenyls as white crystalline solids.

n-alkoxy	Yield %	purity	Compound number
C ₅ H ₁₀ O-	85	99.5% (HPLC)	(7a)
C ₆ H ₁₂ O-	89	99.6% (HPLC)	(7b)

The melting points, mesomorphic transition temperatures and other data for compounds (7a) and (7b) are presented in the Results and Discussion chapter, pages 145-147.

<u>Typical spectral results</u>: Compound (7b)

m/z 416 (M⁺) ; υ_{max} (KBr) 2942, 2863 (CH alkane), 2224 (C≡N), 1604, 1494 (C=C aromatic), 1520, 1351 (N-O), 1278, 1246, 1178, 1033 (CO ether), 826, 750 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl₃) 7.95 (1H ,d ,ArH), 7.80 (4H, q, ArH), 7.64 (3H, m, ArH), 7.17 (4H, m, ArH), 4.26 (2H, t, CH₂O), 4.17 (2H, t, CH₂O), 2.01-1.72 (8H, m, CH₂ alkyl).

In order to assign the aromatic protons more precisely a 2D COSY (Correlated Spectroscopy) ¹H NMR spectrum of compound (7b) was recorded (Fig. II.4).





Figure II.4 : 2D ¹H-¹H COSY NMR Spectrum of (7b)

II.3.3.3. 4-Bromo-4'-[6-(2-nitrophenoxy)hexoxy]biphenyl {or α -(4-bromobiphenyl-4'oxy)- ω -(2-nitrophenoxy)hexane} ; Compound (8)

4-Bromo-4'-[6-(2-nitrophenoxy)hexoxy]biphenyl was prepared by using the procedure described in page 85 for compound (6), using 4-bromo-4'-hydroxybiphenyl (5.01 g, 20.1 mmol), anhydrous potassium carbonate (13.5 g, 97.7 mmol), 2-(6-bromohexoxy) nitrobenzene (2e) (6.15 g, 20.4 mmol) and cyclohexanone (150 cm³) with constant stirring under an atmosphere of nitrogen overnight. The crude product was crystallised from methylated spirit. The solid obtained was purified by column chromatography on silica gel, eluting with a mixture of dichloromethane : petroleum spirit 60-80°C (1:1), and then recrystallised from methylated spirit to yield 4-bromo-4'-[6-(2-nitrophenoxy)hexoxy] biphenyl as a white crystalline solid 6.43 g (68%), purity 99.5% ; **m/z** 469, 471 (M⁺) ; v_{max} (KBr) 2945, 2863 (CH alkane), 1606, 1474 (C=C aromatic), 1533, 1353 (N-O), 1242, 1174, 1036, 997 (CO ether), 805, 743 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl₃) 7.82 (1H, d, ArH), 7.54-7.40 (7H, m, ArH), 7.08-6.95 (4H, m, ArH), 4.12 (2H, t, CH₂O), 4.02 (2H, t, CH₂O), 1.87 (4H, m, CH₂).

The melting point, mesomorphic transition temperatures and other data for compound (8) are presented in the Results and Discussion chapter, pages 145-147.

II.3.4. SCHEME 4 : Synthesis of 4-Biphenyl 4'-[6-(2-nitrophenoxy)hexoxy] carboxylic acid and Ester Derivatives

$\begin{array}{c} \begin{array}{c} \begin{array}{c} 0 - (CH_2)_{0} - 0 & 0 & 0 \\ \hline \\ -NO_2 & (7b) & 1 \\ \hline \\ \end{array} \end{array} \begin{array}{c} 1 \\ (7b) & 0 \\ \hline \\ \end{array} \end{array}$

- [i] H₂SO₄ aq /CH₃COOH
- [iii] $(CF_3CO)_2O/CH_2Cl_2/$ HO-O-CN [iii] $(CF_3CO)_2O/CH_2Cl_2/$ HO-O-OCH₃

II.3.4.1. 4-Biphenyl 4'-[6-(2-nitrophenoxy)hexoxy]carboxylic acid {or α -(4-biphenyl carboxylic acid-4'-oxy)- ω -(2-nitrophenoxy)hexane}; Compound (9)

4-Cyano 4'-[6-(2-nitrophenoxy)hexoxy]biphenyl (7b) (5.0 g, 12 mmol) was added to a mixture of 50% (w/w) aqueous sulphuric acid (50 cm³) and glacial acetic acid (125 cm³). After heating under gentle reflux for 18h, the solution was poured into ice cooled distillated water (250 cm³). The solid was filtered off and washed with water (100 cm³) followed by a small amount of cold methylated spirits. The residue was recrystallised from methylated spirits to yield 4-biphenyl 4'-[6-(2-nitrophenoxy)hexoxy]carboxylic acid as a white solid 5.08 g (97%), purity 99.9% ; m/z 436 (M⁺) ; v_{max} (KBr) 2936, 2858 (CH alkane), 2672, 2551 (OH acid), 1678 (C=O aryl acid), 1603, 1430 (C=C aromatic), 1529, 1348 (N-O), 1286, 1250, 1199, 995 (CO ether), 830, 773 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (DMSO) 9.72 (1H, s, OH, D₂O exchanged), 7.98 (2H, d, ArH), 7.85 (1H, d, ArH), 7.76-7.57 (5H, m, ArH), 7.36 (1H, d, ArH), 7.13-7.03 (3H, m, ArH), 4.17 (2H, t, CH₂O), 4.03 (2H, t, CH₂O), 1.76-1.49 (8H, m, CH₂ alkyl).

The melting points, mesomorphic transition temperatures and other data for the acid are presented in the Results and Discussion chapter, pages 147-155.

In order to assign the aromatic protons more precisely a 2D COSY (Correlated Spectroscopy) ¹H NMR spectrum of compound (9) was recorded (Fig. II.5).

<u>II.3.4.2. 4-Cyanophenyl-4'-[6-(2-nitrophenoxy)hexoxy]biphenyl-4-carboxylate {or α-[(4cyanophenyl-biphenyl-4-carboxylate)-4'-oxy]-ω-(2-nitrophenoxy)hexane}</u>; <u>Compound (10)</u>

The 4-hydroxybenzonitrile (0.68g, 5.74 mmol) was added to a stirred mixture of the carboxylic acid (9) (2.50g, 5.74 mmol) and trifluoroacetic anhydride (1.90g, 9 mmol) in dry dichloromethane (170cm³) contained in a flask fitted with a CaCl₂ guard tube. This mixture was stirred for 5 days. Water was then removed slowly by azeotropic distillation (Dean-Stark apparatus) over 2 days. The remaining solvent was removed by rotary evaporation to yield a creamy solid which was purified by column chromatography on silica gel, eluting with a mixture of chloroform : ethyl acetate (9:1). Recrystallisation from methylated spirits yielded 4-cyanophenyl-4'-[6-(2-nitrophenoxy)hexoxy]biphenyl-4-carboxylate as a white solid 2.11g (69%), purity 99.5% ; m/z 536 (M⁺) ; v_{max} (KBr) 2942, 2868 (CH alkane), 2228 (C=N), 1744 (C=O ester), 1604, 1500 (C=C aromatic), 1526, 1350 (N-O), 1276, 1248, 1062 (CO ether), 1186 (CO ester), 826, 750 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl₃) 8.22 (2H, d, ArH), 7.70-7.84 (5H, m, ArH), 7.60 (2H, d, ArH), 7.51 (1H, t, ArH), 7.39 (2H, d, ArH), 7.03 (4H, m, ArH), 4.13 (2H, t, CH₂O), 4.05 (2H, t, CH₂O), 1.88-1.59 (8H, m, CH₂ alkyl).

The melting point, mesomorphic transition temperatures and other data for compound (10) are presented in the Results and Discussion chapter, pages 147-155.

In order to assign the aromatic protons more precisely a 2D COSY (Correlated Spectroscopy) ¹H NMR spectrum of compound (10) was recorded (Fig. II.6).





Figure II.5 : 2D ¹H-¹H COSY NMR Spectrum of (9)

<u>II.3.4.3. 4-Methoxyphenyl-4-[6-(2-nitrophenoxy)hexoxy]biphenyl-4'-carboxylate {or α-</u> <u>[(4-methoxyphenyl-biphenyl-4-carboxylate)-4'-oxy]-ω-(2-nitrophenoxy)hexane</u>} ; Compound (11)

The 4-methoxyphenol (0.287g, 2.31 mmol) was added to a stirred mixture of the carboxylic acid (9) (1g, 2.30 mmol) and trifluoroacetic anhydride (0.89g, 4.25 mmol) in dried dichloromethane (70cm³) contained in a flask fitted with a CaCl₂ guard tube. This mixture was stirred during 5 days. The solvent was removed by rotary evaporation to yield an orange brown oil which was purified in hot methylated spirit. The product was purified by column chromatography on silica gel, eluting with a mixture of chloroform : ethyl acetate (9:1). Recrystallisation from methylated spirits yielded 4-methoxyphenyl-4-[6-(2-nitrophenoxy)hexoxy]biphenyl-4'-carboxylate as a white solid 0.423g (34%), purity 99.6% ; m/z 541 (M⁺) ; υ_{max} (KBr) 3074 (CH aromatic), 2940, 2862 (CH alkane), 1726 (C=O ester), 1605, 1506 (C=C aromatic), 1526, 1363 (N-O), 1277, 1247, 1075, 990 (CO ether), 1175 (CO ester), 826, 770 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl₃) 8.23 (2H, d, ArH), 7.82 (1H, d, ArH), 7.69 (2H, d, ArH), 7.59 (2H, d, ArH), 7.51 (1H, t, ArH), 7.16 (2H, d, ArH), 6.93-7.08 (6H, m, ArH), 4.13 (2H, t, CH₂O), 4.04 (2H, t, CH₂O), 3.84 (3H, s, CH₃O), 1.88-1.59 (8H, m, CH₂ alkyl).

The melting point, mesomorphic transition temperatures and other data for compound (11) are presented in the Results and Discussion chapter, pages 147-155.





Figure II.6 : 2D ¹H-¹H COSY NMR Spectrum of (10)

II.3.5. SCHEME 5 : 4'-Cyanobiphenyl-4-[6-(2-nitrophenoxy)hexoxy]phenyl-4carboxylate {or α-[(4'-cyanobiphenyl-phenyl-4-carboxylate)-4-oxy]-ω-(2nitrophenoxy)hexane} ; Compound (12)



[i] (CF₃CO)₂O/CH₂Cl₂/ HO-O-CN

The 4-cyano-4'-hydroxybiphenyl (1.62 g, 8.3 mmol) was added to a stirred mixture of the carboxylic acid (4e) (3.0 g, 8.3 mmol) and trifluoroacetic anhydride (8.18 g, 38.9 mmol) in dry dichloromethane (250cm³) contained in a flask fitted with a CaCl₂ guard tube. This mixture was stirred for 1 day. The solvent was removed by rotary evaporation, and the residue purified by column chromatography on silica gel, eluting with chloroform. Recrystallisation from methylated spirits yielded 4'-Cyanobiphenyl-4-[6-(2-nitrophenoxy) hexoxy]phenyl-4-carboxylate as a white solid 4.16 g (93%), purity 99.5% ; m/z 536 (M⁺) ; v_{max} (KBr) 2947, 2858 (CH alkane), 2223 (C=N), 1730 (C=O ester), 1605, 1492 (C=C aromatic), 1517, 1346 (N-O), 1249, 1162, 1064, 1004 (CO ether), 852, 749 (CH bend) cm⁻¹. $\delta_{\rm H}$ (CDCl₃) 8.16 (2H, d, ArH), 7.82 (1H, d, ArH), 7.76-7.61 (6H, m, ArH), 7.52 (1H, t, ArH), 7.33 (2H, d, ArH), 7.09-6.98 (4H, m, ArH), 4.13 (2H, t, CH₂O), 4.08 (2H, t, CH₂O), 1.88 (4H, m, CH₂).

The melting point, mesomorphic transition temperatures and other data for compound (12) are presented in the Results and Discussion chapter, pages 147-155.
<u>terphenyl</u>



- [i] *n*-BuLi/dry THF/-78°C
- [ii] $(CH_3O)_3B/-78^{\circ}C$ then HCl dil
- [iii] Pd(PPh₃)₄/EtOH/Toluene/Na₂CO₃ 2M

II.3.6.1. 4-Ethoxyphenylboronic acid ; Compound (13)

n-Butyllithium (31.5 cm³, 50.4 mmol, 1.6 mol dm⁻³ in hexane) was added dropwise to a stirred, cooled (-78°C) solution of 4-bromophenetole (10.1 g, 50 mmol) in dry THF (50 cm³) under dry nitrogen. The reaction mixture was maintained under these conditions for 3.5 h when a previously cooled solution of tri-isopropyl borate (18.8 g, 99.7 mmol) in dry THF (50 cm³) was added dropwise at -78°C. The reaction was allowed to warm to room temperature overnight and then stirred for 2 h with 10% hydrochloric acid (50 cm³). The product was extracted into dichloromethane (3 x 20 cm³), and the combined chlorinated extracts were washed with water (2 x 20 cm³) and dried (MgSO₄). The solvent was removed *in vacuo* and the residue was recrystallised from hexane to yield 4-ethoxyphenylboronic acid as a white crystalline solid 5.07 g (61%); m.p. 165-167°C; m/z 443 (trimer, C₂₄H₂₇O₆B₃), 359, 166 (M⁺); υ_{max} (KBr) 3315 (OH), 3038 (CH aromatic), 2979, 2935 (CH alkane), 1604, 1476 (C=C aromatic), 1246, 1172, 1114, 1044 (CO ether), 846 (CH bend) cm⁻¹; δ_{H} (CDCl₃) 8.16 (2H, d, ArH), 7.0 (2H, m, ArH), 4.13 (2H, q, OCH₂), 1.47 (3H, t, CH₃), no obvious OH absorption.

II.3.6.2. 4"-Methoxy-4-[6-(2-nitrophenoxy)hexoxy]terphenyl; Compound (14)

A solution of 4-ethoxyphenylboronic acid compound (13) (1.38 g, 8.3 mmol) in ethanol (40 cm⁻³) was added to a stirred mixture of compound (8) (3.01 g, 6.4 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.25 g, 0.21 mmol) in toluene (50 cm⁻³) and aqueous sodium carbonate (50 cm³ of 2 mol dm⁻³) at room temperature under dry nitrogen. The stirred mixture was heated under reflux for 24 h (i.e. until tlc analysis revealed a complete reaction). The product was extracted into dicholoromethane (2 x 25 cm³) and the combined chlorinated extracts were washed with brine (50 cm³), water (50 cm³) and dried (MgSO₄). The solvent was removed under pressure and the residue was purified by column chromatography on silica gel, eluting with toluene followed by chloroform, and then recrystallised from a mixture of toluene : ethyl acetate : methylated spirits (3:2:2) to yield 4"-methoxy-[6-(2-nitrophenoxy)hexoxy]terphenyl as a white crystalline solid 2.70 g (83%), purity EA : Found : C, 75.31 ; H, 6.4 ; N, 3.05 %. C₃₂H₃₃NO₅ requires C, 75.13 ; H, 6.5 ; N, 2.74 % ; m/z 511 (M⁺) ; v_{max} (KBr) 2977, 2935, 2859 (CH alkane), 1605, 1492 (C=C aromatic), 1532, 1347 (N-O), 1285 (C-N), 1248, 1187, 1046, 995 (CO ether), 807, 737 (CH bend) cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 7.82 (1H, d, ArH), 7.61-7.48 (9H, m, ArH), 7.08-6.96 (6H, m, ArH), 4.11 (2H, q, CH₂O), 4.03 (4H, t, CH₂O), 1.86 (4H, m, CH₂), 1.59 (4H, m, CH₂), 1.45 (3H, t, CH₃).

The melting point, mesomorphic transition temperatures and other data for compound (14) are presented in the Results and Discussion chapter, pages 155-160.

In order to assign the aromatic protons more precisely a 2D COSY (Correlated Spectroscopy) ¹H NMR spectrum of compound (14) was recorded (Fig. II.7).



Figure II.7 : 2D ¹H-¹H COSY NMR Spectrum of (14)



- [i] K₂CO₃/Cyclohexanone/Benzyl chloride
- [ii] n-BuLi/dry THF/-78°C
- [iii] (CH₃O)₃B/-78°C then HCl dil
- [iv] Pd(PPh₃)₄/EtOH/Toluene/Na₂CO₃ aq./4-Bromobenzonitrile
- [v] H₂/Pd on C/Ethyl acetate

[vi] H_2/Pd on C/EtOH

- [vii] Pyridine/Acetic anhydride then H₂O
- [viii] aq EtOH/KOH then HCl
- [ix] $K_2CO_3/Cyclohexanone/Compound$ (2e)

II.3.7.1. 4-Bromo-(4'-benzyl-oxy)biphenyl; Compound (15)

4-Bromo-(4'-benzyl-oxy)biphenyl was prepared by using the procedure described in Scheme 3 for compound (6), using 4-bromo-4'-hydroxybiphenyl (25.06 g, 101 mmol), anhydrous potassium carbonate (29 g, 210 mmol), benzyl chloride (16.6 g, 131 mmol) and cyclohexanone (150 cm³) and heated under reflux for 1 day. The crude yellow solid obtained was purified by recrystallisation from methylated spirit to yield 4-bromo-(4'-benzyl oxide)biphenyl as a white crystalline solid 32.7 g (96%) ; m.p. 142-146°C ; m/z 338-340 (M⁺) ; v_{max} (KBr) 3086, 3031 (CH aromatic), 2930, 2864 (CH alkane), 1606, 1480 (C=C aromatic), 1286, 1254, 1008, 996 (CO ether), 812, 729, 694 (CH bend) cm⁻¹. $\delta_{\rm H}$ (CDCl₃) 7.55-7.32 (11H, m, ArH), 7.05 (2H, d, ArH), 5.12 (2H, s, CH₂O).

II.3.7.2. 4-Biphenyl 4'-(benzyl-oxy)boronic acid ; Compound (16)

4-Biphenyl 4'-(benzyl-oxy)boronic acid was prepared by using the procedure described in Scheme 6 for compound (13), using n-Butyllithium (1.6 mol dm⁻³ in hexane, 9.21 cm⁻³, 14.7 mmol), the bromo-compound (15) (5.0 g, 14.7 mmol) in dry THF (70 cm³). This was followed by tri-isopropyl borate (5.7 g, 30.3 mmol) in dry THF (11 cm³). The reaction was allowed to warm to room temperature during 2 days and then stirred for 2 h with 10% hydrochloric acid (10 cm³). After extraction and the solvent removed the residue was recrystallised from methylated spirits. The solid obtained was further purified by column chromatography on silica gel, eluting with chloroform, and then recrystallised from methylated spirits to yield 4-biphenyl 4'-(benzyl-oxy)boronic acid as a white crystalline solid 3.31 g (74%) ; m.p. 261-266°C ; m/z 573 (dimer, $C_{38}H_{30}O_4B_2$) (M+1) FAB ; v_{max} (KBr) 3406 (OH), 3035 (CH aromatic), 2908, 2866 (CH alkane), 1604, 1531 (C=C aromatic), 1252, 1024, 999 (CO ether), 814, 743, 699 (CH bend) cm⁻¹. $\delta_{\rm H}$ (DMSO) 8.06 (2H, s, B(OH)₂ removed upon D₂O exchange), 7.85 (2H, d, ArH), 7.64 (2H, d, ArH), 7.60 (2H, d, ArH), 7.50-7.32 (5H, m, ArH), 7.11 (2H, d, ArH), 5.17 (2H, s, CH₂O).

II.3.7.3. 4"-Cyano-4-(benzyl-oxy)terphenyl ; Compound (17)

4"-Cyano-4-(benzyl-oxy)terphenyl was prepared by using the procedure described in Scheme 6 for compound (14), using compound (16) (1.0 g, 3.29 mmol) in ethanol (70 cm⁻³), 4-bromobenzonitrile (0.46 g, 6.4 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.1 g, 0.09 mmol) in toluene (20 cm⁻³) and aqueous sodium carbonate (2 mol dm⁻³; 20 cm⁻³). The product was extracted into chloroform (2 x 25 cm³) and the combined chlorinated extracts were washed with brine (50 cm³) and dried (MgSO₄). The solvent was removed under pressure and the residue was purified by column chromatography on silica gel, eluting with chloroform to yield 4"-cyano-4-(benzyloxy)terphenyl as a white crystalline solid 0.78 g (86%) ; **m/z** 361 (M⁺) ; v_{max} (KBr) 3035 (CH aromatic), 2935, 2859 (CH alkane), 2229 (C=N), 1602, 1490 (C=C aromatic), 1251, 1043 (CO ether), 818, 740, 696 (CH bend) cm⁻¹. $\delta_{\rm H}$ (CDCl₃) 7.74 (4H, s, ArH), 7.66 (4H, s, ArH), 7.58 (2H, d, ArH), 7.48-7.35 (5H, m, ArH), 7.08 (2H, d, ArH), 5.14 (2H, s, CH₂O). $\delta_{\rm H}$ (DMSO) 7.95 (4H, s, ArH), 7.85 (2H, d, ArH), 7.78 (2H, d, ArH), 7.71 (2H, d, ArH), 7.51-7.35 (5H, m, ArH), 7.14 (2H, d, ArH), 5.19 (2H, s, CH₂O).

The melting point, mesomorphic transition temperatures and other data for compound (17) are presented in the Results and Discussion chapter, pages 155-160.

II.3.7.4. 4-Cyano-4"-hydroxyterphenyl ; Compound (18)

4-Cyano-4"-benzyl-oxyterphenyl (17) was dissolved in a minimum quantity of the appropriate solvent in a glass-lined autoclave, and a catalytic amount of 10% palladium on charcoal was added. This was subjected to a positive pressure of hydrogen at the appropriate temperature with constant agitation during the required time. On cooling, the catalyst was filtered off and the solvent was removed under vacuum by rotary evaporation to yield a solid.

Different conditions have been studied in order to selectively remove the benzyl group without reducing the nitrile group (Table II.1). In the cases (c) and (d), we obtained a mixture of the cyano and the methyl compounds, in the case (a) the methyl product (19) has been obtained, whereas in the case (b) the desired compound (18) was obtained but with a low yield. The reaction was also difficult to reproduce on a larger scale.

Test	Solvent	Temperature (°C)	Pressure (psi)	Time (h)	Product	Yield (%)
(a)	Ethyl Acetate	65	50	4	(19)	100
(b)	Ethyl Acetate	45	30	3	(18)	40
(c)	Ethanol	60	35	4	Mixture 18 + 19	60
(d)	Ethanol	70	40	3	Mixture 18 + 19	60

Table II.1 : Different Conditions Used for Debenzylation and their Results

The product obtained in the case (a) was recrystallised from methylated spirit to yield 4methyl-4"-hydroxyterphenyl (**19**) as a white crystalline solid 0.36 g (100%) ; m.p. 261-262°C ; **m/z** 260 (M⁺) ; υ_{max} (KBr) 3418 (OH), 3030 (CH aromatic), 2914, 2879 (CH alkane), 1610, 1492 (C=C aromatic), 1263 (CO), 805 (CH bend) cm⁻¹. $\delta_{\rm H}$ (**DMSO**) 7.66 (4H, s, ArH), 7.58 (3H, d, ArH), 7.49 (1H, s, ArH), 7.32 (1H, s, ArH), 7.23 (1H, s, ArH), 6.91 (1H, s, ArH), 6.82 (1H, s, ArH), 2.34 (3H, s, CH₃).

The product obtained in the case (b) was purified by column chromatography on silica gel, eluting with toluene to start and then toluene : ether (1:3) to yield 4-cyano-4"-hydroxyterphenyl (**18**) as a white solid 0.03 g (40%) ; **m/z** 271 (M⁺) ; υ_{max} (KBr) 3348 (OH), 3030 (CH aromatic), 2914, 2879 (CH alkane), 2237 (C=N), 1598, 1498 (C=C aromatic), 1219 (CO), 817 (CH bend) cm⁻¹. $\delta_{\rm H}$ (CDCl₃) 7.74 (4H, s, ArH), 7.66 (4H, s, ArH), 7.54 (2H, d, ArH), 6.94 (2H, d, ArH), 4.87 (1H, s, OH removed upon D₂O exchanged).

The melting point, mesomorphic transition temperatures and other data for compounds (18) and (19) are presented in the Results and Discussion chapter, pages 155-160.

In the other cases, it was impossible to separate compounds (18) and (19) by column chromatography due to the high polarity of the hydroxy group in relation to the cyano or methyl groups. Therefore, the mixture was acylated as shown below.

II.3.7.5. Acetylation of a mixture of (18) and (19); Compounds (20) and (21)

The mixture of compounds (18) and (19) (0.20 g) was dissolved in pyridine, and acetic anhydride (7 cm³) was added dropwise keeping the temperature cooled with an ice bath with constant stirring. The solution was stirred at room temperature for 1.5h. The mixture was poured into cold water (100 cm³) with stirring. The precipitate was filtered off under vacuum and washed with water (50 cm³). The mixture obtained was dried under vacuum and subjected to column chromatography on silica gel eluting with toluene to yield 4-cyanoterphenyl-4"-ethanoate (20) 0.10 g (45%); m/z 313 (M⁺) ; v_{max} (KBr) 3030 (CH aromatic), 2914, 2865 (CH alkane), 2230 (C=N), 1760 (C=O ester), 1604, 1490 (C=C aromatic), 1208, 1169, 1003 (CO), 824 (CH bend) cm⁻¹. $\delta_{\rm H}$ (CDCl₃) 7.74 (4H, s, ArH), 7.68 (4H, s, ArH), 7.64 (2H, d, ArH), 7.20 (2H, d, ArH), 2.35 (3H, s, CH₃COO).

The melting point, mesomorphic transition temperatures and other data for compound (20) are presented in the Results and Discussion chapter, pages 155-160.

II.3.7.6. 4-Cyano-4"-hydroxyterphenyl from the ester-derivative ; Compound (18)

Compound (20) (0.10 g) was dissolved in hot 80% aqueous ethanol (40 cm³), potassium hydroxide (0.10 g, 1.8 mmol) was added and this was heated under reflux with constant stirring for 2h. The reaction was cooled and then diluted with water (10 cm³) and acidified with concentrated hydrochloric acid. The white precipitate was filtered off and washed with dilute hydrochloric acid followed by methylated spirits to yield 4-cyano-4"-hydroxyterphenyl (18) 0.06 g (71%). The spectral data were identical to that described previously in section 4 for compound (18).

II.3.7.7. 4"-Cyano-4-[6-(2-nitrophenoxy)hexoxy]terphenyl; Compound (22)

4"-Cyano-4-[6-(2-nitrophenoxy)hexoxy]terphenyl was prepared by using the procedure described in Scheme 3 for compound (6) with 4-cyano-4"-hydroxyterphenyl (18) (0.04 g, 0.15 mmol), anhydrous potassium carbonate (0.10 g, 0.74 mmol), 2-(6-bromohexoxy)nitrobenzene (2e) (0.05 g, 0.16 mmol) and cyclohexanone (10 cm³) heated

under reflux with constant stirring under an atmosphere of nitrogen during 3h. The crude creamy white solid obtained was purified by recrystallisation from methylated spirit to yield 4"-cyano-4-[6-(2-nitrophenoxy)hexoxy]terphenyl as a yellow solid 0.06 g (85%) ; m/z 492 (M⁺) ; v_{max} (KBr) 3070 (CH aromatic), 2944, 2857 (CH alkane), 2222 (C=N), 1604, 1448 (C=C aromatic), 1522, 1351 (N-O), 1280 (C-N), 1248, 1177, 990 (CO ether), 817, 752 (CH bend) cm⁻¹. $\delta_{\rm H}$ (CDCl₃) 7.82 (1H, d, ArH), 7.73 (4H, s, ArH), 7.66 (4H, s, ArH), 7.57 (2H, d, ArH), 7.49 (1H, d, ArH), 7.07 (1H, d, ArH), 7.01 (3H, d, ArH), 4.13 (2H, t, CH₂O), 4.04 (2H, t, CH₂O), 1.88 (4H, m, CH₂), 1.56 (4H, m, CH₂).

The melting point, mesomorphic transition temperatures and other data for compound (22) are presented in the Results and Discussion chapter, pages 155-160.

II.3.8. SCHEME 8 : HYDROGENATION

The next step was the reduction of the substituted 2-nitrobenzenes to the corresponding anilines.





$$R = -C_nH_{2n+1} \text{ where } n = 3 - 5 \text{ (see Table II.2)}$$

A = Complex Structure with x = 5, 6 (see Table II.3)

R	Nitro-compound	Corresponding Aniline-compound
-C ₃ H ₇	1a	23a
-C ₄ H ₉	1b	23ь
-C ₅ H ₁₁	1c	23c

Table II.2 : Aniline-molecule numbers depending on R

The required nitro-compound was dissolved in the appropriate solvent in an autoclave glass liner, and a catalytic amount of 10% palladium on charcoal was added. This was subjected to a positive pressure of hydrogen at the appropriate temperature with constant stirring during the required time. (See Table II.4 for details of conditions for each compound). On cooling, the catalyst was filtered off and the solvent removed by rotary evaporation to yield the appropriate aniline.



 6	. 11	29
 6	12	30 *
 6	14	31

Table II.3 : Aniline-molecule numbers depending on the Structure of A-

The compounds (23a), (23b) and (23c) were purified by high vacuum distillation (Kügelrohr) to yield a pale yellow liquid.

Compound	R	b.p.°C/mmHg	Yield %
23a	$-C_3H_7$	96-98/0.25	94
23b	$-C_4H_9$	100-105/0.4	90
23c	-C ₅ H ₁₁	104-105/0.3	95

These three products showed the expected spectroscopic values and typical results are given for compound (23b) : m/z 165 (M⁺) ; v_{max} (thin film) 3472, 3375 (NH primary amine), 3057, 3032 (CH aromatic), 2957, 2871 (CH alkane), 1614, 1459 (C=C aromatic), 1507 (NH bend), 1342 (C-N), 1275, 1219, 1143, 1041 (CO ether), 737 (CH bend) cm⁻¹ ; $\delta_{\rm H}$ (CDCl3) 6.84 (2H, m, ArH), 6.77 (2H, t, ArH), 4.04 (2H, t, CH₂O), 3.86 (2H, s, ArNH₂ removed on D₂O exchange), 1.86 (2H, quintet, OCH₂CH₂), 1.58 (2H, sextet, CH₂-CH₃), 1.06 (3H, t, CH₃) ;¹³C (CDCl₃) 147 (C=C-O), 136, 121, 118, 115, 111 (C=C aromatic), 68 (OCH₂), 32 (CH₂), 19 (CH₂-CH₃), 14 (CH₃).

Products	Т	Pressure	Time	Solvent	Mass/g
	(°C)	(Bar)	(h)	(Vol/cm ³)	Yield
23a	20	11	3	Ethanol	7.48
				50	94 %
23b	20	11	2	Ethanol	7.58
				50	90 %
23c	20	10	15	Ethanol	2.85
				40	95 %
24d	100	25	2	Ethanol	0.67
				110	90 %
24e	95	20	3	Ethanol	1.15
				120	80 %
25	95	15	2	Ethanol	0.30
				60	98 %
26	70	11	4	Ethanol	1.60
				150	81 %
27	85	20	5	Ethanol	1.40
				150	96 %
28	40	15	5	DMF	0.85
				80	89 %
29	40	15	week	DMF	0.19
				70	58 %
30 *	80	11	5	Ethanol	0.83
				150	84 %
31	50	15	5	DMF	0.82
				150	87 %

 Table II.4 : Hydrogenation Conditions for each Compound

The compounds (24d), (24e) & (25) were purified by recrystallisation from methylated spirit, whereas compounds (26) - (31) were purified by column chromatography and recrystallised or washed with hot methylated spirits (IMS) and immediately polymerised.

Compound	Column Chromatography	IMS
26	Toluene:ethyl acetate (3:1)	Recrystallised
27	Chloroform	Washed
28	Chloroform:ethyl acetate (9:1)	Washed
29	Chloroform:ethyl acetate (9:1)	Washed
30	Chloroform	Washed
31	Chloroform	Washed

After spectroscopic analysis, all the desired aniline products were formed except for compound (30^*) , where in addition, the cyano group had been reduced to a methyl group (and not a primary amine as might have been expected in the case of reduction of the cyano group). This was shown by the following spectroscopic data.

Compound (30*) ; m/z 495 (M⁺) ($C_{32}O_4NH_{33}$) ; v_{max} (KBr) 3468, 3380 (NH primary amine), 3070, 3056 (CH aromatic), 2929, 2860 (CH alkane), 1724 (C=O ester), 1601, 1503 (C=C aromatic), 1253, 1223, 1169, 1066, 993 (CO ether), 796, 728 (CH bend) cm⁻¹. δ_{H} (**CDCl**₃) 8.16 (2H, d, ArH), 7.61 (2H, d, ArH), 7.50 (2H, d, ArH), 7.27 (4H, d, ArH), 6.98 (2H, d, ArH), 6.81-6.70 (4H, m, ArH), 4.07 (2H, t, OCH₂), 4.03 (2H, t, OCH₂), 3.80 (2H, s, ArNH₂ removed on D₂O exchange), 2.41 (3H, s, CH₃), 1.88 (4H, m, CH₂), 1.58 (4H, m, CH₂).

Spectral results : Aniline Compounds

M.S. : All compounds show correct M⁺

I.R. : All compounds show the same bands as their respective nitro compounds excepted the following two bands : vasy(N-O) ArNO₂

 $v_{sym}(N-O)$ ArNO₂ which disappear to give place to ds : 3460 cm⁻¹ vasy N-H ArNH₂

the following two bands : 340

3370 cm⁻¹ vsym N-H ArNH₂

N.M.R.: ¹H All compounds showed similar results as their respective nitro compounds except for the addition of a new peak corresponding to : 4.63 ppm

(2H, s, NH_2 removed upon D_2O exchange), but this peak was not always observed.

The melting point, mesomorphic transition temperatures and other data for the aniline compounds (24) - (31) are presented in the Results and Discussion chapter, pages 161-163.

The purity of the aniline monomers was assessed by HPLC and all the values were equal or above 99.5%.

II.4 : MECHANISMS OF THE SYNTHETIC ROUTES

II.4.1. Preparation of Ethers : Williamson Synthesis

The formation of alkoxynitrobenzenes (Schemes 1, 2, 3 and 7) involves the reaction of a nitro-phenol with alkyl halides. In fact, the Williamson reaction, discovered in 1850, is still the best general method for the preparation of unsymmetrical or symmetrical ethers²⁹¹. It involves nucleophilic substitution of alkoxide ion or phenoxide ion for halide ion. In our case, the reaction involved is shown in Figure II.8 for the formation of compounds (1), (2), (3), (6), (7), (8) and (15). When using dibromo-alkanes a large excess of alkyl halide relative to the substituted-phenol is required in order to give a high yield of the desired monosubstituted product.



Figure II.8 : Williamson Reaction

II.4.2. Alkaline Hydrolysis of Esters

The carboxylic acid (Compound 4) in Scheme 2 is prepared by Alkaline hydrolysis of the ester (Compound 3). Ester hydrolysis is usually catalysed by acids or bases. When bases catalyse the reaction, the attacking species is the more powerful Nucleophile OH. This reaction is called *saponification* and gives the salt of the acid. Acids catalyse the reaction by making the carbonyl carbon more positive and therefore more susceptible to attack by the nucleophile. Both reactions are equilibrium reactions, so that they are practicable only when there is a way of shifting the equilibrium to the right in favour of the salt of the acid. Since formation of the salts does just this, ester hydrolysis is almost always done for preparative purposes in basic solution, unless the compound is basesensitive.

The base promotes hydrolysis of esters by providing the strong nucleophilic reagent OH⁻, and this reaction is essentially irreversible since a resonance-stabilised carboxylate anion shows little tendency to react with an alcohol as shown in one of the possible and most common mechanism²⁹² ($B_{AC}2$)[§] pictured in Figure II.9.



Figure II.9 : Ester Hydrolysis, Mechanism $B_{AC}2$

II.4.3. Esterification of Acids

The esterification of acids with alcohols is the inverse of the hydrolysis (Fig. II.10) and can be accomplished only if a means is available to drive the equilibrium to the right.

 H^+ R-COOH + R'-OH \rightarrow R-COOR' + H₂O

Figure II.10 : Esterification-Hydrolysis Equilibrium

There are many ways of doing this, among which are :

- (i) addition of an excess of one of the reactants, usually the alcohol
- (ii) removal of the ester or the water by distillation
- (iii) removal of water by azeotropic distillation

⁸ B_{AC}2: Most common mechanism for basic catalysis of hydrolysis of an ester involving a tetrahedral mechanism and an acyloxygen cleavage.

Also the most common catalysts are H_2SO_4 and TsOH (*p*-Toluene sulfonic acid).

In our case, R and R' are aromatic groups and therefore give sterically hindered acids and alcohols. So, the ester compounds (5), (10), (11) and (12) have been prepared by using trifluoroacetic anhydride (TFAA). Indeed, Parish et al.²⁹³ have studied the esterification of hindered aliphatic and aromatic carboxylic acids in the presence of TFAA and found yield as high as 97%. A mechanism (Fig. II.11) has been postulated in order to explain such good yields, it was found that solutions of acids in TFAA involve several equilibria²⁹⁴, but the major component in solution is the unsymmetrical anhydride^{295,296}. Acylation is generally ascribed to the oxo-carbonium ion formed by the acid-catalysed ionisation of the anhydride²⁹⁷.



Figure II.11 : Esterification Mechanism with TFAA

The slight dissociation to give acylium and trifluoroacetate ions enables these ions to be largely responsible for acylation, reacting with many compounds much more readily than the molecular anhydride is able to do. Excess of trifluoroacetic anhydride acts as a dehydrating agent and ensures a dry reaction solvent.

The use of TFAA resulted in high yields of most of the ester series, for example the ester

series 4-Methoxyphenyl 4-[x-(2-nitrophenoxy)alkoxy]benzoates (Compounds 5a to 5i) was synthesised with an average yield of 89%. 4'-Cyanobiphenyl-4-[6-(2-nitrophenoxy) hexoxy]phenyl-4-carboxylate (12) have been prepared with 93% yield. 4-Cyanophenyl 4-[4{6-(2-nitrophenoxy)hexoxy}phenyl]benzoate (10) was also synthesised with a relatively high yield of 69% for an esterification. But the massive acid molecule did slow the reaction and removal of some water by azeotropic distillation was necessary. In the case of 4-Methoxyphenyl 4-[4-{6-(2-nitrophenoxy)hexoxy}phenyl]benzoate (11), the azeotropic distillation was not used drastically lowering the yield to 34%.

II.4.4. Hydrolysis of Nitriles

Nitriles can be hydrolysed to give either amides or carboxylic acids²⁹⁸. The amide is initially formed, but since amides are also hydrolysed with acid or base, the carboxylic acid is the more common product. When the acid is desired, acid-catalysed hydrolysis is possible, and hydrolysis of nitriles to carboxylic acids is one of the best methods for the preparation of these compounds.

Compound 4-cyano 4'-[6-(2-nitrophenoxy)hexoxy]biphenyl (7b) was therefore succesfully acid-catalysed hydrolysed to form 4-Biphenyl 4'-[6-(2-nitrophenoxy)hexoxy]carboxylic acid (9) with 97% yield by the mechanism described in Figure II.12.



Figure II.12 : Hydrolysis of a Nitrile to form a Carboxylic Acid

II.4.5. Synthesis of Boronic Acids

4-Ethoxyphenylboronic acid (13) and 4-Biphenyl 4'-(benzyl-oxy)boronic acid (16) were prepared by forming the appropriate aryl-lithium which is then subsequently reacted

with tri-isopropyl borate. Hydrolysis of the borate ester with dilute hydrochloric acid produced the desired boronic acid. Alternatively, boronic acids can be made via Grignard reagent, but in this case the Grignard reagent was difficult to form. Therefore, the metalhalogen exchange method was then adopted.

The exchange reaction between halides and organometallic compounds (Fig. II.13) is almost entirely limited to the cases where X is bromide or iodide²⁹⁹ and with the following reactivity R-I > R-Br.

Ar-X + R-Li = Ar-Li + R-X

Figure II.13 : Metal-Halogen Exchange Reaction

The equilibrium lies towards the side giving the organolithium compound whose organic group is better able to accommodate partial carbanionic character; it is thus particularly useful for preparing aryl- and 1-alkenyllithium. With iodo- and bromo-compounds the reaction is general, and often proceeds remarkably rapidly even at low temperature.

Once the Aryl-lithium formed, it is reacted with tri-isopropyl borate. This reaction is straight forward³⁰⁰ and hydrolysis of the ester with dilute hydrochloric acid produced the desired boronic acid (Fig. II.14).



Figure II.14 : Boronic Acid Synthesis

The boronic acid formed exists as a mixture, dependent on condition of isolation, of the monomer, dimer and trimer with the monomer in the highest concentration. This was characterised for compound 4-ethoxyphenylboronic acid (13) by Mass Spectrometry (Fig. II.15) and TLC (one big spot with two small ones very close).



Figure II.15 : Monomer, Dimer and Trimer of the Boronic Acid

II.4.6. Cross-Coupling between Aryl Boronic acids and Aryl Bromides

Terphenyl compounds (14) and (17) can be formed by coupling reaction between aryl boronic acids and aryl halides in the presence of a catalyst tetrakis(triphenylphosphine) palladium $(0)^{301}$. This catalytic reaction was first reported by Miyaura et al.³⁰² and called the Suzuki reaction. This heterogenous coupling reaction (toluene/sodium carbonate (aq)/Pd(PPh₃)₄) enabled the preparation of unsymmetrical biaryl or multi-aryl systems. A proposed mechanism^{303,304} for the coupling of an aryl halide (Br, I) with an aryl boronic acid is shown in Figure II.16.

The first step in the coupling procedure would involve the addition of the aryl halide, the palladium (0) is oxidised to palladium (II), as two ligands are lost (Oxidative Addition). The next step is a transmetallation step which involves loss of the halide atom and addition of the aromatic species of the boronic acid. The final step involves the liberation of the coupled product and the regeneration of the catalyst, with reduction of the palladium to the (0) oxidation state (Reductive Elimination).



Figure II.16 : Possible Mechanism for Palladium Coupling[§]

II.4.7. Hydrogenation

II.4.7.1. Nitro-compounds

Both aliphatic and aromatic nitro compounds can be reduced to amines in good yield. Many reducing agents have been used to reduce aromatic nitro compounds, among them Zn, Sn or Fe and acid, catalytic hydrogenation, AlH₃-AlCl₃, TiCl₃, formic acid and Pd-C, and sulfides³⁰⁵. In general aromatic nitro compounds can be easily reduced at room temperature and under slight hydrogen pressure with rhodium, palladium or platinum on carriers, with palladium or platinum oxide, or with Raney nickel to give high yields of amines.

The aromatic nitro group, which is reduced more rapidly than any of the intermediates or side products (azo, azoxy, hydrazo compounds), goes directly to the amine (see Figure II.17)³⁰⁶.

 $ArNO_2 \longrightarrow ArNO \longrightarrow ArNHOH \longrightarrow ArNH_2$

Figure II.17 : Reduction of an Aromatic Nitro Compound to an Aniline

b : base

ş

This is probably due to the exothermicity of the reaction which supplies enough energy to aid rapid reduction of the intermediates to the amine. This reaction proceeds best in neutral solution and takes place more slowly in acidic or basic media³⁰⁷. Generally alcohols are the best solvents, and for safety reasons ethyl alcohol is preferred over the more volatile methyl alcohol. Ethylene glycol monoethyl ether and dimethylformamide are especially useful for nitro compounds that are poorly soluble in alcohol³⁰⁸. Palladium, nickel and platinum have been reported to give good results but Pd is extremely useful for the low pressure hydrogenation of many functional groups³⁰⁹ and was our choice for the hydrogenation.

II.4.7.2. Debenzylation

Benzyl ethers C_6H_5 - CH_2 -O-R are very readily cleaved to the corresponding alcohol by catalytic reduction in neutral or acidic solution. Based on rapidity of reaction and high yields of products of reduction the use of palladium on carbon gives the best results³¹⁰.

II.4.7.3. Nitrile groups

During our hydrogenation reactions to reduce nitro groups or debenzylation, we have been faced with the possible reduction of the nitrile groups. In fact, hydrogenation of most nitriles to primary amines is readily carried out. One of the low pressure methods of converting nitriles to primary amine is that of Hartung³¹¹, in which hydrogenation with palladium on carbon is carried out in absolute ethanol containing three equivalents of hydrogen chloride. Generally yields are very good ; at times, however, a large amount of catalyst must be used and/or more vigorous conditions may be necessary³¹². It was therefore necessary to carry out a selective reduction of the aromatic nitro or benzyl group in the presence of a cyano group.

In the case of compounds 4-cyano 4'-[6-(2-nitrophenoxy)hexoxy]biphenyl (7b) and (4cyanophenyl-4'-[6-(2-nitrophenoxy)hexoxy]biphenyl-4-carboxylate (10), the nitrile group was not affected during the reduction of the nitro group. Whereas in the case of compound 4'-cyanobiphenyl-4-[6-(2-nitrophenoxy)hexoxy]phenyl-4-carboxylate (12), the nitrile group was reduced to a methyl group (as shown by spectroscopic data) every time.

This might be explained by the fact that between the first two reactions and that of the compound (12), the equipment had been used with Raney nickel which might have contributed to the activation of the catalyst. Also it was unusual to obtain a methyl group instead of a primary amine but all the spectroscopic data confirmed this fact.

II.5 : SYNTHESES OF POLYMERS

The aniline-based monomers were electropolymerised and polymerised by oxidative chemical polymerisation using three different methods :

- Normal conditions : Acid medium (type 1)
- Addition of an organic acid (type 2)
- Concentrated sulfuric acid (type 3)
- Addition of a surfactant and use of organic solvents : Emulsion polymerisation (type 4)



$$R = -C_n H_{2n+1} \text{ where } n = 1 - 5 \text{ (see Table II.5)}$$

A = Complex structure with x = 5, 6 (see Table II.5)

	D		<u> </u>	Polymerisation
Compound	-K	x	-A	type [§]
100	CII			E.C.
100	-CH ₃			Chemical
				E.C.
101	-C ₂ H ₅			Chemical
	C II			E.C.
102	-C ₃ H ₇			Chemical
	GU			E.C.
103	-C ₄ H ₉			Chemical
104	-C ₅ H ₁₁			Chemical
105		5		Chemical
106		6	—————————————————————————————————————	E.C. Chemical
107		6		Chemical
108		6		E.C. Chemical

[§] Notes : E.C. -Electrochemical

109	6	Соон	Chemical
110	6		Chemical
111	6	{	Chemical
112	6	{O}{O}0C ₂ H ₅	Chemical

Table II.5 : Different types of polymers synthesised

II.5.1. Electropolymerisation

Electrochemical polymerisation was studied by cyclic voltammetry which is used to characterise and study the anodic reactions of the polymer whether a film is grown or not. It involves a three-electrode system : a working electrode which was indium-tin-oxide glass or platinum, a counter electrode which was platinum or silver and the reference electrode which was silver/silver chloride. Cyclic voltammetry consists of cycling the potential of the working electrode immersed in a solution containing the electroactive species and a background electrolyte, and recording the current as a function of potential. The potential of the working electrode is controlled against the reference electrode by a potentiostat. The solutions were studied under static conditions.

2-Methoxyaniline, 2-ethoxyaniline, 2-propoxyaniline and 2-butoxyaniline were electropolymerised. For cyclic growth approximately 0.2M monomer solutions were used, with 1M HCl as solvent. Indium-tin-oxide glass (ITO) was used as the working electrode, with a silver wire as the counter electrode. For each monomer, the potential was cycled repeatedly between predetermined switching potentials at a scan rate of 50 mV s⁻¹. Details of the conditions for each monomer are given in Table II.6.

Monomer	Polymer	Scan rate (mV s ⁻¹)	Potential range (mV)	Mass / g (Concentration)	Volume 1M HCl (cm ³)
1	100	50	-200-+800	0.95 (0.26)	30
1	101	50	-200-+800	0.80 (0.20)	30
23a	102	50	-100-+800	0.4 (0.18)	15
23b	103	50	-200-+800	0.4 (0.16)	15

Table II.6 : Electropolymerisation Conditions for Polymer (100)-(103)

Notes : Concentration in mol cm⁻³

The cyclic voltammograms, anodic and cathodic potential peaks for polymers (100)-(103) will be investigated in the Results and Discussion chapter pages 164-170.

It was attempted to electropolymerise 2-methoxyaniline using concentrated H_2SO_4 as a solvent (with platinum electrodes) in order to develop this method for potential use with our liquid crystalline monomers. But even though an oxidation peak was sometimes observed at 550 mV with its reduction peak at 350 mV, film growth was not achieved. This method was therefore abandoned.

Electropolymerisation of our liquid crystalline monomers was investigated, but due to their low solubility in aqueous media, it was not possible to use 1M HCl or similar aqueous solvents. The monomer (26) was found to be slightly soluble in a mixture of 1M HCl and butanoic acid; therefore this was used as electrolyte. The same monomer (26) and also monomer (24e) were each dissolved in a mixture of propylene carbonate, 1M HCl and

1M dodecylbenzenesulfonic acid (DBSA). Propylene carbonate was even substituted for chloroform in the case of monomer (24e). Details of the conditions for electropolymerisation of 2-[4-cyano 4'(hexoxy-6-oxy)biphenyl]aniline (26) and 2[4-methoxyphenyl 4-hexoxy(6-oxy)benzoate]aniline (24e) are given in Table II.7. ITO was the working electrode and platinum wire was used as the counter electrode.

Monomer	Mass (g) Conc. (mol.cm ⁻³)	Solvents (cm ³)	Scan rate (mV s ⁻¹)	Potential range (mV)
26	0.05 [0.016]	1M HCl (4) butanoic acid (4)	10	-200 +1000
26	0.04 [0.012]	propylene carbonate (3) 1M HCl (3) 1M DBSA (3)	10	-200 +1300
24e	0.10 [0.015]	propylene carbonate (5) 1M HCl (5) 1M DBSA (5)	10	-200 +1200
24e	0.11 [0.017]	CHCl3 (5) 1M HCl (5) 1M DBSA (5)	8	0 - +900

Table II.7 : Electropolymerisation conditions for monomers (26) and (24e)

In the cases of the side-chain liquid crystalline monomers (26) and (24e), the first cycles of the cyclovoltammograms showed an increase of the oxido-reduction peaks, leading to the expectation of film formation on the electrode, but no film was ever obtained. In fact, after the peaks had increased during the first cycles, they began to decrease later, indicating the formation of oligomers only.

The cyclic voltammograms will be further investigated in the Results and Discussion chapter, pages 164-170.

II.5.2. Chemical Polymerisation

II.5.2.1. NORMAL CONDITIONS : Polymerisation of 2-Alkoxyanilines

The appropriate 2-alkoxyaniline (35 mmol) was dissolved in 1M hydrochloric acid (100 cm³) in a beaker placed in a ice bowl on a magnetic stirrer. A few mg of iron (II) chloride tetrahydrate were added. Then, a solution of ammonium persulfate (8.7 g, 38 mmol) in 1M HCl (60 cm³) was added dropwise to the monomer solution down a glass rod at temperatures ranging 0-5°C with constant stirring during 3 hours. The solution was stirred at 5-10°C for one day. The black precipitate obtained was filtered off and washed with 1M HCl followed by diethyl ether to yield a black solid poly(2-alkoxyaniline) which was dried in a vacuum oven.

Alkoxy-	Mass (g)	Yield %	Compound
-OCH ₃	4.39	90	(100)
-OC ₂ H ₅	4.88	91	(101)
-OC ₃ H ₇	4.86	83	(102)
-OC₄H9	5.97	94	(103)
-OC ₅ H ₁₁	3.69	54	(104)

The polymers obtained were in their protonated (doped) form. Thus in order to calculate the % yield it was necessary to take into account that each repeat unit has half an HCl molecule. Therefore, the molar mass of the repeat unit will be equal to :

MM polymer = MM monomer -
$$2H(2.016) + \frac{1}{2}HCl(18.254)$$

Deprotonation of the polymers was achieved by addition of 70 cm^3 of 50:50 ammonia:water to 3g of the previously synthesised polymer, and stirred for 5 days at room temperature. The precipitate was filtered off to yield a black solid.

The IR spectral assignments of poly(2-alkoxyanilines) are given in Table II.8.

Compound	υ _{N-H}	δ _{C-H}	U _{C=N}	υ _{C=C}	U _{C-N} U _{C-O-C}	δ _{с-н}
100	1	1	1583	1493	1294, 1256, 1206, 1122, 1011	822 745
100 undoped	3386	2950, 2922, 2833	1577	1509	1259, 1213, 1171, 1121, 1028	849 751
101	1	2978, 2933	1572	1489	1293, 1197, 1024	811
101 undoped	3364	2974, 2929	1590	1506	1256, 1189, 1120, 1033	853 807
102	1	2967, 2935, 2870	1577	1500	1254, 1190, 1121, 997	814 745
102 undoped	3347	2961, 2931, 2873	1579	1508	1254, 1212, 1117, 1000	808 747
103	1	2956, 2930, 2881	1578	1497	1298, 1250, 1201, 1123, 999	833 749
103 undoped	3420	2956, 2931, 2869	1578	1508	1249, 1195, 1115	836 741
104	1	2926, 2855	1578	1498	1289, 1256, 1200, 1122, 1000	817 744
104 undoped	3411	2927, 2857	1584	1508	1250, 1190, 1113, 1043	815 742

Table II.8 : IR Absorptions of Poly(2-alkoxyanilines) (Wavenumbers in cm⁻¹)

The two main bands characteristic of polyaniline in its emeraldine form have been assigned by Tang et al.³¹³ as follows :

 $\upsilon_{C=N}$ from the iminoquinoid phenyl rings at about 1600 cm^{-1}

 $\upsilon_{C=C}$ from the benzenoid phenyl rings at about 1500 cm⁻¹

The benzenoid / quinoid area ratio is characteristic of the degree of oxidation of the polymer and in our case was equal to :

Alkoxy-	B/Q
Methoxy	1.60
Ethoxy	1.52
Propoxy	1.58
Butoxy	1.46
Pentoxy	1.55

The emeraldine form of PANI which is the most conducting (see pages 48-52) should have an ideal benzenoid / quinoid ratio equal to 3/2 = 1.5. The experimental errors obtained in the case of our poly(2-alkoxyaniline) are due to the difficulty to measure the area of the peaks.

It is assumed that the doped and undoped (protonated or deprotonated) forms of substituted polyanilines can be distinguished by the long absorption tail between 1650 and 4000 cm⁻¹. In fact, when the polymer is protonated and therefore conducting, this tail is characteristic of the absorption between the valence band and the lowest non-bonding level of the bipolaron structure (see page 38). Therefore, as expected for protonated polyaniline this absorption tail is higher in intensity, characteristic of the bigger electron delocalisation and presumably higher conductivity values.

In the doped state, the peaks between 1300-1110 cm⁻¹ are broader than the undoped ones. All these features can be observed in typical spectra of doped and undoped poly(2-butoxyaniline) given in Figures II.17 and II.18.



Figure II.17 : IR Spectra of Doped Poly(2-butoxyaniline)



Figure II.18 : IR Spectra of Undoped Poly(2-butoxyaniline)

The N.M.R. data for each polymer are given below :

 $\begin{array}{l} \underline{\text{Compound (100) :}} \\ \delta_{\text{H}} (\text{CDCI}_{3}) \ 7.2\text{-}6.5 \ (\text{m, ArH}), \ 3.85 \ (\text{s, OCH}_{3}). \\ \underline{\text{Compound (101) :}} \\ \delta_{\text{H}} \ (\text{CDCI}_{3}) \ 7.2\text{-}6.5 \ (\text{m, ArH}), \ 3.72 \ (2\text{H, q, OCH}_{2}), \ 1.24 \ (3\text{H, t, CH}_{3}). \\ \underline{\text{Compound (102)}} \\ \delta_{\text{H}} \ (\text{CDCI}_{3}) \ 7.45\text{-}6.8 \ (\text{m, ArH}), \ 3.98 \ (\text{m, OCH}_{2}), \ 1.74 \ (2\text{H, m, CH}_{2}), \ 1.01 \ (3\text{H, m, CH}_{3}). \\ \underline{\text{Compound (103)}} \\ \delta_{\text{H}} \ (\text{CDCI}_{3}) \ 7.45\text{-}6.75 \ (\text{m, ArH}), \ 4.02 \ (\text{m, OCH}_{2}), \ 1.85 \ (\text{m, CH}_{2}), \ 1.53 \ (\text{m, CH}_{2}), \ 1.00 \ (\text{m, CH}_{3}). \\ \underline{\text{Compound (104)}} \end{array}$

 $\delta_{\rm H}$ (CDCl₃) 7.45-6.8 (m, ArH), 3.87 (m, OCH₂), 1.70 (m, CH₂), 1.32 (m, 2xCH₂), 0.85 (m, CH₃).

All the NMR spectra obtained were difficult to assess due to the low solubility of the polymers, unlike the data for the monomers the base line was very noisy and it was impossible to take into account the integrals. This is often observed in polymer NMR spectroscopy. In all the case, there was no evidence of N-H group. The doped and undoped NMR spectra were similar.

The melting points, glass transition temperatures, thermal analysis, conductivity measurements, UV-visible spectra, solubility tests and molecular weight distributions are presented in the Results chapter.

II.5.2.2. ADDITION OF AN ORGANIC ACID

The aniline monomers (25) and (26) (1.5 mmol) were dissolved in 40 cm³ of 1M HCl : butanoic acid (1:1) in a beaker placed in a ice bowl on a magnetic stirrer. A few mg of ferrous chloride tetrahydrate were added. Then, a solution of ammonium persulfate (0.37 g, 1.65 mmol) in 20 cm³ of 1M HCl : butanoic acid (1:1) was added dropwise to the monomer solution down a glass rod at 0°C with constant stirring. The solution was left stirring at a temperature of 5-10°C for 3 days. The black precipitate obtained was filtered off and washed with 1M HCl, followed by diethyl ether to yield a black solid which was

dried in a vacuum oven. The polymers obtained were in their doped (protonated) form.

Polymer	Yield %
(107)	89 (0.50 g)
(108)	61 (0.37 g)

Spectral results :

Compound (107) : v_{max} (KBr) 3442 (NH secondary amine), 3030 (CH aromatic), 2934, 2855 (CH alkane), 2554 (NH, Amine salt), 1608 (C=N), 1520, 1499 (C=C aromatic), 1291, 1266 (C-N), 1248, 1188, 1003 (CO ether), 833, 764, 752, 698 (CH bend) cm⁻¹. The benzenoid / quinoid ratio (bands 1499/1608) was equal to 1.48. **N.M.R. :** no sign of -NH group.

Compound (108) : Doped : v_{max} (KBr) 3037 (CH aromatic), 2938, 2861 (CH alkane), 2223 (C=N), 1602, 1581 (C=N), 1523, 1495 (C=C aromatic), 1289, 1248 (C-N), 1178, 1115, 999 (CO ether), 822, 749 (CH bend) cm⁻¹. The benzenoid / quinoid ratio (bands 1495/1602) was equal to 1.15. **Undoped :** v_{max} (KBr) 3423 (NH secondary amine), 3037 (CH aromatic), 2938, 2861 (CH alkane), 2223 (C=N), 1603, 1582 (C=N), 1523, 1495 (C=C aromatic), 1290, 1248 (C-N), 1178, 1114, 999 (CO ether), 822, 745 (CH bend) cm⁻¹. $\delta_{\rm H}$ (CDCl₃) 7.79 (3H, s, ArH), 7.61 (3H, m, ArH), 7.35 (1H, m, ArH), 7.11 (4H, m, ArH), 4.16 (4H, m, OCH₂), 2.00 (4H, m, CH₂), 1.70 (4H, m, CH₂), no evidence of N-H group.

The typical infra-red spectra of doped and undoped poly{2-[4-cyano 4'-(hexoxy-6-oxy)biphenyl]aniline} (108) are illustrated in Figures II.19 and II.20.

The same technique was used for monomer (24e) but no polymer was obtained.

The melting points, glass transition temperatures, thermal analysis, conductivity measurements, UV-visible spectra, solubility tests and molecular weight distributions are presented in the Results and Discussion chapter.



Figure II.19 : IR spectra of doped polymer (108)



Figure II.20 : IR spectra of undoped polymer (108)

II.5.2.3. CONCENTRATED SULPHURIC ACID

Attempts were made to polymerise 2-methoxyaniline and some of the mesogenic side chain monomers in a medium of pure (98%) concentrated sulfuric acid. The polymerisations were followed by UV/visible spectroscopy.

2-Methoxyaniline was polymerised by using the procedure described in Chapter 1, pages 54-55, using 2-methoxyaniline (1 g, 8 mmol), concentrated H_2SO_4 (20 cm³) and ammonium persulfate (2 g, 8.8 mmol) in conc. H_2SO_4 (10 cm³). Immediately, the solution became dark blue. It was then left sealed under constant stirring at a temperature ranging from 5-10 °C for 4 days.

UV/ visible spectra of the solution in DMF as illustrated in Fig. II.21 revealed two absorption bands at 323 and 632 nm. The optical band at 323 nm was associated with the π - π * transition of the polymer backbone benzenoid rings. This band can vary a lot depending on the conjugation length of the polymer formed. The second band at 632 nm is usually ascribed to an exciton, located in the quinoid ring arising from charge transfer from the adjacent benzenoid rings, with each side contributing half an electron on average,

+½ -1 +½ -B-NH-B-N=Q=N-B-NH-

i.e.



Figure II.21 : UV/visible Spectra of Polymerisation of 2-Methoxyaniline in conc. H_2SO_4

130
Therefore, we concluded that a highly conjugated polymer was formed and the solution was poured on ice (100 cm³) but no polymers were ever precipitated. The solution was neutralised, in an attempt to precipitate the polymer in IMS but it proved impossible to recover any polymers. Our conclusion was that the polymer formed was probably hydrolysed when the concentrated sulphuric acid was poured on ice, or possibly that some water was absorbed by the acid during the experiment, again leading to hydrolysis.

Polymerisation with concentrated sulphuric acid as solvent was also investigated with the side chain monomers (26), (27), (28) and (31).

In the case of the monomer 4-cyano 4'-[6-(2-aniline-oxy)hexoxy]biphenyl (26), a dark green solution was formed ; whereas for 4-biphenyl 4'-[6-(2-aniline-oxy)hexoxy] carboxylic acid (27) a dark brown solution was formed, and for 4-cyanophenyl 4'-[6-(2-aniline-oxy)hexoxy]biphenyl-4-carboxylate (28) a black-green solution was formed. In all these case, the absorption bands were around 320 nm for the first peak and 400-450 nm for the second peak. After deactivation of the concentrated acid, almost no polymers were formed and when a tiny portion of polymer was recover the IR spectra revealed inconsistent absorptions with the expected polymers. For example, the cyano band disappeared, the C=O stretching ester peak was no longer visible, and many other peaks were inexplicable.

The monomer 4"-methoxy-4-[6-(2-aniline-oxy)hexoxy]terphenyl (31) was more extensively studied as its structure did not possess any sensitive functional group which could be hydrolysed in conc. H_2SO_4 (unlike the ester or the cyano groups in the previous monomers). The reaction was followed by UV/visible spectroscopic analysis.

At time equal to 0 (monomer in conc. H_2SO_4), 2 strong absorption bands at 253 and 306 nm were revealed as well as 2 small absorption bands at 396 and 814 nm. The solution was slightly green coloured. The monomer is therefore oxidised by the concentrated acid and oxygen of the air without addition of any oxidant.

The persulphate oxidant was then added and the observations shown in Table II.9 were made. The first peak at 205 nm was associated with 100% in intensity and the other peaks intensity were calculated with respect to this peak. After 5 days, as the intensity of the peaks above 300 nm seemed to decrease more oxidant (1 equi.) was added.

Time	λ max	λmax	λmax	λmax	λmax	λ max
	205 nm	280 nm	447 nm	482 nm	673 nm	806 nm
30 mn	100 %	46 %	17 %	14 %	42 %	14 %
1 h	100 %	51	18	15	44	16
2 h	100 %	43	21	17	43	15
3 h	100 %	23	23	17	35	12
19 h	100 %	42	39	32	60	23
24 h	100 %	46	35	29	59	20
43 h	100 %	75	38	30	73	25
5 days	100 %	89	24	19	43	19
6 days	100 %	87	40	33	52	19
7 days	100 %	80	41	36	63	1
13 days	100 %	63	15	13	20	8
26 days	100 %	88	15	14	1	1

Table II.9 : UV/Visible Analysis of Polymerisation of Monomer (31) in Conc. H_2SO_4



Figure II.22 : UV/ Visible Spectra of Polymerisation of (31) in conc. H₂SO₄ after 2 days



Figure II.23 : UV/Visible Spectra of Polymerisation of (31) in conc. H_2SO_4 after 26 days

The maximum intensity of the peaks at 447, 482 and 673 nm were reached after 2 days, and then started to decrease. Addition of more oxidant after 5 days allowed increase of these absorption bands at first ; then a massive decrease occurred after a few days. The UV/visible spectra indicated the formation of coloured products during the first week then as the sulphuric acid became slightly wet, hydrolysis of the conjugated species occurred. This highly coloured appearance could also have been due to formation of azo-groups by polymerisation head-to-head but it was impossible to support any theory as no polymers could be isolated.

Therefore, even if head-to-tail conjugated materials were formed, in all the case it was impossible to isolate some real polymer for intensive study, this method was then abandoned.

II.5.2.4. EMULSION POLYMERISATION

The monomers (24d), (24e), (26), (27), (28), (30*) and (31) were dissolved in the appropriate solvent (chloroform or acetone). The solution was emulsified with an equal volume of a mixture of 10% aqueous surfactant (dodecylbenzenesulfonic acid 1M) and 90% HCl (1M). A few mg of iron (II) chloride tetrahydrate were added, and the resulting mixture was cooled to 0°C and stirred during the addition along a glass rod of a solution of ammonium persulfate (1 equiv.) in 5-10 cm³ of 1M HCl. This was stirred continuously for at least 24 h after the appearance of a dark precipitate of polymer. This mixture was then poured into a large amount of water (200 cm³) to deactivate the surfactant. The precipitate was filtered off and washed with 1M HCl to yield a black solid which was dried in a vacuum oven.

Details of the conditions of polymerisation for each monomer are given in Table II.10.

Monomer	Polymer	Solvent (Vol/cm ³)	Time (day)	Mass/g Yield (%)
24d	105	CHCl ₃ (20)	2	0.10 (60)
24e	106	CHCl ₃ (20)	2	0.80 (98)
26	108	CHCl ₃ (20)	1	0.60 (98)
07	100	Acetone (60)	2	0.93 (98)
21	109	CHCl ₃ (15)	5	0.31 (72)
28	110	CHCl ₃ (15)	5	0.39 (75)
30*	111	CHCl ₃ (20)	5	0.44 (98)
31	112	CHCl ₃ (20)	5	0.20 (68)

Table II.10 : Emulsion Polymerisation Conditions for each Monomer

The melting points, glass transition temperatures, thermal analysis, conductivity measurements, UV-visible spectra, solubility tests and molecular weight distributions are presented in the Results chapter.

Polymer (105) : υ_{max} (**KBr**) 2951, 2891 (CH alkane), 1730 (C=O ester), 1606 (C=N), 1510 (C=C aromatic), 1249 (C-N), 1196, 1165, 1071, 1032, 1006 (CO ether), 870, 845, 764 (CH bend) cm⁻¹.

Polymer (106) : υ_{max} (**KBr**) 3430 (NH secondary amine), 2934, 2874 (CH alkane), 1734 (C=O ester), 1606 (C=N), 1510 (C=C aromatic), 1253 (C-N), 1196, 1166, 1071, 1006 (CO ether), 845, 764, 747 (CH bend) cm⁻¹.

Polymer (108) : υ_{max} (**KBr**) 3038 (CH aromatic), 2928, 2856 (CH alkane), 2225 (C=N), 1603 (C=N), 1495 (C=C aromatic), 1291, 1250 (C-N), 1180, 1125, 1034, 1009 (CO ether), 823, 752 (CH bend) cm⁻¹.

Polymer (109) : υ_{max} (**KBr**) 3448 (NH secondary amine), 3048 (CH aromatic), 2938, 2864 (CH alkane), 2667, 2545 (OH acid), 1685 (C=O acid), 1604 (C=N), 1526, 1498 (C=C aromatic), 1250 (C-N), 1187, 1116, 1000 (CO ether), 829, 775 (CH bend) cm⁻¹.

Polymer (110) : υ_{max} (**KBr**) 3024 (CH aromatic), 2931, 2854 (CH alkane), 2230 (C=N), 1732 (C=O ester), 1602 (C=N), 1500 (C=C aromatic), 1264 (C-N), 1213, 1185, 1167, 1064 (CO ether), 828, 754 (CH bend) cm⁻¹.

Polymer (111) : υ_{max} (**KBr**) 3430 (NH secondary amine), 3028 (CH aromatic), 2925, 2855 (CH alkane), 1735 (C=O ester), 1605 (C=N), 1509, 1498 (C=C aromatic), 1256 (C-N), 1205, 1165, 1071, 1005 (CO ether), 845, 797, 763 (CH bend) cm⁻¹.

Polymer (112) : v_{max} (**KBr**) 3035 (CH aromatic), 2936, 2862 (CH alkane), 1607 (C=N), 1508, 1498 (C=C aromatic), 1255 (C-N), 1218, 1187, 1116, 1024 (CO ether), 821, 751 (CH bend) cm⁻¹.

All the IR results are for doped polymers.

The benzenoid / quinoid ratio was very difficult to assess due to the other conjugated benzene rings of the different side chains.

N.M.R. : All the polymers did show the characteristic chemical shifts of the side chain but there was no evidence of chemical shift of ¹H of NH- group. All the spectra were difficult to interpret fully because of the very noisy background due to the partial insolubility of the polymers in the solvents (CHCl₃ and DMSO).



III.1 : INTRODUCTION

The previous chapter of this thesis has been concerned with the design and synthesis of aniline monomers bearing pendant mesogenic groups and their polymerisation. This chapter describes the characterisation of the liquid crystal properties of the monomers and other intermediates synthesised and then the optical, mechanical, electrical and liquid crystal properties of the resultant polymers.

The first part of this chapter will only be concerned with low molecular weight compounds such as the 2-substituted nitrobenzenes and then the 2-substituted anilines. In order to synthesise monomers based on aniline *ortho*-substituted with liquid crystalline moieties, it was necessary to prepare a series of *ortho*-substituted nitrobenzene molecules which were subsequently reduced to the required anilines. We will then describe the liquid crystal phase behaviour of these monomers and intermediates, as determined by investigation with hot-stage polarising microscopy and differential scanning calorimetry. To explain some of the results, a computer modelling package was used. Some of the liquid crystalline phases were not easily identified either by microscopy or thermal analysis, therefore a few samples were sent away for X-ray diffraction studies. These results will be shown in Appendix 2.

The second part of this chapter will deal with the polymers synthesised. They were identified, as described in the previous chapter, by infra-red and NMR spectroscopy. In this chapter studies of the properties of these polymers will be discussed, such as solubility measurements, ultra-violet/visible spectroscopy, molecular weight characterisation, thermal analysis, liquid crystal properties, and measurements of electrical conductivity.

III.2 : MONOMERS : Liquid Crystal Transition Temperatures and Phase Behaviour

III.2.1. 4-Methoxyphenyl 4-[x-(2-nitrophenoxy)alkoxy]benzoates



Nine esters (5a to 5i) were prepared in this series (x = 2 to 10) as described in Scheme 2. These compounds were investigated by hot stage optical polarizing microscopy to determine their liquid crystal transition temperatures and identify the phase type ; the results are presented in Table III.1. A complementary evaluation of the thermal behaviour by differential scanning calorimetry (DSC) is reported in Table III.2. DSC is a valuable aid by which phase transition temperatures and transition enthalpies can be conveniently measured or calculated.

x	C - I (°C)	N - I (°C)	I - C (°C)	N • C (°C)
2	119.4	(62.0)		60
3	104.0		< -35	
4	108.8	(58.4)		46
5	107.2		< -60	
6	88.3	(56.5)		35
7	78.0		24	
8	81.9	(56.0)		40
9	64.5		38	
10	68.5	(54.2)		< -40

 Table III.1 : Transition temperatures for the 4-Methoxyphenyl 4-[x-(2-nitrophenoxy)alkoxy]benzoates

Notes : Symbols

- C Crystal
- I Isotropic
- N Nematic
- () Monotropic liquid crystal (exhibited liquid crystalline properties only on cooling).

The heating rate for the DSC study was $10^{\circ}C$ / min on heating and $2^{\circ}C$ / min on cooling.

x	Т _{с.і} (°С)	Τ _{N-I} (°C)	Τ _{I-C} (°C)	T _{N-C} (°C)
	ΔH_{C-I} (kJmol ⁻¹)	ΔH _{N-I} (kJmol ⁻¹)	ΔH_{I-C} (kJmol ⁻¹)	ΔH_{N-C} (kJmol ⁻¹)
2	117.5	I - N - C	64.9	
	43	same peak	43	
	102.5			
3	44			
4	108.2	(56.6)		52.3
4	42	1		38
_	105.0			
5	51			
	88.4	(55.9)		
D	49	1		
7	77.5		36.1	
/	53		35	
0	82.4	(54.1)		46.2
0	46	2		40
0	64.9		38.9	
9	44		44	
10	68.4	(52.6)		
10	55	2		

Table III.2 : Transition temperatures and Transition Heats (ΔH) of the Ester series by DSC

In general, the results obtained by microscopy and by DSC were consistent. The minor differences can be ascribed to experimental errors due to the different rates of heating or cooling used between the microscope and the DSC and the type of calibration used.

An example of DSC heating and cooling curves is given in Figure III.1 for molecule (5e).



Figure III.1 : Differential Scanning Calorimetry Heating and Cooling Curves of 4-Methoxyphenyl 4-[6-(2-nitrophenoxy)hexoxy]benzoate (5e)

In the case of the even spacer number the esters were nematic in character, whereas the molecules with odd spacer length did not exhibit any liquid crystal properties at all. The liquid crystalline molecules (x = 2, 4, 6, 8 and 10) showed a monotropic nematic phase with a Schlieren texture (as illustrated in the Photograph III.1). A monotropic liquid crystal is a molecule which exhibits liquid crystalline properties only on cooling below the melting point.

The magnification of all the photomicrographs was 20 times.



Photograph III.1 : Nematic Schlieren texture of 4-Methoxyphenyl 4-[6-(2nitrophenoxy)hexoxy]benzoate (5e) ($T = 55^{\circ}C$)

In the Schlieren texture, the black bands or Schlieren occurring throughout the texture are regions of extinction and are often referred to as "Schlieren brushes" as illustrated in Figure III.2. These brushes meet at point singularities in the texture, or rather, point singularities are the origins of the brushes. The points are in effect the intersection of vertical lines of singularity with the surface. For Schlieren textures in nematics, two types of point singularity are observed, one in which two brushes originate from the centre, and one in which four brushes originate from the centre.

Nehring and Saupe³¹⁴ were able to show that the point singularities are characterised by :

$$S \mid = \frac{\text{number of brushes}}{4}$$

The singularities have a positive sign when the brushes rotate in the same direction as that in which the polariser and analyzer are simultaneously rotated in the crossed position, and a negative sign when they turn in the opposite sense. Thus, singularities with $S = +\frac{1}{2}, -\frac{1}{2},$ +1, -1 are known for nematics. In the case of compound (5e) illustrated in Photograph III.1, the schlieren texture exhibited two brushes.



(a) point singularity with four brushes(b) point singularity with two brushes

Figure III.2 : Schlieren Texture with Point Singularity with Four and Two Brushes

We also observed that the ester series showed a strong odd-even effect. A plot of the transition temperatures (°C) against the number of carbon atoms in the alkyl chain (x) is shown in Figure III.3.

In fact, when x was equal to an even number (2, 4, 6, 8 and 10) the molecules were liquid crystalline whereas in the case of an odd number (3, 5, 7 and 9) the molecules did not show any liquid crystalline behaviour.

The odd-even phenomenon is common for many liquid crystals but is not usually so dramatic. Generally, it is characterised by a regular alternation like the melting points of our series. Indeed, with the exception of the pentyl homologue, the melting points showed a regular alternation on increasing x, the even-numbered spacers exhibiting the higher values.

The fact that the molecules with even spacers were liquid crystalline whereas the odd members were not, can be related to Imrie's³¹⁵ elegant work on dimeric liquid crystals, in which a large odd-even alternation was interpreted in terms of an alternation in the long-range orientational order.



Figure III.3 : Transition Temperature (°C) Against the Number of Carbon Atoms x for the 4-Methoxyphenyl 4-[x-(2-nitrophenoxy)alkoxy]benzoate Series

A simplistic explanation of our own results assumes that the spacer exists predominantly in an *anti* conformation in the nematic phase. Thus, for even numbered spacers the two terminal aromatic moieties are almost parallel and the molecules are more linear than those with odd spacer lengths. Use of the computer modelling package, Desktop Molecular Modeller version 2.0 (DTMM) to draw the isolated molecules in their minimum energy configurations (Figure III.4) tends to corroborate this explanation.

In fact, DTMM showed that in the case of an odd spacer group, the molecule is not linear whereas with an even spacer the molecule is mainly linear and more likely to exhibit liquid crystal properties.



Figure III.4 : Molecular modelling of molecules (7a) and (7b) in their most probable conformation

III.2.2. Various Other Substituted Nitrobenzenes

III.2.2.1. Substituted Biphenyl Nitrobenzenes

Some substituted biphenyl molecules were synthesised by the route shown in Scheme 3 and studied by polarising hot-stage microscopy and DSC. The resulting transition temperatures and transition heats are presented in Table III.3.



Compound	X	T _{C-I} (°C) T _{C-K1} † (°C) ΔH (kJmol ⁻¹)	T _{N·I} (°C) T _{K1-I} † (°C) ΔH (kJmol ⁻¹)	T _{I-C} (°C) ΔH _{I-C} (kJmol ⁻¹)
(6)	6	71.0†	83.9†	28.2
(6)	0	48	5	38.5
(7-)	E	115.5		85.8
(7a)	2	47		47
(71-)	¢	95.3	(55.3)	
(70)	0	52	2	
(9)	6	93.5	•	82.4
(8)	6	38		13

Table III.3 : Transition temperatures and transition heats for various biphenyls substituted nitrobenzenes

Notes : K₁ = Crystal phase

The molecules 4-[6-(2-nitrophenoxy)hexoxy]biphenyl (6) and 4-bromo 4'-[6-(2-nitrophenoxy)hexoxy]biphenyl (8) did not exhibit mesogenic properties whereas 4-cyano 4'-[6-(2-nitrophenoxy)hexoxy]biphenyl (7b) exhibited a monotropic nematic phase. This can be explained by the fact that the cyano group is more efficient than the bromo group or hydrogen atom at inducing the formation of nematic liquid crystalline phases. This trend has been discussed in Chapter I page 19.

Compound (8) exhibited two crystal phases, a property which is often observed in organic materials.

The same odd-even phenomenon described previously for the 4-methoxyphenyl 4-[x-(2-nitrophenoxy)] benzoates was also observed for 4-cyano 4'-[x-(2-nitrophenoxy)] biphenyls. In the case of an even spacer length (x=6, compound (7b)) the molecule was liquid crystalline whereas for an odd spacer length (x=5, compound (7a)) it was not. A photograph of the nematic schlieren texture exhibited by the molecule (7b) is illustrated in Photograph III.2. In this case, the brushes are not very distinctive.



Photograph III.2 : Nematic Schlieren Texture of 4-cyano 4'-[6-(2-nitrophenoxy) hexoxy]biphenyl (7b) $(T = 54.5^{\circ}C)$



The observations are supported by differential scanning calorimetry data. Heating and cooling curves for compound (7b) are displayed in Figure III.5.

Figure III.5 : Differential Scanning Calorimetry Heating and Cooling Curves of 4-cyano 4'-[6-(2-nitrophenoxy)hexoxy]biphenyl

III.2.2.2. High Transition Temperature Monomers

After investigation of the polymer glass transition temperatures (T_g) of substituted polyanilines, we realised that to be useful our liquid crystalline moieties should possess mesogenic transitions at least above the backbone T_g . Therefore, the molecules previously synthesised with transition temperatures around 55°C did not appear to produce polymers with liquid crystalline properties. We then decided to synthesise monomers with transition temperatures above 100°C.

Therefore, four types of molecules with higher liquid crystal transition temperatures and fixed spacer group length (x=6) were synthesised initially, as shown in Schemes 4 and 5. The results obtained using polarising hot-stage microscopy and DSC of their liquid

crystalline properties, are presented in Table III.4.



Compound	С - N С - S† (ДН)	N - I (ДН)	S _c - N S _A - N‡ (ΔH)	$S_1 - S_C$ $S_1 - S_A \ddagger$ (Δ H)	S ₂ - S ₁ (ΔH)	$N - C$ $S_1 - C \ddagger$ $S_2 - C \$$
•	157.3†	227.3	214.0	175.7	146.0	118.0§
9	(37)	(4.2)	(3.3)		(14)	(24)
	136.0	190.1				78.7
10	(51)	(1)				(23)
	134.6†	181.4	115.2‡	72.5‡		36.8‡
11	(50)	(1.2)	(0.65)	(1.7)		(2.4)
	124.0	199.8				66.3
12	(39)	(1)				(30)

Table III.4 : Transition Temperatures (°C) and Transition Heats $(\Delta H / kJ mol^{-1})$ of Substituted Nitrobenzenes

<u>Symbols</u>: S smectic with S_1 and S_2 not yet identified

The observations are supported by the differential scanning calorimetry heating and cooling data. The plots for compounds (9), (10) and (11) are displayed for example in Figures III.6,



Figure III.6 : Differential Scanning Calorimetry Heating and Cooling Curves of 4-Biphenyl 4'-[6-(2-nitrophenoxy)hexoxy]carboxylic acid (9)

Compound (9) undergoes polymorphism, in fact it shows more than one type of mesomorphic structure as the conditions of temperature are changed. It exhibites a nematic phase as well as a number of smectic phases. Compound (9) is a carboxylic acid and as a result of dimerisation by hydrogen bonding (see page 21) a longer molecule is produced which raises liquid crystal transition temperatures and generates the polymorphic properties.



Figure III.7 : Differential Scanning Calorimetry Heating and Cooling Curves of 4-Cyanophenyl-4'-[6-(2-nitrophenoxy)hexoxy]biphenyl-4-carboxylate (10)



Figure III.8 : Differential Scanning Calorimetry Heating and Cooling Curves of 4-Methoxyphenyl-4-[6-(2-nitrophenoxy)hexoxy]biphenyl-4'-carboxylate (11)

The nematic phase of compound (9) showed a Schlieren texture with four brushes as illustrated in Photograph III.3. The first smectic phase shown upon cooling the nematic phase is a smectic C with a Schlieren texture as illustrated in Photograph III.4. The brushes are not very distinctive, but only centres with four derived brushes can be observed in smectic C as all the point singularities are of the $S = \pm 1$ type. The domains between the Schlieren become faint lines, due to the layer stress as the tilt angle changes, forming the so called lined Schlieren texture.



Photograph III.3 : Nematic Schlieren Texture of 4-Biphenyl 4'-[6-(2nitrophenoxy)hexoxy]carboxylic acid (9) (T = 227.2°C)

Two other smectic phases were distinguished and illustrated in Photograph III.5 and III.6 respectively, but it was not possible by means of optical observations or DSC measurements to identify their phases. A doubt remained with the smectic 2 phase which could either be a highly ordered smectic phase as suggested by the microscope observations or a recrystallisation phenomenon as indicated by DSC and the high transition enthalpy exhibited (14 kJ mol⁻¹). X-ray diffraction is the only method that will resolve this. The sample has been sent for X-ray analysis and the results are available in Appendix 2.



Photograph III.4 : Smectic C Schlieren Texture of 4-Biphenyl 4'-[6-(2nitrophenoxy)hexoxy]carboxylic acid (9) (T = 194°C)



Photograph III.5 : Smectic 1 Phase of 4-Biphenyl 4'-[6-(2nitrophenoxy)hexoxy]carboxylic acid (9) $(T = 167^{\circ}C)$



Photograph III.6 : Smectic 2 Phase of 4-Biphenyl 4'-[6-(2nitrophenoxy)hexoxy]carboxylic acid (9) $(T = 145^{\circ}C)$

Compounds (10) and (11) exhibited homeotropic textures in their nematic and smectic phases. A homeotropic phase is shown when the orientation of the director is perpendicular to a surface. The homeotropic texture (also called pseudoisotropic texture) when observed using an optical microscope, with crossed polarizers, appears black, except in the neighbourhood of deformations, e.g. around air bubbles or particles of impurity. These areas are often ringed by bright birefringent regions due to structural imperfections at the edge of the bubble or impurity. The photograph of the homeotropic texture of the nematic phase of compound (10) and (11) (Photograph III.7 and III.8 respectively) illustrates this behaviour perfectly. This kind of texture is observed because the molecules are aligned with an average orientation perpendicular to the surfaces of the microscope slides.

Compound (11) also exibited a smectic A phase with an homeotropic texture as illustrated in Photograph III.9. The smectic A phase is formed on cooling the nematic phase and therefore is dependent to some degree on the texture of the nematic phase. If the nematic phase is homeotropic, then it is probable that the smectic A phase will exhibit a homeotropic texture, as shown in this case.



Photograph III.7 : Nematic Homeotropic Texture of 4-Cyanophenyl-4'-[6-(2nitrophenoxy)hexoxy]biphenyl-4-carboxylate (10) (T = 186°C)



Photograph III.8 : Nematic Homeotropic Texture of 4-Methoxyphenyl-4-[6-(2nitrophenoxy)hexoxy]biphenyl-4'-carboxylate (11) ($T = 166^{\circ}C$)



Photograph III.9 : Smectic A Homeotropic Texture of 4-Methoxyphenyl-4-[6-(2nitrophenoxy)hexoxy]biphenyl-4'-carboxylate (11) (T = 112°C)

Compound (11) exhibited another smectic phase which could not be identified by optical microscopy or differential scanning calorimetry. X-ray diffraction studies are being carried out at the moment and the results should be available in the appendix section. Compound (12) exhibited a nematic phase with a classical Schlieren texture.

The four molecules synthesised did show liquid crystalline behaviour at a high temperature, above the polymer backbone T_g , but they all possessed potentially reactive groups such as cyano, ester and carboxylic acid. In fact, the cyano group has proven to be sensitive in the hydrogenation process, whereas the ester group can easily be hydrolysed. In the case of the carboxylic acid group, it might react with the amine group once formed, creating an intramolecular amide or alternatively a cross-linked polymer. In order to avoid these problems, it was decided to synthesise some terphenyl molecules (Schemes 6 and 7) with fixed spacer group.

Terphenyls are also known to exhibit high liquid crystalline transition temperatures. Therefore, two terphenyl-based molecules were synthesised and their liquid crystalline properties were investigated by polarising hot-stage microscopy and by differential scanning calorimetry. The results are given in Table III.5 as well as the transition temperatures of



Compound	С - N С - K ₁ † С - I‡ (ДН)	N - Ι K ₃ - Ι† (ΔΗ)	K ₂ - K ₃ † N - S ₁ (ΔH)	N - C I - C \ddagger K ₁ - K ₂ \ddagger S ₁ - C¶
14	133.7†	223.5†	178.9†	147.1†
14	(14)	(26)	(1)	(2)
17	222.5	291.0		191.2
1/	(37)	(2)		(14)
18	215	330		
10	264.9‡			259.4‡
19	(47)			(32)
20	228.0	328		195.5
22	156.2	197.5	125.7	78.3¶
22	(50)	(1)	(7)	(24)

Table III.5 : Transition Temperatures (°C) and Transition Heats ($\Delta H / kJ mol^{-1}$) of Terphenyl Type Molecules and their Intermediates

<u>Notes</u>: K_1 , K_2 , K_3 and S_1 are crystal or highly ordered smectic phases but they have not yet been identified.

The compounds (17), (18), (20) and (22) exhibited a classical nematic Schlieren texture as illustrated in the previous pages. Molecule (19) does not possess any liquid crystalline properties; in fact when the cyano group was substituted by a methyl group, the molecule no longer showed any mesogenic properties. This is in agreement with the terminal group efficiency order quoted in Chapter 1 page 19.

The compound 4"-cyano-4-[6-(2-nitrophenoxy)hexoxy]terphenyl (22) also exhibited a smectic phase (as illustrated in Fig. III.9 by the differential scanning calorimetry heating and cooling curves) which could not be identified either by optical microscopy or DSC, and is currently the subject of X-ray studies.



Figure III.9 : Differential Scanning Calorimety Heating and Cooling Curves for 4''cyano-4-[6-(2-nitrophenoxy)hexoxy]terphenyl (22)

The compound (14) 4"-methoxy-4-[6-(2-nitrophenoxy)hexoxy]terphenyl exhibited

three phases which could not be identified. Some of the observations like the rigidity of the phases and the similarity of the textures under microscope oriented our conclusion to crystal phases whereas the reversibility of the peaks by DSC influenced our conclusion towards highly oriented smectic phases. X-ray studies are again being run at the moment and will be the definitive method. To support our preliminary conclusion, the differential scanning calorimetry heating and cooling curves are available in Figure III.10 as well as the photographs of the different phases observed (Photographs III.10-12).



Figure III.10 : Differential Scanning Calorimety Heating and Cooling Curves for 4"-Methoxy-4-[6-(2-nitrophenoxy)hexoxy]terphenyl (14)



Photograph III.10 : K_3 Texture of 4''-Methoxy-4-[6-(2-nitrophenoxy)hexoxy]terphenyl (14) (T = 223°C)



Photograph III.11 : K_2 Texture of 4''-Methoxy-4-[6-(2-nitrophenoxy)hexoxy]terphenyl (14) (T = 170°C)



Photograph III.12 : K_1 Texture of 4''-Methoxy-4-[6-(2-nitrophenoxy)hexoxy]terphenyl (14) (T = 140°C)

III.2.3. Aniline Monomers

The results given in the previous part of this chapter were for the *ortho*-substituted nitrobenzene molecules. For the *ortho*-substituted aniline compounds the results were similar. Of course, the transition temperatures were different because the chemical constitution was different, but the phases behaviour of the molecules were the same.

- Compounds (5e), (7b), (9), (10), (11) and (12) which have respective aniline equivalent compounds (24e), (26), (27), (28), (29) and (30*) were all liquid crystalline. In contrast, compounds (5d) and (6) which have respective aniline equivalent compounds (24d) and (25), showed no liquid crystal phases.



Almost the same conclusions can then be pointed out for the aniline group of molecules. - Like their nitro-equivalents, compounds (24e) and (26) exhibited liquid crystalline properties only on cooling, so they were monotropic liquid crystals. - The even-odd correlation was also valid for the aniline compounds. Indeed, the compounds (24d) and (24e) just had a different spacer length with x = 5 and 6 respectively. In the first case (odd number), the molecule did not show any liquid crystalline behaviour whereas in the second case (even number) the molecule was liquid crystalline.

- Compounds (24e), (26), (27), (28), (29) and (30*) all showed a nematic phase like their nitro-equivalents.

- The compound (31) exhibited three phases, but only a nematic phase could be identified whereas the phase called S_1 was almost certainly a highly ordered smectic phase, the phase called K_1 could not be distinguished between a smectic or a crystal phase.

All these results can be explained by the fact that the nitro or aniline groups were not directly attached to the main mesogenic core and therefore would have a limited effect on the liquid crystalline behaviour.

In all cases, only the nematic phases were definitely identified. Indeed, for all the aniline molecules it seemed difficult to assess clearly the temperature dependence, as there was some evidence of decomposition of the molecules. The amine group is known to be a reactive functional group and it is easily oxidised by air at relatively low temperature. To obtain more reliable results, all the measurements by differential scanning calorimetry were done under a nitrogen atmosphere, but for the optical microscopy this condition was not always easy to achieve as the equipment used was not always set for work under nitrogen. However, the results of the transition temperatures of the aniline molecules are given in Tables III.6-III.8. The aniline molecules synthesised were polymerised almost immediately in order to avoid any oxidation during storage.

Compound	С - К ₁ С - І†	K ₁ - I	N - I
(24d)	72.8†		
(24e)	70.6	100.5	(65.9)

Table III.6 : Transition Temperatures (°C) of the Ester Compounds (24d) and (24e)

Notes : $K_1 = crystal$

Compound	С - К ₁ † С - І	K ₁ - I† N - I	I - C† N - C
(25)	82.9†	84.0†	27.5†
(26)	87.2	(75.6)	53.3

Table III.7 : Transition Temperatures (°C) of the Biphenyl Compounds (25) and (26)

Commonwead	C-S	NI	E N	C V	N • C
Compound	C - N ₁ ‡	N - 1	5 ₁ - N	5 1 - K 1	$S_1 - C_1^*$ $K_1 - C_2^*$
(27)	157.0	222.3			
(28)	125.0	164.5	140.0		127.9†
(30*)	151.0†	180.1			72.7
(31)	147.7‡	230.3	222.0	159.2	141.2‡

Table III.8 : Transition Temperatures (°C) for Compounds (27), (28), (30*) and (31)

Notes : K_1 and S_1 crystal or highly ordered smectic phases not identified.

III.3 : POLYMERS

III.3.1. Electropolymerisation

As described in section II.5.1., 2-methoxyaniline, 2-ethoxyaniline, 2-propoxyaniline and 2-butoxyaniline were electropolymerised in an exploratory study. Cycling of the ITO working electrode potential produced electrochromic changes from yellow (reduced form, leucoemeraldine) to green (at the first oxidation stage, emeraldine) and to blue-violet (at the second one, pernigraniline), reproducing the behaviour of polyaniline. The first oxidation peak involves firstly the removal of an electron to give a cation radical system, then at almost the same potential this polaron is oxidised further to the bipolaron (dication) as illustrated in Figure III.12. The second oxidation peak is caused by the emeraldine type species being oxidised.



Figure III.12 : Mechanism of Oxidation

The anodic potential peaks E_{pa} and the cathodic potential peaks E_{pc} for each monomer were calculated and are listed in Table III.9. When cycling the films formed it was possible to see the typical electrochromic properties of polyaniline depending on the potential applied.

Compound	First [§] E _{pa} (mV)	Second [§] E _{pa} (mV)	First [§] E _{pc} (mV)	Second [§] E _{pc} (mV)	Comments
methoxy-	273	413	193	338	Electrochromic
ethoxy-	318	450	186	332	Electrochromic
propoxy-	306	440	239	386	Electrochromic
butoxy-	335	471	211	404	Electrochromic

Table III.9 : Electrochemical Data for 2-Alkoxyanilines

The voltammograms of the four 2-alkoxyanilines are illustrated in Figure III.13

2-Methoxyaniline in HCI 1M

Cyclic Voltammogram



[§] Notes : Peak potentials with respect to Ag/AgCl reference



2-Propoxyaniline in HCI 1M

Cyclic Voltammogram




Figure II.13 : Cyclic Voltammograms of 2-Alkoxyanilines

Electropolymerisation of our liquid crystalline monomers was investigated, but due to their low solubility in aqueous media, it was not possible to use 1M HCl or similar aqueous solvents. The voltammogram obtained for monomer (26) in a mixture of butanoic acid and 1M HCl is illustrated in Figure III.14. The oxidation potential was 439 mV and the reduction one was 367 mV. The first cycles showed an increase of the oxido-reduction peaks, leading to the expectation of film formation on the electrode, but no film was ever obtained. In fact, after the peaks had increased during the initial cycles, they began to decrease later.



Figure II.14 : Cyclic voltammogram of 2-[4-Cyano 4'-(hexoxy-6-oxy)biphenyl]aniline in a mixture of butanoic acid and HCl 1M (1:1)

The same monomer (26) and also (24e) were each dissolved in a mixture of propylene carbonate, HCl 1M and dodecylbenzenesulfonic acid (DBSA) 1M and then cycled under the same conditions. The two voltammograms obtained are displayed in Figures III.15 and III.16. The same phenomenona was observed as previously, with oligomer formation but no polymer.

Propylene carbonate was replaced by chloroform in the case of monomer (24e) but the same results were obtained (see voltammogram in Figure II.17).



Figure II.15 : Cyclic voltammogram of 2-[4-Cyano 4'-(hexoxy-6-oxy)biphenyl]aniline (26) in a mixture of propylene carbonate, HCl 1M and DBSA



Figure II.16 : Cyclic voltammogram of 2-[4-methoxyphenyl 4-hexoxy(6oxy)benzoate]aniline (24e) in a mixture of propylene carbonate, HCl 1M and DBSA



Figure II.17 : Cyclic voltammogram of (24e) in a mixture of CHCl₃, HCl 1M and DBSA

III.3.2. Oxidative Chemical Polymerisation

We have seen in Section 4 of the Introduction that polyaniline can be synthesised by oxidative chemical polymerisation in a Bronsted acid medium¹⁸¹. Typically, this leads to a predominantly *para*-linked head-to-tail polymer which is partly protonated at the nitrogen atoms. Reaction of anilines with ammonium persulfate in 1M HCl with a trace of ferrous chloride as catalyst produces polyanilines in their emeraldine type protonated (salt) form (see pages 48-54). Initially, the following reaction sequence is thought to occur as illustrated in Figure III.18. The full mechanism has been described in pages 52-54.



Figure III.18 : First Steps of the Aniline Polymerisation Mechanism

In order to achieve these reactions, our monomers had to be dissolved in aqueous HCl (1M). This was possible with 2-methoxyaniline, 2-ethoxyaniline, 2-propoxyaniline, 2butoxyaniline and 2-pentoxyaniline which were polymerised using these normal conditions. But as we increased the length of the ortho-substituted group, the monomers became progressively more insoluble in acidic aqueous media. In the case of 4-[6-(2-anilineoxy) hexoxy]biphenyl (25) and 4-cyano 4'-[6-(2-anilineoxy)hexoxy]biphenyl (26) we used an organic acid (butanoic acid) in conjunction with 1M HCl to solubilise the monomer and allow polymerisation. Moreover as the ortho-substituted group became even bigger, this method was no longer efficient and a new method was devised using emulsion polymerisation. This one-step polymerisation technique was carried out in an emulsion comprising 1M HCl and an organic solvent (chloroform or acetone) in the presence of the functionalised protonic acid dodecylbenzenesulfonic acid. Use of an organic solvent allowed solubilisation of the monomers. The oxidative agent was dissolved in 1M HCl and the surfactant (via micelle formation) enabled contact between the oxidant and the aniline group with the required conditions (50% oxidation and protonation) to form head-to-tail polymers.

Investigations of the infra-red spectra of the polymers formed by all of these three methods did not reveal any bands characteristic of head-to-head or tail-to-tail polymerisation such as azo-group or primary amine group. Instead, the bands characteristic of head-to-tail coupling such as benzenoid and quinoid stretching peaks were detected. For simple substituted polyanilines such as poly(2-alkoxyanilines) the study of their spectra was relatively straightforward and easily comparable with published results on similar polymers. As the side groups became bulkier it was much more difficult to interpret the spectra. In fact, due to the conformation of the polymer, the functional groups on the side-chain were much easier to detect than the polymer backbone ones. We found in all cases that the sidechains were not affected by the oxidative polymerisation process ; they all remained intact. It was almost impossible to assess the degree of oxidation-reduction of the polymer backbone as the benzenoid / quinoid ratio was unclear as a result of the multiple benzene rings of the mesogenic side chains.

Hence, there was no evidence for non-regular polymers, and so it was assumed that the substituted polymers that had been prepared were regular head-to-tail in 50% oxidised protonated forms (Figure III.19). In fact, care was taken to ensure that the overall acid concentration was 1M and that the amount of oxidant was equal to 1.1 equivalent.



Figure III.19 : Polyaniline Emeraldine Protonated Salt form

The emulsion polymerisation technique used was optimised in order to assess the best quantity of surfactant required to obtain a stable emulsion of suitable sized micelles.

As an example, some simplified mathematical calculations have been performed on the polymerisation of monomer (27) in chloroform in order to estimate the number of micelles in the solution and the number of monomer molecules per micelle.

Number of micelles :

We assumed that the micelles are spherical and have a radius of 2.5 nm. The number of surfactant molecules was 0.0015 x N_A (N_A = Avogadro number).

Volume of an empty micelle is equal to : $4/3 \pi R^3 = 6.6 \times 10^{-26} m^3$ Surface of an empty micelle is equal to : $4 \pi R^2 = 7.9 \times 10^{-17} m^2$

Effective cross-sectional area of surfactant molecule (i.e. area of the shaded part) : π r² = 7.9x10⁻¹⁹ m²

Surfactant Molecule

Therefore, the number of surfactant molecules per micelle is equal to :

 $\frac{7.9 \times 10^{-17}}{7.9 \times 10^{-19}} = 100$

Therefore, the number of micelles is equal to :

 $\frac{0.0015 \text{ x N}_{\text{A}}}{100} = 9 \text{ x } 10^{18} \text{ micelles}$

Number of monomer molecules per micelle :

The number of monomer molecules was 0.001 x N_A

Therefore, the average number of monomer molecules per micelle is equal to :

 $\frac{0.001 \text{ x N}_{\text{A}}}{9 \text{ x } 10^{18}} = 67 \text{ monomer molecules per micelle}$

The value of 67 was found to be an optimum value to allow the synthesis of polymers with repeatable properties, in fact a much smaller number of monomers would produce only oligomers. The number was also not too large, in order to avoid production of insoluble and non-processable polymers.



III.3.3. Solubility Studies and Ultra-Violet/Visible Spectra

The solubilities of the protonated and deprotonated polyaniline derivatives were determined in a large range of solvents by eye and then by UV studies. This was investigated for the purpose of making thin films. The results of the solubility tests are given in Table III.10.

Polymer	DMSO	DMF	THF	CHCl ₃
100 Doped	S d.green	S d.green	s.S red	s.S pink
Undoped	S d.blue	S d.blue	I	s.S d.blue
101 Doped	S d.green	S d.green	I	S green
Undoped	S d.blue	S blue-purple	s.S blue	S green
102 Doped	S d.green	S green-brown	s.S brown-red	s.S d.red
Undoped	S d.blue	S blue-purple	s.S blue-purple	S red
103 Doped	S d.green	S d.green	S brown-red	S green
Undoped	s.S d.blue	S d.blue	S blue-purple	S blue-purple
104 Doped	S d.green	S d.green	s.S d.green	s.S d.green
Undoped	s.S d.purple	S purple-blue	S purple	s.S purple
105	S d.red	S d.red	S d.red	S d.red
106	S burgundy	S burgundy	s.S burgundy	1
107	S brown-red	S brown	s.S brown	s.S brown
108	S burgundy	S burgundy	S burgundy	s.S burgundy
109	S d.red	S red	S burgundy	S burgundy
110	S orange	S red-brown	S brown-red	S brown
111	S red	S red	S red	S red
112	S red	S red	S red	S brown

Table III.10 : Solubility Results for Polymers

Notes :

S = Soluble

- s.S = slightly Soluble
- I = Insoluble

d. = dark

All the side-chain liquid crystalline polymers did not show any visible colour changes between the doped and undoped forms.

Most of the poly(2-alkoxyanilines) were insoluble or only slightly soluble in most organic solvents. They seem soluble only in a limited range of polar solvents such as DMF and DMSO, but the use of dodecylbenzenesulfonic acid can make polyanilines soluble in a variety of common organic solvents and so ease the processing of polyanilines in the conducting form. In fact all the side chain liquid crystalline polyanilines synthesised by emulsion polymerisation were more soluble than polymers synthesised by other means in solvents like chloroform and tetrahydrofuran. As well as acting as a surfactant, dodecylbenzenesulfonic acid can also act as a dopant. The main problem was to remove this dopant, which was not as easy as for HCl.

We have seen in the Introduction chapter that PANI can exhibit a wide range of colours from pale yellow to blue for both thin and thick films, depending on the degree of protonation and the oxidation-reduction potential. The absorption in the visible range is due to allowed transitions between the electronic levels of the polymer. Chromophores corresponding to the aromatic amine, the radical cation and the quinone-diimine forms are correlated to the reduced-insulating, the conductive and the oxidised-semiconducting forms of the polymer respectively.

Figure III.20 shows the optical absorption spectrum of undoped poly(2-methoxyaniline) dissolved in dimethylformamide. There are two broad bands with maxima at 308 nm (4.03 eV) and 598 nm (2.07 eV). The band at 308 nm has been assigned to the main optical band gap (π - π *) transition, whereas the second band can be either attributed to the transition from the valence band to the upper polaron (p*) (E₁), or between the non-bonding orbitals localised on the imine nitrogen corresponding to a partially filled polaron-type band (p) to the upper anti-bonding π * band (E₃) as illustrated in Figure III.21.





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Figure III.20 : UV/Visible Spectra of Poly(2-methoxyaniline) Base in DMF

Figure III.22 shows the optical absorption spectrum of PANI hydrochloride (emeraldine salt) dissolved in concentrated H_2SO_4 . In this case, there are three primary bands with maxima at 306 nm (4.05 eV), 494 nm (2.51 eV) and a low energy absorption maximum beyond 900 nm (<1.38 eV). The last band originates from a partially filled polaron-type band (p) to the corresponding upper polaron (p*) band (E₂ in Figure III.21).



Figure III.22 : UV/Visible Spectra of Poly(2-methoxyaniline) Salt in Conc. H_2SO_4

The other chemically synthesised alkoxy-substituted polyanilines and side chain liquid crystalline polymers were also studied by UV/Visible spectroscopy. The data are presented in Table III.11 with λ in nm.

Compound	Conditions	λ max	λmax	λ onset $1^{st} \pi - \pi^*$	λ max	λmax
Compound	Conditions	$2^{ m nd}$ π - π^*	$1^{ ext{st}} \pi$ - π^*	Eg (eV)	π-р*	p-p*
100	DMF	1	308	416 (2.98)	598	
100	CHCl ₃	241	280	359 (3.46)	520	
101	DMF	1	314	408 (3.04)	609	
101	CHCl ₃	239	276	355 (3.5)	450	> 900
102	film	-	312	429 (2.89)	510	
102	film salt		286	353 (3.52)	524	000
- 103	film base		307	421 (2.95)	554	880
104	DMF	1.	290	426 (2.91)	567	
104	CHCl3	241	286	436 (2.84)	450	
100	DMF		288	395 (3.14)	532	
100	CHCl ₃		261	302 (4.11)	420	
	DMF	1	297	337 (3.68)	504	
108	CHCl ₃	241	298	339 (3.66)	540	
	film	1	296	349 (3.56)	549	
	DMF	1	294	331 (3.75)	509	
109	CHCl ₃	241	294	345 (3.60)	504	
	H ₂ SO ₄	247	335	400 (3.10)	495	<u>682</u>
	DMF	1	306	360 (3.45)	400	
110	CHCl ₃	241	303	349 (3.56)	433	
	film	1	298	382 (3.25)	416	865
	H ₂ SO ₄	258	321	396 (3.13)	483	<u>600</u>
111	CHCl ₃		285	361 (3.44)	540	
111	film		292	367 (3.38)	515	

 Table III.11 : UV/Visible Spectra Results for Substituted Polyanilines

Notes :

The underlined values in the last column correspond to the p- π^* transition.

The first conclusion that can be drawn is that the average band gap determined from thin film spectra for the side chain liquid crystal polymers is about 3.4 eV which is relatively high compared with that of poly(2-methoxyaniline) $(3.0 \text{ eV})^{316}$. This may be explained by the large size of the mesogenic group, the steric effect of which presumably causes twisting of the polymer backbone and results in less effective conjugation.

The intensity of the π -p* transition band is also smaller in the case of the side chain liquid crystalline polymers, as illustrated in Figure III.23 for poly{2-[hexoxy-6-oxy-(4-cyanobiphenyl)]aniline}.



Figure III.23 : UV/Visible Spectra of Polymer (108) in DMF Solution

III.3.4. Molecular Weight and Molecular Weight Distribution

One of the most fundamental characteristics of a molecule is its relative size and one of the most important features which distinguishes polymers from low-molecular weight species is the existence of a distribution of chain length and therefore degree of polymerisation and molecular weight. This distribution can be illustrated by plotting the weight of polymer of a given molecular weight against the molecular weight, as in Fig. III.24.



Figure III.24 : Distribution of Molecular Weights in a Typical Conducting Polymer

Because of the existence of the distribution in any finite sample of polymer, most experimental measurements of molecular weight can give only an average value. Several different averages are important depending on the methods used for estimating the molecular weight of polymers.

For example, some methods of molecular weight measurement such as osmotic pressure in effect count the number of molecules in a known mass of material. This information provides the number-average molecular weight \overline{Mn} of the sample defined by :

$$\overline{\mathbf{M}}\mathbf{n} = \frac{\sum N_i M_i}{\sum N_i}$$

where N_i is the number of molecules of species i of mass M_i .

From light scattering measurements, a method depending on the size rather than the number of molecules, a weight average molecular weight $\overline{\mathbf{M}}\mathbf{w}$ is obtained. This is defined as :

$$\overline{\mathbf{M}}\mathbf{w} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Because heavier molecules contribute more to $\overline{\mathbf{M}}\mathbf{w}$ than light ones, $\overline{\mathbf{M}}\mathbf{w}$ is always greater than $\overline{\mathbf{M}}\mathbf{n}$, except for a hypothetical monodisperse polymer. The quantity $\overline{\mathbf{M}}\mathbf{w}/\overline{\mathbf{M}}\mathbf{n}$ is a useful

measure of the breadth of the molecular weight distribution curve and is termed the polydispersity.

In order to check and calibrate the results obtained by gel permeation chromatography, vapour pressure osmometry and viscosity measurements were investigated for poly(2-methoxyaniline).

By using an Ubbelohde type viscometer, the intrinsic viscosity $[\eta]$ was estimated and the viscosity average molecular weight ($\overline{\mathbf{M}}\mathbf{v}$) determined by the following equation :

$$[\eta] = K \overline{\mathbf{M}} \mathbf{v}^{a} \qquad \text{with} \qquad \overline{\mathbf{M}} \mathbf{v} = \frac{\sum N_{i} M_{i}^{1+a}}{\sum N_{i} M_{i}^{a}}$$

Where K and a are the Mark-Houwink parameters for a particular polymer/solvent pair at a given temperature, and a is normally slightly less than unity.

III.3.4.1. Viscosity

The intrinsic viscosity and then the viscosity average molecular weight of undoped poly(2-methoxyaniline) were determined by viscosity measurements in dimethylformamide at 30°C.

It has been seen previously that the constants K and a are particular for a polymer/solvent pair, but no values were available in any publication or in the Polymer Handbook for this type of polymer. Values were found for some polymers in DMF at $30^{\circ}C^{317}$.

Polymer	a	K (10 ⁻³ ml/g)
Polyacrylonitrile	0.75	20.9
Poly(2-hydroxyethyl methacrylate)	0.70	10.6
Poly(5-vinyl-2-methylpyridine)	0.76	13
Poly(oxy 1-oxo-hexamethylene)	0.73	19.1

For these numbers, an average value of a and K was established :

$$a = 0.73$$

K = 16 x 10⁻³ cm³/g

Five solutions of poly(2-methoxyaniline) in DMF were prepared, ranging from 0% to 0.5% w/v and the flow time for a given volume, through the capillary tube in an Ubbelohde viscometer was measured at the constant temperature of 30°C. The calculations were carried out using the following equations :

Viscosity ratio :
$$\eta_{rel} = t / t_0 = \eta / \eta_0$$

Specific viscosity:
$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_{rel} - 1$$

Viscosity number : $\eta_{red} = \eta_{sp} / c$

where η_{rel} = relative viscosity η solution and η_0 solvent η_{red} = reduced viscosity c = concentration in g/ml

In order to determine [η], we plotted η_{sp}/c against c (Fig. III.25) and read of the value of the former obtained by extrapolating to c = 0. The results are given in Table III.12.

C (x10 ⁻³ g/cm ³)	t average (s)	$\eta_{ m sp}$	η _{sp} / c
0	90.47	1	I
0.824	91.45	0.01086	13.51
2.06	93.25	0.03073	14.92
3.005	94.56	0.0452	15.04
5.008	98.40	0.08765	17.50

 Table III.12 : Concentration, Flow Time and Specific Viscosity Results of Poly(2methoxyaniline)



Figure III.25 : Plot of Viscosity Number against Concentration of Poly(2methoxyaniline) (g.cm⁻³)

The intercept [η] was equal to 12.73, therefore $\overline{\mathbf{M}}\mathbf{v} = 9410$ for poly(2-methoxyaniline).

III.3.4.2. Vapour Pressure Osmometry

Most of the traditional methods for the determination of molecular weights are concerned with the colligative properties of solutions, and hence if used for polydisperse systems they would give a number average molecular weight. Three methods, commonly used for the determination of the molecular weights of small molecules are :

- lowering of vapour pressure
- elevation of the boiling point
- depression of the freezing point

As most polymer solutions do not behave ideally the methods adopted for polymers are somewhat comparative rather than completely absolute.

The vapour pressure of solutions containing doped poly(2-methoxyaniline) was studied in DMF for different concentrations and calibrated with a known concentration of benzil in DMF using a Knauer vapour pressure osmometer. DMF and solutions of different concentration were introduced into the measuring cell and allowed to equilibrate at 90°C. The benzil standard solutions were measured first to obtain a calibration curve of R/C as a function of the concentration (where R was the reading on the chart recorder and C was the concentration in mol.kg⁻¹ for the benzil standard) as illustrated in Figure III.26. Then, the poly(2-methoxyaniline) solutions were measured and R/C was plotted against C with C in g.kg⁻¹ for the polymer solutions (Figure III.27).



Figure III.26 : Calibration Curve for Benzil in DMF at 90°C

Benzil solutions :

Linear Regression : intercept = K_{cal} = 565 kg.mol⁻¹ slope = -4480 kg².mol⁻²

Poly(2-methoxyaniline) solutions :

Linear Regression : intercept = $K = 0.20 \text{ kg.g}^{-1}$ slope = -0.00244 kg².g⁻²

 $\overline{\mathbf{M}}\mathbf{n}$ of polymer = Kcal / K = **2825 g mol**⁻¹

This corresponds to a number average of 20 2-methoxyaniline units.



Figure III.27 : Experimental Curve for Poly(2-methoxyaniline) in DMF at 90°C

III.3.4.3. Gel Permeation Chromatography or Size Exclusion Chromatography

Gel permeation chromatography (GPC) is a method used to separate molecules by size. Basically, any soluble polymer molecules can be separated by GPC, small ones of less than 100 molecular weight as well as large ones of several millions. This method can be very valuable for polymer investigations ; in fact a macromolecule can show the specific properties of a polymer only if it has more than a certain number of repeat units. Being able to know the molecular weight distribution of a polymer can be essential to ensure reproducible properties. The separation of the molecules is usually carried out on columns that are tightly packed with a gel or some other porous material and completely filled with solvent. The same solvent is used to dissolve the sample before introducing it into the column and for elution ; in our case dimethylformamide (DMF) was used. Small sample molecules can diffuse into the pores of the gel, large ones are excluded, others of intermediate size can penetrate some of the larger pores. As the solvent is pumped through the column, the large molecules which are always or mostly excluded from the pores are therefore eluted first, whereas the small ones which are mostly inside the pores come out last.

A big advantage of this method, in our case, was the small amount of sample required. The

synthesised polymers were sent for analysis to Rapra Technology. GPC analysis gave us the molecular weight distributions of our polymers and the results calculated by Rapra using their standard programmes as well as the results found from the available curves are given in Table III.13. Some examples of the GPC curves obtained are available in Appendix 3. Where it is not specified if the polymer is doped or undoped in Table III.13, it indicates that the polymer was submitted for analysis as produced, and therefore it was believed to be in a doped form.

Samples of polyvinylpyrrolidone and polystyrene of known molecular masses were also analysed. The polyvinylpyrrolidone calibrants had average molecular weight above 10 000, and the GPC analysis performed by Rapra Technology found molecular weights on average twice as big as would have been expected. In the case of almost monodisperse polystyrene calibrants which had molecular weight ranging from 1900-3650, the values found by GPC analysis were half of the expected theoretical values.

The system used for the work carried out by Rapra was calibrated with polyethylene oxide (PEO) and polyethylene glycol (PEG) and all the results were expressed as the "PEO/PEG equivalent" molecular masses. In view of the difference in chemical type between the samples, our calibrants and Rapra's calibrants, there is a possibility of considerable difference between the calculated molecular masses and the actual molar masses of the samples. It would have been ideal if it had been possible to send a polyaniline sample, of known molecular weight, as calibrant in order to reduce the uncertainties related to the solvational and conformational properties of the polymer backbone in DMF. Another factor is that measurements were made using a refractive index detector. Better results would probably have been found with a UV/visible detector as the samples were very colourful compounds, but this equipment was not available at the time. During their computer analysis Rapra did not take into account the fact that in most of our samples there was not only one peak but two, three and even four peaks in some cases. The results they calculated were therefore largely irrelevant to the molecular weight distribution profile of our samples (Polydispersities as high as 500 were quoted). A peak by peak analysis was therefore calculated in order to understand the composition of our samples. The numerical values given in the Table III.13 were calculated from the curves and need to be considered with reservation, as all the necessary mathematical data were not available. Emphasis needs to be placed on any observed differences between the different side-chains and chemical polymerisation methods used rather than on the crude numerical values. Therefore, in our further discussion, we will use the term "oligomers" instead of giving a precise number.

	Rapra Computer Calculations		Results from Curves				
Polymer	Mw	Mn	PD	Peak	Mn	Mw	PD
100 Doped	3600	1000	3.7	1 broad	1401	15672	11.2
Undoped	11700	1700	7.1	1 broad	5309	53915	10.2
101 Doped	32000	1500	21.3	1 big-broad	4819	34402	7.1
				1 small-broad	325233	755177	2.3
Undoped	4800	1300	3.7	1 broad	3548	21951	6.2
102				1 sharp	229	297	1.3
Undoned	140900	800	176	1 broad	590	1750	3.0
				1 small-broad	314422	1000000	3.2
103				1 broad	742	1394	1.9
Undoped	293900	1350	218	1 broad	3108	13010	4.2
Chuopou				1 small-broad	395380	1773194	4.5
104 Doped	3600	800	4.8	1 broad	1122	14007	12.5
Undoped	2400	600	3.8	1 broad	755	9454	12.5
107	1300	500	28	1 sharp	266	389	1.5
107	1.500	500	<i>4.0</i>	1 small-broad	841	4685	5.6
				1 sharp	239	315	1.3
106	1200	500	2.4	1 medium	524	1658	3.2
				1 small	4307	8308	1.9
				1 sharp	215	291	1.4
108	1100	400	2.4	1 medium	487	1401	2.9
				1 small	4072	7988	2.0
100	500	400	14	1 sharp	211	638	2.0
107	500	400	1.7	1 small	2075	4072	2.0
				1 sharp	399	532	1.3
110	550000	1030	534	1 sharp	866	1142	1.3
110		1000		1 sharp	4833	14227	2.9
				1 small	3009324	1000000	3.3
				1 medium	363	443	1.2
111	57200	680	84	1 medium	701	1243	1.8
				1 small	31442	41869	1.3

 Table III.13 : Molecular weights and polydispersity values from GPC Analysis

Notes : PD = polydispersity

It has to be underlined that some samples were not completely soluble in DMF, resulting probably in the neglect of higher molecular weight polymers.

If we use the GPC as a comparative technique, the following point can be made :

- In the case of poly(2-methoxyaniline), viscosity measurements, vapour pressure analysis and GPC analysis can be compared (molecular weights in g.mol⁻¹). Doped sample : GPC (Rapra) $\overline{Mn} = 1000$, $\overline{Mw} = 3600$; VPO $\overline{Mn} = 2825$ Undoped sample : GPC (Rapra) $\overline{Mn} = 1700$, $\overline{Mw} = 11700$; Viscometry $\overline{Mv} = 9410$ The first set of results is not very consistent, indeed the number average molecular weight of the VPO method is three times the value by GPC.

The second set of results is more consistent as the viscosity average number value is intermediate between the number average molecular weight and the weight average molecular weight values, which is quite usual behaviour.

The main conclusion drawn is a careful interpretation of the values given.

- When the side-chain was bigger than the well-known methoxy and ethoxy goups, the molecular weight distribution was no longer a one peak system any more but the samples were constituted of mixtures of monomers, oligomers and a smaller proportion of higher polymers. This information needs to be kept in mind during the interpretation of the following results ; in fact a lot of the properties such as thermal analysis and conductivity will be highly influenced by the proportion of oligomers in the samples. A macromolecule can show the distinctive properties of a polymer only if there is more than a certain number of repeat units (usually over 100 in classical polymer science but in our case we assumed that 10-20 repeat units will be enough for preliminary investigation). Most of our samples were therefore washed extensively in order to remove the lower oligomers as much as possible before further investigation.

III.3.5. Thermal Analysis

At sufficiently low temperatures all polymers are hard rigid solids. As the temperature rises, each polymer eventually obtains sufficient thermal energy to enable its chains to move freely enough for it to behave like a viscous liquid (assuming no degradation has occurred). There are two ways in which a polymer can pass from the solid to the liquid phase, depending on the organisation of the chains in the sample.

A polymer may be completely amorphous in the solid state, which means that the chains in the specimen are arranged in a random fashion. The polymer is therefore a glass at low temperatures. Large-scale chain motion becomes possible as it passes through a temperature T_g , called the glass transition temperature, beyond which the polymer softens and becomes rubber-like.

If a polymer could also be perfectly crystalline, all the chains would be incorporated in regions of three-dimensional order and no glass transition would be observed, because of the absence of disordered chains in the sample. The crystalline polymer, on heating, would exhibit a melting point T_m at which the polymer would become a liquid.

Perfectly crystalline polymers are not encountered in practice and instead polymers may contain varying proportions of ordered and disordered regions in the sample. Therefore, these semi-crystalline polymers usually will exhibit both T_g and T_m .

The substituted polyanilines synthesised in the present project are also potential liquid crystalline polymers.

In order to characterise the melting, glass-transition and liquid crystalline transition processes, a broad range of thermal analysis techniques were used in complementary fashion.

At first, investigation of the thermal stability of some alkoxy and liquid crystal substituted polyanilines was carried out by thermogravimetry.

Secondly, the alkoxy and liquid crystalline side chain polyanilines were studied by differential scanning calorimetry (DSC) in order to assess the behaviour of the glass transition temperature with increasing side chain length, and then to identify the possible liquid crystalline transition temperatures.

Studies on liquid crystal polymers have shown that the liquid crystalline phases in polymeric materials are sometimes difficult to identify unequivocally. Several techniques can be used that provide information on the nature of the molecular organisation within the

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phase, and if used in a complementary fashion these can provide reliable information on the state of order of the mesogenic groups. Polarised hot-stage optical microscopy was therefore combined with differential scanning calorimetry. The nature of the phases can often be identified by observing the characteristic textures shown by thin layers of the polymer when viewed through a microscope using a linearly polarised light source. The DSC technique is used as a means of analysing thermotropic mesophase transitions ; they are identified in most cases as first-order endothermic transitions.

III.3.5.1. TGA, DSC and TMA

(i) Thermogravimetric Analysis (TGA)

Thermogravimetry is a technique in which the mass of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.

The substituted polyanilines have been studied under an atmosphere of nitrogen and the results obtained are given in Table III.14.

The first weight loss is due to moisture, free HCl and unreacted monomer. The second one is due to the elimination of the dopant (combined HCl) which is in the case of the protonated polymer more important. The third loss is due to the pyrolysis of the polymer ; all the polymers in this project were found to be stable up to 300°C. Polymers with transition temperatures up to 300°C could therefore be studied by thermal analysis techniques without destroying the polymer backbone.

It has to be emphasised that the polymers (108)-(111) synthesised by emulsion polymerisation have a starting second weight loss step at much higher temperatures (200-300°C) than for polymers synthesised only in acidic media (140-300°C). It appears that the composition of the dopant was not only HCl but a mixture of HCl and dodecylbenzenesulphonic acid.

The results found were in agreement with the literature on doped and undoped PANI. Examples of the thermogravimetric (TG) and differential thermogravimetric (DTG) curves obtained for doped and undoped poly(2-ethoxyaniline) (101), the carboxylic acid polymer

(109) and the polymer (111) are illustrated in Figures III.28-31.

Polymer	1 st weight loss step	2 nd weight loss step	3 rd weight loss step
(100) - (101)	30-130°C	130-310°C	310-440°C
protonated	15%	14%	20%
(100) - (101)	25-130°C	130-310°C	310-440°C
deprotonated	3%	4%	30%
(102) - (104)	30-130°C	130-310°C	310-500°C
protonated	5%	18%	35%
(102) - (104)	30-130°C	130-310°C	310-500°C
deprotonated	2% .	10%	45%
(107)	30-140°C	140-310°C	310-450°C
(protonated)	2%	25%	45%
(108)	30-200°C	200-300°C	300-440°C
(protonated)	1%	15%	50%
(109)	30-230°C	230-320°C	320-450°C
(protonated)	7%	11%	40%
(110)	30-230°C	230-300°C	300-440°C
(protonated)	4%	30%	35%
(111)	30-230°C	230-310°C	310-440°C
(protonated)	3%	25%	45%

 Table III.14 : Thermogravimetry Analysis of Substituted Polyanilines

Notes : The polymers (107) - (111) have been analysed "as-prepared" and should be protonated.



Figure III.28 : TG and DTG Curves of Doped Poly(2-ethoxyaniline) (101)



Figure III.29 : TG and DTG Curves of Undoped Poly(2-ethoxyaniline)



Figure III.30 : TG and DTG Curves of Polymer (109)



Figure III.31 : TG and DTG Curves of Polymer (111)

(ii) Differential Scanning Calorimetry (DSC) and Thermomechanical Analysis (TMA)

DSC is a technique in which the difference in heat flow to a sample and to a reference is monitored against temperature, while the temperature of the sample, in a specified atmosphere, is programmed. TMA is a technique in which the deformation of the sample under non-oscillating stress is monitored against temperature, while the temperature of the sample, in a specified atmosphere, is programmed.

TMA was used as a complementary technique for only few polymers to identify their glass transition temperature, but the equipment was not found to be sensitive enough for our measurements. This was probably due also to the general difficulty in interpreting the PANI curves. In fact, the glass transition temperature, T_g , of the emeraldine base films of PANI was observed for the first time at around 140°C indicated by sharp decreases in the storage modulus and a peak of the loss modulus in dynamic mechanical analysis (DMA)³¹⁸. DSC studies of PANI by Chan et al.²⁴⁰ did not report a T_g . They concluded that T_g was not observed because it was masked by the other overlapping enthalpic changes in the polymer. In fact, two endothermic peaks were observed on heating for PANI. The first broad endothermic peak, of enthalpy change 192 J.g⁻¹, was observed between 94-212°C with a peak temperature at 141°C. This was attributed to the energy required to expel the dopant. The second smaller endothermic peak was observed between 270-312°C with a peak temperature at 293°C. This was attributed to morphological changes within the polymer matrix, but no visual changes were detected by hot-stage microscopy.

The results of the DSC analysis, under an atmosphere of nitrogen, for the synthesised substituted polyanilines are given in Table III.15. Some of the DSC curves are available in Appendix 4. The DSC results were very difficult to interpret, in fact no T_g curve shape were observed in all the recorded samples. Instead, a first endothermic peak has been observed for poly(2-alkoxyanilines) with decreasing peak temperature as the alkoxy group lengthens (from 135°C for undoped poly(2-methoxyaniline) to 58°C for undoped poly(2-pentoxyaniline). Even if the curves were not characteristic of a glass transition, this peak is attributed mainly to the softening of the polymer going from a crystalline to a glassy state. Glass transition temperatures of the synthesised liquid crystalline polymers should then occur at temperature no more than 140°C (PANI T_g). But in the case of the side chain liquid crystal groups, interpretation was even more complex and microscope analysis was required for better understanding. The conclusions are given in the next section.

Polymer State		1 st transition	2 nd transition	3 rd transition
Polymer	State	peak (°C)	peak (°C)	peak (°C)
	damad	sharp endo		
100	uopeu	128 (peak temp.)		
100	undonad	110-175 (endo)	175-245 (exo)	
	unuopeu	135 (peak temp.)	220 (peak temp.)	
	doned	115-185 (endo)		245-275 (endo)
101	doped	135 (peak temp.)		265 (peak temp.)
101	undoped	115-160 (endo)	160-215 (exo)	
	undoped	140 (peak temp.)	180 (peak temp.)	
	doped	70-145 (exo)	145-200 (endo)	
102	uopea	100 (peak temp.)	175 (peak temp.)	
_ 102	undoned	100-120 (endo)	120-150 (exo)	sharp endo
	undoped	113 (peak temp.)	130 (peak temp.)	154 (peak temp.)
	doped	90-140 (exo)	140-180 (endo)	
103	doped	120 (peak temp.)	160 (peak temp.)	
	undoned	80-125 (endo)	125-190 (exo)	250-300 (endo)
	undoped	100 (peak temp.)	155 (peak temp.)	280 (peak temp.)
104	undoned	55-65 (endo)	230-245 (endo)	262-300 (endo)
104	undoped	58 (peak temp.)	232 (peak temp.)	280 (peak temp.)
105	doped		180-270 (exo)	270-330 (endo)
105	uopeu		225 (peak temp.)	270-330 (endo)
	orga. acid	sharp endo	55-120 (endo)	sharp endo
108	undoped	46 (peak temp.)	90 (peak temp.)	224 (peak temp.)
100	emulsion	sharp endo	115-175 (exo)	
	doped	42 (peak temp.)	145 (peak temp.)	
100	doped	125-150 (endo)	exo	210-250 (endo)
109	uopeu	139 (peak temp.)	200 (peak temp.)	240 (peak temp.)
110	doned	65-125 (endo)	130-160 (endo)	
110	uopeu	105 (peak temp.)	134 (peak temp.)	
111	doned	endo	sharp endo	170-300 (exc)
111	doped	50 (peak temp.)	134 (peak temp.)	170-300 (CAU)

Table III.15 : DSC Analysis of Substituted Polyanilines

III.3.5.2. Optical Microscopy Investigation

The polymers (108), (109), (110) and (111) have been investigated by hot stage polarising microscopy to identify any phase transitions and determine transition temperatures which could not be seen by DSC, the results are listed in Table III.16.

Polymer	T _g (°C)	g-N (°C)	N-I (°C)	I-N (°C)
108	1	1	1	1
109	139	225	261	246
110	115	120	175	.155
111	60	1	1	1

Table III.16 : Transition Temperatures (°C) of Polymers (108)-(111)

Notes :

g = glass

Nothing was observed for polymer (108)

Studies using polarised light on the hot stage microscope revealed evidence of liquid crystalline behaviour in two polymer systems (109) and (110). In both cases, a nematic Schlieren texture was observed, which flashed when subjected to mechanical stress, providing evidence of liquid crystalline behaviour. These polymers had to be annealed for about one hour on the hot-stage before the liquid crystal textures developed fully. Photograph III.13 shows the nematic Schlieren texture of polymer (110) after annealing.

The fact that the polymers did not show liquid crystal behaviour immediately explain the DSC results which shows endothermic peaks on a broad range of temperature (210-250°C for polymer (109) and 130-160°C for polymer (110)) instead of sharp peaks. The softening of the polymers was also observed by DSC at 139°C for polymer (109), 105°C for (110 and 50°C for (111), which is well in relation with the microscope observations. The T_g values for the side chain liquid crystal polymers range from 50°C to 140°C depending on the side chain type and obviously on the molecular weights of the polymers. These values are therefore very difficult to predict and can be influenced by a lot of parameters.

Furthermore, the phase transitions in polymeric materials were usually difficult to identify because the polymer samples had a broad distribution of molecular masses, so the phase transition temperature was not as precisely defined as in materials consisting of identical molecules. The exact temperature at which a polymer changes phase depends on the chain length. If the sample contains molecules with different numbers of monomers, all molecules do not behave identically when the temperature is changed. The result is a phase transition that is spread over a range of temperatures. It has been shown by gel permeation chromatography that our polymers had been synthesised with a wide range of molecular weights, so the phase transitions were spread over a range of temperatures and are therefore difficult to assess. Therefore it was necessary to quote both the nematic to isotropic and the isotropic to nematic transition temperatures. In addition, the observed hysteresis was normally 15-20°C, due in part to the slow development of the textures. Moreover, the transitions were detected optically which involves some degree of personal judgement.

The aim of this thesis was to synthesise side chain liquid crystalline conducting polymers based on polyaniline. The two polymers (109) and (110) illustrated in Figure III.32 were liquid crystalline, and having conjugated polymer backbones, they were potential semi-conductors ; the next step was to study the electrical conductivities and their temperature dependences.



Figure III.32 : Liquid Crystal Polymers (109) and (110)



Photograph III.13 : Nematic Schlieren Texture of Polymer (110)

III.3.6. Conductivity

III.3.6.1. Room Temperature Measurements

The electrical properties of poly(2-alkoxyanilines) and the liquid crystalline side chain polyanilines have been studied. The DC conductivities of pressed pellets or films were measured using the van der Pauw technique as 4-probes, 2-probes or interdigitated cells.

Room temperature results are given in Table III.17 depending on the state of protonation and the method used.

Table Notes :

S.C = Semi-Conductor

I = Insulator

The term "doped state" in brackets means that the conductivity of the polymer had been measured from the polymer as synthesised without any additional reprotonation, whereas " H_2SO_4 doped" means that the polymer film had been reprotonated by dry sulphuric acid vapour during two days under a static vacuum equal to 0.1 mmHg and a temperature of 35°C.

Polymer	State	Method	Conductivity (S m ⁻¹)	Type of material
100	protonated deprotonated	4 probes	8.2 10 ⁻⁹	S.C I
101	protonated deprotonated	4 probes	0.12 10 ⁻⁹	S.C I
102	protonated deprotonated	4 probes	0.19 10 ⁻⁹	S.C I
103	protonated deprotonated	4 probes	0.14 10 ⁻⁹	S.C I
104	protonated deprotonated	4 probes	9x10 ⁻⁴ 10 ⁻¹¹	S.C I
107	(protonated)	2 probes	3x10-6	S.C
108	(protonated)	2 probes	6x10 ⁻⁸	I
109	(protonated) H_2SO_4 proto. deprotonated	2 probes	2x10 ⁻⁴ 0.12 6x10 ⁻¹⁰	S.C S.C I
110	(protonated) deprotonated	interdigitated cell 2 probes	7x10 ⁻⁴ 2x10 ⁻¹⁰	S.C I
111	deprotonated	2 probes	4x10 ⁻¹⁰	I

Table III.17 : Conductivity Values (S cm⁻¹) at Room Temperature

The first conclusion which can be drawn from the results confirmed the theory elaborated on pages 48-52, that the protonated (doped) forms of our polyaniline compounds were semi-conductors whereas the deprotonated (undoped) forms were insulators. The carboxylic acid polymer (109) was a typical example with a conductivity of $2x10^{-4}$ S m⁻¹ when measured from the polymer as synthesised, but when the film was deprotonated by use of a base (ammonia) the conductivity dropped drastically to $6x10^{-10}$ S m⁻¹ to form an insulating polymer. When exposed to H_2SO_4 vapour the polymer film exhibited a conductivity as high as 0.12 S m⁻¹, typical for quite a good semi-conductor. Therefore, the polymers synthesised needed to be in their protonated (salt) form to have the conductivity properties of a semi-conductor.

III.3.6.2. Conductivity as a Function of Temperature

The two polymers (109) and (110) showed liquid crystalline and semi-conducting properties. The aim of this thesis was to improve the electrical properties of the polyaniline backbone by introducing liquid crystalline groups as side chains. The conductivity of these two polymers was therefore studied as a function of temperature to investigate the possible influence of the mesogenic phases on the polymer backbone. If the liquid crystal groups become ordered at the transition temperature it was hoped that this would allow the backbone to improve its order and so the delocalisation of the electrons might be increased. A film of polymer (109) and (110) was made on a platinum interdigitated ceramic cell as described in page 76 seated on a hot-stage with precise temperature control.

Initially, we determined the conductivity of the polymers at different temperatures by the 2-probe method given on page 76 and the results are listed in Table III.18

Delumon			Conductiv	ity (S m ⁻¹)		
rotymer	20°C	70°C	120°C	170°C	220°C	260°C .
(109)	1.2x10 ⁻⁵	4.1x10 ⁻⁵	5x10 ⁻⁵	3.2x10 ⁻⁴	8x10 ⁻⁴	3x10 ⁻⁴
(110)	8x10 ⁻⁴		8x10 ⁻⁴	9x10 ⁻⁴	4x10 ⁻⁵	

Table III.18 : Conductivity at Various Temperatures for Polymer (109) and (110)

The applied voltage was then fixed at 100 V and the current and the resistivity recorded as a function of the temperature on heating and cooling. Figure III.33 represents two heating and cooling cycles for the carboxylic acid polymer (109).



Figure III.33 : Current (10⁻⁹ A) against Temperature for Polymer (109)

During the first cycle there is a large increase in the current (and hence a large increase in conductivity) as the temperature approaches the liquid crystalline transition at about 220°C, then during the second cycle there is a corresponding increase but much smaller. The difference between the first and second cycle may be due to the loss of protonation, indeed HCl is evolved at about 140°C. The most important point is that the current increases substantially at a temperature corresponding to the transition from a soft amorphous state to a nematic liquid crystalline phase.

The same measurements were realised with polymer (110). An increase in current was also observed during the first cycle as the temperature reached 130-140°C but not as distinctively as for polymer (109). This increase was stable up to 170° C then a significant decrease in current was observed above this temperature. During the second cycle no increase was observed and the current even dropped drastically (large increase in resistivity), and conductivities as low as $3x10^{-6}$ S m⁻¹ were measured. Like in the first case, this can be explained by the lost of protonation (HCl doping), but the main point is the increase in current at a temperature corresponding to the transition from the glassy state to

a nematic phase.

In both polymers (109) and (110) which exhibit liquid crystalline properties, the electrical conductivity significantly increases as the polymer reaches the transition temperature, by a factor of 67 for polymer (109) and 2 for polymer (110). The only problem remaining is the thermal de-doping of the polymer, in fact as the liquid crystal transition temperature is reached the conductivity increases due to the better ordering of the polymer, but as it tends to do so the protonation is lost, causing a dramatic decrease in the conductivity. Therefore, polymers doped with less volatile dopant than HCl have to be produced in order to obtain long term repeatable results. Work with dried concentrated sulphuric acid vapour as dopant was initiated in order to study the stability of the polymers in such strong acid vapours. A room temperature conductivity as high as 0.12 S m⁻¹ was observed for polymer (109).

III.3.7. Laser Alignment

Attempts to organise side chain liquid crystalline polymers have been almost entirely limited to those containing saturated backbones^{319,320,321,322}. The liquid crystalline moieties in these polymers may be aligned at the clearing temperature in the presence of magnetic or electric fields, or by differential cooling after laser addressing. The contrast between the aligned and non-aligned regions have been reported³²² to be extremely high making these compounds of technological interest as optical storage devices.

A laser has been used to directly write onto the liquid crystalline side chain polyanilines synthesised, in order to align the polymers and enhance the conductivity. Photograph III.14 shows the results of a slow diagonal movement of polymer (109) relative to the laser beam. The width of the aligned areas produced (15 μ m) was in keeping with the diameter of the focused laser beam. The irradiated region was viewed microscopically between crossed polars, and was seen to be birefringent, implying that the optically anisotropic mesogenic side groups were aligned in a plane perpendicular to the incident laser beam. This is thought to have been caused by the gaussian temperature profile across the track, where cooling occurs in the outer edges initially undergoing the isotropic to nematic transition, followed by cooling of the higher temperature region at the centre. The aligned tracks could be erased either by heating the entire sample to the isotropic phase

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or by dissolving the sample and recasting a film. This process could be repeated several times without any apparent loss in alignment capability.



Photograph III.14 : Laser written texture on a film of polymer (109)

The laser was then used to produce a set of about 50 parallel lines of an undoped film of polymer (109). After doping using H₂SO₄ vapour, the electrical conductivity was measured using the two probes method. σ_{\parallel} and σ_{\perp} represent the conductivities parallel and perpendicular to the direction of the laser scans.

	$\boldsymbol{\sigma}_{\#}$ (S m ⁻¹)	$\boldsymbol{\sigma}_{\perp}$ (S m ⁻¹)	Anisotropy
Polymer (109)	4x10 ⁻⁵	2x10 ⁻⁵	2

A minor but observable anisotropy in the conductivity values has been shown. The conductivity values were relatively low for sulphuric acid doping compared with the previous investigations on different films (0.12 S m⁻¹). It was assumed that the film was not fully protonated.

The results were preliminary work on the subject but since an anisotropy was still shown even on partially protonated films of polymer (109), it is anticipated that this technique could be of great potential interest as a method of local conductivity enhancement.
CHAPTER IV CONCLUSIONS AND FURTHER WORK

IV.1 : CONCLUSIONS

The work presented in this thesis involved the synthesis of side chain liquid crystalline conducting polymers based on polyaniline and the investigation of their chemical and physical properties.

The first goal of this research was to synthesise some aniline monomers with mesogenic groups attached in the *ortho*-position. For ease of synthesis, the different liquid crystal moieties were attached to nitrobenzene via a flexible spacer. A large number of suitable *ortho*-substituted nitrobenzenes with potential liquid crystalline properties were synthesised and investigated.

Study of the 4-methoxyphenyl 4-[x-(2-nitrophenoxy)alkoxy]benzoate series, with x = 2-10, revealed that only the molecules with even spacer lengths showed liquid crystal behaviour whereas the ones with odd spacers length did not. All the even molecules were nematic in character, but with low transition temperatures ranging from 54 to 62°C.

Some substituted biphenyl nitrobenzenes were also synthesised and 4-cyano 4'-[6-(2-nitrophenoxy)hexoxy]biphenyl (7b) exhibited a monotropic nematic phase at 55.3°C.

A large variety of other *ortho*-substituted nitrobenzenes with higher transition temperatures were also synthesised (compounds (9)-(12), (14) and (22)) and all exhibited liquid crystalline properties. Depending on the structure, nematic and some smectic phases were characterised by microscopy and differential scanning calorimetry.

The *ortho*-substituted nitrobenzene molecules were subsequently reduced to the required anilines. Investigation of their properties revealed similar liquid crystalline behaviour to their respective nitro-compounds.

Once these mesogenic *ortho*-substituted aniline precursors had been achieved, the second goal of this thesis was the polymerisation of these monomers. Electropolymerisation as well as oxidative chemical polymerisation was studied. 2-Alkoxyaniline monomers were successfully polymerised by the two classical methods well known for the synthesis of polyaniline.

Cyclic voltammetry of some of the liquid crystal substituted anilines (24e) and (26) was investigated but even when some oxido-reduction peaks were revealed, no polymer film was formed.

Oxidative chemical polymerisation for the 2-substituted liquid crystal anilines had to be modified due to the low solubility of the monomers in acidic aqueous media. An emulsion polymerisation system was devised and several potentially liquid crystalline polymers were synthesised. The polymers obtained were then fully characterised by spectroscopic analysis.

The third part of this thesis describes an investigation of the properties of these polymers. Whereas poly(2-alkoxyanilines) were mainly soluble in a limited range of solvents such as DMF and DMSO and slightly soluble in CHCl₃ and THF, the potentially liquid crystal polymers synthesised were soluble in all these four solvents. UV/visible analysis revealed a relatively large band gap of 3.4 eV for the liquid crystal polymers compared with poly(2-alkoxyaniline). Molecular weight investigations of the liquid crystal polymers revealed the presence, in all samples, of some oligomers and some higher polymers in smaller proportions. The polymerisation will need to be further optimised in order to allow the oligomers to react and to produce polymers with higher molecular weights. The stability of the synthesised polymers up to 300°C was characterised by thermogravimetric analysis.

DSC combined with microscopic investigation showed that two polymers (109) and (110) exhibited liquid crystalline properties. These were nematic in character.



Electrical conductivity studies revealed a drop in conductivity from the poly(2-alkoxyanilines) to the side chain liquid crystal polymers. These first results were contradicted by the values obtained for the film reprotonated by H_2SO_4 vapour of polymer (109) which exhibited a conductivity as high as 0.12 S m⁻¹. This latest result suggested that the polymers as obtained initially were probably not fully doped (protonated).

A study of the conductivity as a function of the temperature for polymers (109) and (110) revealed that there was an increase in conductivity at a temperature corresponding to the transition from the amorphous ("rubbery") state to the nematic liquid crystal phase.

A reasonable conclusion is that when the liquid crystal side chains are ordered, they can influence the order of the polymer backbone and hence enhance its conductivity.

Films of polymer (109) were laser aligned and a study of the conductivity along or across the written lines revealed a small anisotropy. Further investigation of this technique could arouse a great interest in molecular electronics as a method of localised conductivity enhancement.

IV.2 : FURTHER WORK

Much of the work performed in this study could be carried further. The author suggests the following main ideas :

i) Further studies should be made on the emulsion polymerisation system in order to produce more regular polymers with higher molecular weights.

ii) Protonation of the liquid crystal polymers with less volatile dopants such as concentrated sulphuric acid or toluene sulphonic acid should be fully investigated in order to produce doped polymer films stable at temperatures up to 200°C.

iii) Laser alignment of the liquid crystal polymers as a way to enhance the conductivity should be further investigated on fully protonated samples.

iv) Investigation of the polymers under electric or magnetic fields could be studied as another way to align these polymers and enhance the conductivity.



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COURSES ATTENDED DURING Ph D

During the course of my research work at Kingston University (October 1992 to December 1995) I have attended nearly all of the colloquia arranged within the Department of Applied Chemistry as part of my coursework requirements. I gave two talks, the first one on "Polymer Liquid Crystals" on the 25th March 1993 and the second one on "Synthesis of Side Chain Liquid Crystalline Conducting Polymers" on the 12th October 1995.

In addition I have also attended the following talks organised by different societies :

- i) "Liquid Crystals" by Dr R. Richardson at SCI London, 27/10/1992
- ii) "Prediction of Liquid Crystallinity and Associated Structures in Polymers" by Prof. A.H. Windle at the University of Surrey, 25/11/1992
- iii) "Liquid Crystals" by G.W. Gray at the Royal Society, London, / /199

I attended the two days workshop of the British liquid crystal society organised at Leeds University between the 16th and 17th of December 1992. I also went to the British liquid crystal society conference in Hull between the 28th and 30th March 1994.

I attended the International Conference on Liquid Crystal Polymers held in Beijing (China) 6-9th September 1994, where I presented a poster entitled "Synthesis and Properties of Liquid Crystalline Conducting Polymers".

I also attended the Second International Conference on Materials Chemistry held at the University of Kent at Canterbury 17-21 July 1995, where I presented a poster entitled "Synthesis and Properties of Liquid Crystalline Monomers and Conducting Polymers".

In addition to these conferences, I have also attended a one day symposium on Polymer Liquid Crystals held at the Institute of Physics, London, the 8th February 1995.

X-RAY DIFFRACTION RESULTS

X-ray crystallography was investigated for monomers (9) and (14) in order to assess with more precision the different phases observed by hot-stage polarised microscopy and differential scanning calorimetry.



Compound (9) was assessed as follows :

$C - S_c$	$S_{G} - S_{C}$	$S_{c} - N$	N — I	$S_G - C$
157.3°C	(146°C)	214.0°C	227.3°C	118.0°C

Compound (14) was assessed as follows :

It exhibited two crystal phases but no liquid crystalline phases were identified.





LOG M





DSC of Polymers







PUBLICATIONS

L.I. Gabaston, P.J.S. Foot, J.W. Brown, Proc. Int. Conf. Liq. Cryst. Polymers, Beijing (China), p. 97, 6-9 Sept. (1994)

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