

Synthesis and Properties of Novel Thiophene-Based Liquid Crystalline

Conducting Polymers (LCCPs)

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Abstract

Side chain liquid crystalline polythiophenes have been synthesised and investigated in order to study the effects of liquid crystalline moieties on the polymer and their possible effect on the electronic properties.

Initially some mesogenic groups with a structure of two benzene rings were synthesised as the rigid core of the mesogen. This synthesis was followed by the attachment of mesogens through a six-methylene unit spacer to 3-thiophene methanol and the preparation of thiophene-based monomers. The chemical structure of the prepared monomers was confirmed by characterisation techniques such as NMR, GCMS and ATR etc. The investigation of the liquid crystalline behaviour of the monomers was carried out by polarised hot-stage optical microscopy (HSM), differential scanning calorimetry (DSC) and X-Ray diffractometry (XRD)

The resulting monomers were polymerised chemically into the form of powders in order to measure their conductivity. A thin film of polymers was prepared on silicon and ITO glass substrate. The liquid crystalline properties of the polymer films were studied using DSC and HSM. XRD was used to investigate the effect of a magnetic field on the monomers and polymers.

Polymerisation and electroactivity of monomers were studied on an ITO glass substrate by cyclic voltammetry technique. Polymers were modelled using Quantum Cache (Scigress) to predict their geometry and the calculated molecular dimensions were compared with the results of the X-ray diffraction analysis.

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ABBREVIATIONS

GCMS	gas chromatography-mass spectroscopy
HSM	polarised hot-stage optical microscopy
ATR	Attenuated total reflectance
DSC	differential scanning calorimetry
XRD	X-Ray diffractometry
ΙΤΟ	indium-tin oxide
НОМО	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
LEDs	light emitting diodes
PEDOT	poly(3,4-ethylenedioxythiophene)
LG	linkage group
LCDs	liquid crystal displays
SCLCPs	side-chain liquid crystalline polymers
LC	liquid crystalline
NMR	Nuclear magnetic resonance
DMSO	dimethyl sulfoxide
THF	tetrahydrofuran
DMF	dimethylformamide
TGA	thermogravimetric analysis
UV	Ultraviolet
CV	cyclic voltammetry
MF	magnetic field
RPM	revolution per minute
SCE	saturated calomel electrode
TBAF	tetrabutylammonium tetrafluoroborate
Α.	Angstrom (0.1 nanometre)

Chapter I:

Introduction

1.1 Conducting Polymers

Polymers have generally been used in electrical and electronic applications as insulators as they have localized electrons and are unable to provide electrons or any other charge carriers to move along the polymer chain. Since the first report of a conducting polymer in 1977 by Shirakawa, Heeger and MacDiarmid¹, conducting polymers have attracted the interest of researchers as they show interesting electrical, electronic, magnetic and optical properties. The possibility of combining in these new materials the properties of organic polymers and the electronic properties of semiconductors has been the driving force for various applications²⁻⁴.

The search for conducting polymers became exciting when a large increase in conductivity $(1 \times 10^{5} \text{ Sm}^{-1})$ was observed in polyacetylene as a result of a chemical doping process. Despite being the highest crystalline conducting polymers, polythiophenes can be easily oxidised and are sensitive to humidity ⁵. As a result, the synthesis of conjugated polymers was then rapidly extended to other aromatic and heterocyclic compounds such as thiophene, furan, pyrrole, aniline etc.

Polypyrrole

Polythiophene

Polyacetylene

Polyaniline

Figure 1: Examples of conjugated polymers

However the application of conducting polymers is restricted due to their intractability and insolubility, although this drawback has been resolved by the use of substituted polythiophenes, polyaniline derivatives and other conjugated polymers. The resulting polymers were not only fusible and soluble but also able to be characterized by chemical and physical methods.

Among conducting polymers, polythiophene (PT) has always been one of the most promising candidates due to its high stability in the doped and undoped states and the simplicity of modification of its structure. Researchers have intensively studied the highly processable poly(3-alkylthiophene)s and other derivatives in the last few years ⁶.



Figure 2: Measured magnitudes of the room-temperature conductivities of different conducting polymers: polythiophene (PT), poly(3-methyl thiophene) (PMeT), poly(3,4ethylenedioxythiophene) (PEDOT) and poly(p-phenylene) (PPP)⁷

1.1.1 Mechanism of Conductivity in Conjugated Polymers

A π -conjugated backbone structure of a polymer is not sufficient to produce appreciable conductivity on its own. Partial charge extraction from the polymer chain is also required, which is achieved by a chemical or an electrochemical process referred to as doping. By exposing a π -conjugated polymer to a dopant, it is possible to add or remove an electron from the conjugated polymer backbone chain. This process will generate a positive hole or a negative charge, resulting in a polaron or bipolaron defect on the polymer chain⁸.



Figure 3: Polythiophene oxidation, forming a polaron and then a bipolaron

The high density of electrons and the zero energy gap in metals make them conductive. These features in metals make it possible for electrons to move freely from the valence band (which extends up to the highest occupied molecular orbital) to the conduction band (which begins at the lowest unoccupied molecular orbital) through the lattice. Some aspects of the conduction in conjugated polymers can be elucidated using the band theory. When an electron is removed during the doping process from the conjugated polymer, this will cause an alteration in the polymer lattice, and consequently an upward shift of the highest occupied molecular orbital (HOMO) and downward shift of the lowest unoccupied molecular orbital (LUMO). This ultimately leads to a smaller energy gap and a conductivity that can be almost as good as those of metals.

In heteroaromatic polymers like polypyrrole, by chemical or electrochemical redox doping it is possible to extract electrons from the polymer chain (Fig 3). During the doping process, the conductivity of neutral polypyrrole is remarkably changed from an insulating regime to a metallic one 9,10 .



Figure 4: Electronic energy diagrams for polypyrrole

1.1.2 Chemical Polymerisation

Polythiophene can be synthesised from the monomer, using a chemical oxidant. Due to the limited solubility of thiophene, the process must be carried out in nonaqueous media. Copper (II) perchlorate has been used as an oxidizing agent ¹¹. Alternatively, a Grignard or similar coupling reaction can be used to synthesise polythiophene ¹². Some workers ¹³ have used a chemical polymerization process that ensures the production of well-defined head- to-tail (HT)-coupled poly(3-alkylthiophenes).

Making controlled chemical synthesis of polythiophenes was first reported in 1980; which metal-catalyzed coupling of 2,5-dibromothiophene was used. The dibromothiophene substrate was first reacted with Mg in THF, replacing either the 2- or 5-bromo substituent with MgBr^{14,15}.

The oxidative polymerization of a thiophene monomer has also been applied to make polythiophene, for instance using $FeCl_3$ in organic solvents such as chloroform. MoCl₅ has also been employed as both the oxidant and dopant ^{16,17}.

Despite the low molecular weight of polythiophenes, unsubstituted polythiophenes are insoluble in THF and other common organic solvents, and are also infusible. The poor processability has led to studies of alkyl- and alkoxy-substituted polythiophenes in order to improve their solubility and processibility in organic solvents ¹⁸.



Figure 5: Polymerization mechanism of thiophene ¹⁹.

In the chemical method, a monomer such as thiophene is often polymerized in nonaqueous solutions with an oxidant like iron (III) chloride or molybdenum (V) chloride (figure 5). The chemical method is suitable for commercial mass production because it is easy to control the molecular weight and structure 20 .

1.1.3 Electrochemical Polymerisation

Conducting polymers can be synthesised chemically or electrochemically. Electrochemical polymerisation is very popular since it is a clean method and the thickness of the polymer growth and the morphology can be controlled. Films of electronically conducting polymers are generally deposited onto a supporting electrode surface by anodic oxidation (electropolymerization) of the corresponding monomer in the presence of an electrolyte solution. In this method, the monomer, dissolved in an appropriate solvent containing the desired anionic doping salt, is oxidized at the surface of working electrode by application of an anodic potential (oxidation). As a result of the initial oxidation, the radical cation of the monomer is formed and reacts with other monomers present in solution to form oligomeric products and then the polymer. The extended conjugation in the polymer results in lowering of the oxidation potential compared to the monomer. Therefore, the synthesis and doping of the polymer are generally done simultaneously. The anion is incorporated into the polymer to ensure the electrical neutrality of the film and, at the end of the reaction, a polymeric film of controllable thickness is formed at the anode. The anode can be made of a variety of materials including platinum, gold, glassy carbon, and tin or indium-tin oxide (ITO) coated glass 21,22 .



Figure 6: A three electrode cell for electrochemical polymerisation. The working, counter and reference electrodes are denoted as WE, CE and RE, respectively.

The electropolymerization is generally achieved by potentiostatic (constant potential) or galvanostatic (constant current) methods. A typical setup (three-electrode cell) for these measurements is schematically shown in Fig 6.

1.1.4 Applications of Conducting Polymers:

The main applications for conducting polymers are based on their electroactivity and conductive properties. By coating an insulator with a very thin layer of conducting polymer, it is possible to prevent the build-up of static electricity. Electromagnetic radiation generated from electrical devices can be absorbed by coating the inside of the plastic casing with a conductive surface ²³. There are some other applications including anti-corrosion coatings, sensors, batteries and supercapacitors, and more recently light emitting diodes (LEDs) ²⁴, electrochromic devices ²⁵ and transparent

electrode materials. Among different conducting polymers, great attention has been recently devoted to poly(3,4-ethylenedioxythiophene) (PEDOT), which shows quite high conductivity, stability and optical transparency in its conducting state ²⁶.

The application of conducting polymers for metallic corrosion protection has been an interesting subject. A great amount of work has been done on the protection of metals like Fe, Al, Cu etc using conducting polymers like polyaniline, polypyrrole, polythiophene and their derivatives ²⁷.

The unique electrical, electrochemical and optical properties of conducting polymers have made them interesting candidates for electrochemical sensors, potentiometric sensors, ion sensors, biosensors, etc. By using their capabilities, it is possible to convert chemical information like concentration, activity and partial pressure into electrical or optical signals 28 .

Since the first discovery of electroluminescence in poly(p-phenylene vinylene), luminescent polymers like poly(p-phenylene vinylene), polythiophene derivatives, polyfluorene derivatives etc have attracted much attention in the research area ²⁹.

To improve the poor mechanical properties and processibility of conducting polymers, conducting polymer composites have combined the electrical properties of polymers like polypyrroles, polythiophenes and polyaniline with the mechanical properties of polystyrene, polyethylene oxide, etc. The resulting polymer blends have practical applications in the field of electromagnetic shielding, microwave absorption, heating elements conducting glues, etc 30 .

There have also been intensive research activities on rechargeable lithium cells by the application of conducting polymers like polyacetylene and polyaniline. The electrochemical doping and undoping of conducting polymers are used in this application ³¹.

Several electrochromic devices based on polyaniline have been developed in the visible light range. The device changes from colourless to pale blue by a cathodic lithium ion incorporation 32 .

1.2 Liquid Crystals

Friedrich Reinitzer in 1888 noticed that cholesteryl benzoate, an ester of cholesterol had more than one melting point. In 1890 Lehmann further studied Reinitzer's samples with an optical polarising microscope and they soon realized that they had discovered liquid crystals as the fourth state of matter in addition to the known states of solid, liquid and gas ^{33,34}.

Generally when a solid melts to a liquid, the strongly-organized molecular structure of the solid collapses to give a disordered liquid where the molecules rotate without restraint 35 . At the melting point, the molecules undergo large and rapid simultaneous changes in rotational, positional, and orientational order. However, when the melting process can lead to liquid-crystalline behaviour there is usually a stepwise breakdown in the order. The steps of this decay occur with changing temperature, producing a variety of thermodynamically stable intermediate states between the solid and the liquid. This collection of structurally unique phases constitutes the thermotropic liquid crystalline (mesomorphic) state 36 .

1.2.1 Thermotropic Liquid Crystals

The thermotropic liquid crystals exhibit liquid-crystalline mesophases on melting from the crystal phase or cooling from the isotropic liquid. Both calamitic and discotic liquid crystals discussed here are thermotropic liquid crystals since the liquid crystal phases are stable within a certain temperature interval.

1.2.1.1 Calamitic Liquid Crystals

The most common kind of molecule that forms liquid crystal phases is rod-shaped. These molecules are termed calamitic liquid crystals and can display many diverse phases. In calamitic liquid crystals, one axis of the molecule is much longer than the other two axes.



Figure 7: Structure of a calamitic molecule

Figure 7 shows a general template for the structure of the calamitic liquid crystal materials. The core units are often aromatic units such as 1,4-phenyl-2,5-pyrimidinyl. The core is the most fundamental unit in the structure of these molecules and is the rigid part of the structure. The core units are connected together by a linkage group (LG). In order to increase the length and polarisibility anisotropy of the molecular core, linkage groups such as ester, azo, imine (Schiff's base) and ethylene are used to attach the rigid units together. A lateral substituent such as fluoro, chloro, nitro or methyl is often attached to the side of the rigid core. Lateral substituents properties such as their size, polarity and position can directly affect the mesophases in the liquid

crystals. The terminal groups can be a small polar group like a cyano group or a straight alkyl/alkoxy chain. These groups are attached to the end of the rigid core. Polar groups enable substantial intermolecular forces, which stabilise the orientation of the molecules ³⁷.



Figure 8: Typical molecular structure of liquid crystals

1.2.1.2 Discotic Liquid Crystals:

In disc-like molecules, one molecular axis is much shorter than the other two axes. The core section of these molecules is usually based on benzene, triphenylene or truxene ³⁸. Much work has been done on the molecular structure of discotic liquid crystals, and the structure of a typical discotic molecule is illustrated in Figure 9.



Figure 9: Structure of a discotic molecule

1.2.2 Liquid Crystal Phases:

Liquid crystals are typically defined as the orientationally ordered phases that occur between the breakdown of positional order on melting a solid and the breakdown of orientational order on melting to a liquid. There are many types of liquid crystal states. Generally, there are three main phases, nematic, cholesteric and smectic, depending upon the amount of order in the materials.



Crystalline

Smectic A

Smectic C

Nematic

Isotropic

Figure 10: A schematic representation of crystalline, liquid crystalline and isotropic molecular arrangement.

The degree of the alignment of the molecules with the director is named as order parameter ³⁹:

$S=\frac{1}{2}(3\cos^2\beta-1)$

Where β is the angle between the long axis of molecule and the director. When the order is zero it suggests that the phase has no order. This value for liquid crystals is between 0.3 to 0.9, for a nematic phase this value is in a range of 0.4 to 0.7. A perfect crystal would have a value of 1.

1.2.2.1 Nematic Phase

Liquid crystal phases can be recognized by their birefringent texture under crossed polarising microscope. Nematic is Greek for "thread-like", as the optical texture of these compounds appears as optically extinct threads on a coloured background. Both calamitic and discotic molecules can generate the nematic phase.



Figure 11: Polarising microscopy photo of Schlieren nematic texture 40

The nematic phase is basically ordered in one dimension, in which the molecules are orientationally ordered. In this phase the rod-like molecules tend to align parallel to each other with their long axes all pointing approximately in the same direction (Figure 10,11). Subject to the molecular orientation, the nematic phase displays different textures under polarised optical microscope. Nematic liquid crystals show Schlieren and Marbled textures. The nematic Schlieren textures present two and four brushes, which meet at dark points (Figure 11).

1.2.2.2 Smectic Phase

In addition to the orientational order found in a nematic phase, positional order that comes from the centre of molecules can put the molecules into layers and form a new phase. If the director is perpendicular to the layers it can be named as smectic A, in this phase the molecules are organised randomly in layers perpendicular to the layer plane and have the freedom to spin around their long axes ⁴¹.



Figure 12: Polarising microscopy photo of smectic texture 42

There are also tilted smectic phases where the director angle is other than 90° , this phase can be named as smectic C, in this phase the molecules are organised in the same style of smectic A phase but they are not perpendicular to the plane of the layer (Figure 10,12).

1.2.2.3 Cholesteric Phase

The cholesteric liquid crystal phase is usually composed of nematic mesogenic molecules, which contain a chiral centre. Due to the presence of this chiral centre in the cholestric or chiral nematic liquid crystals they are optically active. This phase was first observed in cholesterol derivatives and this phase took its name from cholesterol ⁴³.

1.2.3 Lyotropic Liquid Crystals:

Lyotropic liquid crystals are amphiphilic molecules, where each molecule contains both hydrophilic and hydrophobic groups. As a result of the interaction between the compound and an appropriate solvent at a certain concentration, the molecules arrange themselves into spheres, rods or discs ⁴⁴. The lyotropic materials exhibit liquidcrystalline mesophases when mixed with a particular solvent. Detergents like sodium stearate (Figure 13) have a carboxylate salt as the polar group and a chain of hydrocarbon. The lamellar, hexagonal and cubic phases are broadly known as lyotropic liquid crystal phases.



Figure 13: Lyotropic liquid crystal detergent

1.2.4 Applications of Liquid Crystals

The liquid crystal materials' response to temperature, solvents and external field can be used in applications like nematic liquid crystal displays, LCD technology, spatial light modulators, temperature sensors, etc. The thermo-optical properties of chiral nematics (for instance cholesterol-based materials) has led to many interesting applications such as simple and inexpensive thermometry devices ⁴⁵.

The great progress achieved in liquid crystal displays (LCDs) have been possible through extensive research in the field of liquid crystals materials. LCDs have become significant in our daily life due to their compact size, low power consumption and high-resolution density ⁴⁶.

1.2.5 Liquid Crystalline Polymers

Liquid crystal polymers have been investigated intensively in the past decades. These polymers have found application in high strength plastics for use in construction. The spontaneous orientational of the liquid crystalline polymers can be frozen during the process of fabrication and yield stronger fibres like Kevlar, which is a highly crystalline aromatic polyamide with remarkable mechanical and thermal properties.

1.2.5.1 Main Chain Liquid Crystalline Polymers

Main chain liquid crystalline polymers have repeating mesogenic monomer units, which form long chains. The degree of flexibility and the structural combination control the mesomorphic properties of main-chain liquid crystalline polymers. These polymers can be formed from calamitic or discotic units ⁴⁷.



Figure 14: Typical structure of main-chain liquid crystalline polymers

1.2.5.2 Side-Chain Liquid Crystalline Polymers

In side-chain liquid crystalline polymers the mesogenic unit is attached to the backbone of the polymer through a flexible spacer ⁴⁸. The flexible spacer is usually a series of methylene units, oxyethylene or siloxane.



Figure 15: Typical structure of side-chain liquid crystalline polymers

1.3 Literature Review

In recent years, side-chain liquid crystalline polymers (SCLCPs) have attracted significant interest due to their improved properties, such as wider phase transition temperature range, relative higher viscosity, etc, than their low molecular weight counterparts, and their potential applications in many fields, such as nonlinear optical devices, optical data storage materials etc.⁴⁹ Among them, polysiloxane-based SCLCPs have received extensive attention because of the excellent physical properties of organosilicon polymers, such as super flexibility, weatherability, low surface tension, water resistance, etc.⁵⁰

A work by Wang ⁵¹ described the synthesis of a graft liquid crystalline polysiloxane with a biphenyl mesogenic unit (figure 16). The results showed that both the monomer and the graft liquid crystalline polymer were smectic liquid crystals. However, the monomer showed both smectic B and smectic C phases, but the polymer only showed a smectic C phase with a wider liquid crystalline range.



Figure 16: Graft liquid crystalline polysiloxane with biphenyl mesogenic unit ⁵¹.

An article by Yang and Hsu⁵² reviewed the syntheses and electro-optical applications of some main-chain and side-chain liquid crystalline conjugated polymers such as poly(*p*-phenylene vinylene)s (PPV), polyfluorenes, polythiophenes and other conjugated polymers.

Many synthetic routes have been proposed and widely used to prepare poly(*p*-phenylene vinylene) derivatives. Attachment of long alkyl chains or mesogenic groups to the *p*-phenylene vinylene monomer structure has improved the solubility of the resulting polymers in common organic solvents. According to the results obtained from polarising optical microscopy, most of the LC PPV derivatives (figure 17) show nematic textures when in their LC state.



P1 m = 4, 7, 9, 12, 16

Figure 17: Dialkoxy-PPV ⁵².

Some substituted PPV derivatives like poly(2-methoxy-5-(2-ethylhexyloxy)-1,4phenylene vinylene) (MEH-PPV), poly(2,5-dioctyloxy-1,4-phenylenevinylene) (DO-PPV), and poly(2,5,2,5-tetrahexyloxy-8,7-dicyano-di-p-phenylenevinylene) (DH-CNPPV), are found to exhibit nematic-like optical textures. X-ray observation of DO-PPV (Figure 18) annealed at 200 °C revealed that the lamellar mesophase was growing with an increase of temperature. DO-PPV and DH-CNPPV exhibit lamellar mesophases in the bulk, while MEH-PPV has biaxial nematicity ⁵².


Figure 18: X-RD diffractograms of DO-PPV film annealed at 200 °C ⁵².

The polycyclic aromatic rings of polyfluorene main chains can also serve as the mesogenic unit. Long or branched alkyl chains incorporated on the C-9 position of fluorene act as soft spacers. While poly(9,9-dihexylfluorene) is generally considered as amorphous, PFs with longer alkyl side chains like poly(9,9-dioctylfluorene) or poly(9,9-bis(2-ethylhexyl)fluorene) (figure 19) display LC behaviour.



Figure 19: Poly(9,9-dialkylfluorene) 52.

The alignment of LC conjugated polymers can be achieved both by direct rubbing of the active layer and by thermal annealing of additional alignment layers. Both the methods mentioned above are always carried out in the LC temperature range, to fulfill self-organization of the LC materials.

Rubbing a thermotropic LC phase induces the alignment of mesogenic side groups along the rubbing direction and the alignment of polymer backbones perpendicular to the rubbing direction (figure 20).



Figure 20: Illustration of the alignment of LC side chains and polymer backbones due to rubbing treatment ⁵².

The field of liquid crystalline conducting polymers is of increasing importance, with the potential to have a wide range of commercial applications. There has been a great amount of work on SCLCCPs. Much of this activity was pioneered in the UK, for example at Kingston University, where the first reported processible liquid crystal polyanilines and polypyrroles were synthesised.

Gabaston et al ⁵³ studied the synthesis and properties of liquid crystalline aniline monomers and semiconducting polyaniline with mesogenic side-chains (figure 21) and showed a possible way to control the conductivity of conducting polymers by attaching mesogenic side groups in order to give better ordering.



Figure 21: Precursors for preparation of polyaniline ⁵³

Brown et al ⁵⁴ studied liquid crystalline conducting polymers and demonstrated the first work on the synthesis of laser-alignable liquid crystalline conducting polymers. They established some synthetic routes to three series of liquid crystal conducting polymers (based on pyrrole, thiophene, and aniline monomers) (figure 22) and reported the best possible conditions for polymer preparation. These polymers showed increased conductivity when laser-aligned.



Figure 22: Pyrrole, thiophene, and aniline monomers attached to liquid crystalline moieties ⁵⁴.

Hosseini ⁵⁵ showed that in spite of the generally low processability of polypyrroles they could synthesise a kind of polypyrrole containing an azo dye side group with excellent solubility. The polymer was soluble in common organic solvents such as CHCl₃, DMF and DMSO and well processible into a homogeneous thin film, this property permits the possible application of the LC polypyrrole in biological systems and various industries. The polymer consisted of benzenoid and quinonoid units in the polypyrrole backbone, with azo chromophore moiety as a mesogenic core. A mosaic type of texture, which is a typical liquid crystal texture of smectic phases, was observed.

Onoda et al ⁵⁶ synthesised poly(p-phenylene vinylene) derivatives substituted with a long side-chain containing alkoxybiphenyl mesogenic units (figure 23), and studied their electrical and optical properties. They confirmed the liquid-crystalline molecular alignment and layer structure by optical microscopic observation and X-ray diffraction measurements. These polymers showed a typical microscopic texture for the liquid-crystalline phase and a sharp X-ray diffraction peak due to the smectic layer structure.



Figure 23: Poly(p-phenylene vinylene) with alkoxybiphenyl mesogenic unit ⁵⁶.

Unsubstituted polythiophenes are conductive after doping, and have good environmental stability compared with some other conducting polymers such as polyacetylene, but are intractable and soluble only in certain solvents. Much progress has been made in the past decades to solve the problems of solubility and processability of thiophene-based polymers. This problem was overcome by the incorporation of substituents at the 3-position of the thiophene ring, which not only produced processable conducting polymers but also allowed the complete chemical and physical characterization of the prepared materials ⁵⁷.

Other work by Brown et al ⁵⁸ produced a novel thiophene-based conducting copolymer with mesogenic groups attached parallel to the conducting polymer backbone (Figure 24). According to their results, after the non-mesogenic intermediate polymer was converted into a liquid-crystalline polymer there was a major rise in conductivity (from 2.2×10^{-5} to 1.4×10^{-2} Sm⁻¹).



Figure 24: Thiophene base copolymer with mesogenic groups ⁵⁸.

Li ⁵⁹ and Chen ⁶⁰ in a similar work combined the mesogenic cyanobiphenyl to polythiophenes (Figure 25) in order to achieve highly stable and ordered liquidcrystalline conjugated materials. The orientation of cyanobiphenyl mesogen delivers polymer films with a well-ordered morphology and as a result, enhanced properties. After irradiation by UV, the blend film formed a cross-linked network, which not only enhanced the polymer stability, but also maintained the ordered nanostructure.



Figure 25: Incorporation of the mesogenic cyanobiphenyl onto polythiophenes ⁵⁹.

Zhao and colleagues ⁶¹ synthesized a series of azobenzene-functionalized liquidcrystalline (LC) polythiophene derivatives (Figure 26). Their results indicated that these azobenzene-functionalized polythiophene derivatives had wide mesophase temperature ranges and good photoactivity.



Figure 26: Azobenzene-functionalized liquid-crystalline polythiophene derivatives ⁶¹.

Armelin et al ⁶² synthesized a polythiophene derivative with a malonic acid dimethyl ester substituent attached to the 3-position (Figure 27) by chemical oxidative-coupling polymerization. They showed that the electrical conductivity of the new material, which was soluble in polar solvents except water, was higher than that typically found for poly(3-alkylthiophene) derivatives.



Figure 27: Malonic acid dimethyl ester substituent attached to 3-position of polythiophene⁶².

Jin et al ⁶³ prepared poly{3-(4-methoxy-4'-hexyloxybiphenyl)oxymethylthiophene} (Figure 28) to examine the effect of liquid crystalline properties on the conducting polymer structure. The monomer showed an enantiotropic smectic liquid crystalline mesophase. Cyclic voltammetry results showed that there was an overall increase in current with repeated scanning, which was due to the fact that the deposited conducting polymer was increasing the effective surface area of the electrode.



Figure 28: Poly{3-(4-methoxy-4'-hexyloxybiphenyl)oxymethylthiophene}⁶³

Side chains are an important component of some semiconducting polymers, and were originally introduced as the solubilizing group. Linear and branched alkyl groups are major side chains that are introduced into semiconducting polymers. While linear alkyl groups have been used for classical semiconducting polymers such as poly(3-alkylthiophene)s, branched alkyl groups are often used in donor-acceptor polymer systems with strong intermolecular interactions with solvents in order to ensure the solubility. It is also important to note that, as revealed by recent studies, the use of branched alkyl groups is a key to altering the backbone orientation, while preserving the solubility and crystallinity. A number of studies on the backbone orientation and the influence on the device properties have been reported to date. Osaka ⁶⁴ has summarized the correlation of the orientation with the polymer structure, such as the backbone and side chain, and processing methods.

Subramaniyan and colleagues ⁶⁵ synthesised new thiazolothiazole-dithienosilole copolymer semiconductors (Figure 29) bearing side chains of different type, size, and topology and demonstrated the influence of side chains on morphology, charge transport and photovoltaic properties.



Figure 29: Thiazolothiazole-dithienosilole copolymer⁶⁵.

High performance (5.0% PCE (average power conversion efficiency)) bulk heterojunction solar cells were developed from a new polymer with branched alkyl side chains and perpendicular orientation of $\pi - \pi$ stacking to the substrate. In contrast, bulk heterojunction solar cells based on polymers with linear side chains and π stacking that was parallel to the substrate, had average efficiencies of 2.1–4.1% PCE. Transient optical studies indicated that these differences in photovoltaic device performance correlated with differences in charge photogeneration, assigned primarily to differences in geminate recombination losses.

Somanathan ⁶⁶ studied the influence of fused polyaromatic side chains on polythiophene absorption and photoluminescence (Figure 30).



Figure 30: Structures of polymers of (a) 3,4-diphenyl thiophene (poly DPT), (b) 3-biphen-4-ylthiophene (poly BPT), (c) 3-(1, 1, 4, 1)terphen-4-yl)thiophene (poly TPT), (d) 3-(10-phenyl-anthracen-9-yl) thiophene (poly PAT), (e) 3-(9,10-diphenylanthracen-2-yl) thiophene (poly DPAT) ⁶⁶.

According to their results, with an increase in the number of phenyl rings, the emission peak intensity increased and the wavelength was more red-shifted. The emission range extended from the UV to the visible range. By appropriately substituting the phenyl ring, the wavelength and intensity of the emission can be modified in polythiophenes. Self-polarization due to ordered stacking which was produced by molecular crowding helped to enhance the charge carrier mobility.

Soto et al ⁶⁷ synthesised 3-alkyloxymethylthiophenes substituted with a biphenyl group involving a functionalised alkyl chain, from 8 to 12 carbon atoms (Figure 31). DSC spectra of the monomers did not show the presence of mesophases. They also used polarised light microscopy, but no mesophase was observed.

This was due to the insolubility and infusibility of these polymers, which can be related to the high molecular weight of the chains or to a high degree of crosslinking; hence the researchers were limited to studying the electrical and thermal properties.



Figure 31: 3-alkyloxybiphenylthiophenes⁶⁷.

Jang et al ⁶⁸ polymerised 3-hexylthiophene from the vapour phase instead of conventional methods of solution-based thin film fabrication. By evaporating a film of ferric chloride and 3-hexylthiophene monomer, it resulted in the formation of conducting poly(3-hexylthiophene) thin films on the substrate.

Jang et al estimated a band gap of 1.91 eV from the UV-visible transmittance spectrum of a vapour-phase-polymerized P3HT film formed on a glass substrate; this value is similar to that of conventional PTs corresponding to the 70% regioregular head-to-tail poly(3-hexylthiophene) case.

Yoon ⁶⁹ synthesised a series of polythiophene derivatives with decyloligo(oxyethylene) side groups (PD*n*ET) (Figure 32) by oxidative coupling polymerization. As n was increased from 1 to 4, the polymers with longer oligo(oxyethylene) units exhibited an increase in liquid crystalline phase with wellordered lamellar structures (except for n=4). Polymers with n=1 and n=2 had shorter oligo(oxyethylene) groups than PD3ET and showed less-ordered structures of the liquid-crystalline phase observed.



Figure 32: Poly(thiophene)s having decyl oligo(oxyethylene) side-chains ⁶⁹.

An alternative way to align LC conjugated polymers has been studied by using magnetic field. Akagi et al ⁷⁰ produced highly oriented conducting polyacetylene films by applying magnetic force to a polymerization system consisting of nematic liquid crystals. Molecules of liquid crystalline conjugated polymers substituted with liquid crystalline side groups and even non-liquid crystal polymer have also been aligned by applying magnetic force.

Osawa ⁷¹ investigated the conditions for molecular orientation of electrochemically synthesised polythiophenes. The polymerizations were carried out in a magnetic field. With the magnetic field parallel to the electrode surface, the thiophene chains were oriented along the electrode surface. On the other hand, a magnetic field perpendicular to the electrode surface hindered the molecular orientation (Figure 33). This was associated with the degree of stability based on the magnetic susceptibility of thiophene rings.



Figure 33: (a) Schematic illustration of the polymerization cell in a magnetic field. (b) The geometry of magnetic fields parallel and perpendicular to the electrode surface direction ⁷¹.

In another work Cho⁷² synthesised poly(3,4-ethylenedioxythiophene) (PEDOT) films by electropolymerisation under an applied magnetic field on ITO glass in order to study the effects of the magnetic field on the electrochemical polymerization of EDOT. With cyclic voltammetry, it was shown that the current was much higher when the film was fabricated using magneto-electropolymerization (1.17 T). Increasing the electropolymerization time also caused an increase in the current of the cyclic voltammogram, and the applied magnetic field sped up the polymerization. SEM results also clearly revealed that the parallel applied magnetic field induced the formation of a sharper crystalline structure.

1.4 Aims of the Project:

In this project, a range of thiophene-based conducting polymers and monomers with terminally and laterally attached mesogens will be prepared, in order to investigate their switchable anisotropic optoelectric properties. The liquid crystal groups provide the potential for electric or magnetic switching of the molecular orientation.

Heterocyclic monomer of thiophenes with mesogenic substituents will be synthesised using established synthetic routes, and will be polymerised by oxidative coupling. The monomers and polymers will be characterised in solution by nmr and chromatographic methods.

The degree of anisotropy of the electro-optic properties of the polymers when exposed to electric/magnetic fields will be determined by these two spectrometric techniques and, if possible, also by x-ray diffractometry and electronic conductivity measurements. The electrochromic switching kinetics of the polymers will be determined by cyclic voltammetry.

The initial aim of this project is to synthesise novel polymers with liquid crystal units bonded onto stable conductive polymer backbones. They may show externally switchable conductivity or strongly anisotropic electronic properties when thin films are subjected to electric/magnetic fields or laser induced LC alignment, due to increased π -backbone planarity when in an aligned LC phase. It is also hoped to gain an understanding of the structure-properties relationships in these potentially useful materials.

The main programme objectives are:

(i) to synthesise conducting polymers having side-chains terminated by suitable mesogens.

(ii) to gain some understanding of how the side-groups affect the electrical and optical properties, by systematically modifying their structure.

(iii) to study the processibility of the polymers and the effect of applied magnetic/electric fields and thermal treatment on the chain alignment and electronic anisotropy.

Chapter II:

Experimental

2.1 Introduction

This chapter is concerned with the synthesis of thiophene-based monomers and the polymerisation of these monomers in order to study the liquid crystal properties and their influences on the alignment of the polymer backbone and their conductivity. The flexible spacer was an alkoxy chain of six methylene units, and the mesogenic groups were two ring-based structures.

The polymerisations were carried out chemically and electrochemically to study the conductivity and the effects of liquid crystal pendant groups on their alignment and conductivity.

2.2 Materials and Apparatus

All the chemicals, reagents and solvents were purchased from Sigma Aldrich.

The Gas chromatography-mass spectra were obtained with a Hewlett Packard 5890 series II gas chromatograph/Hewlett Packard 5971 series mass-selective detector.

Nuclear magnetic resonance (NMR) and proton nuclear magnetic resonance (¹H NMR) spectra were measured using a Bruker 400 MHz FT-NMR with ACD/NMR Processor Academic Edition Software.

The thermal stability of the polymers was studied by TGA using a Mettler Toledo balance operating at a heating rate of 20 $^{\circ}$ C min⁻¹ under N₂ atmosphere. The heating scan was carried out on 3-5 mg of sample up to 600 $^{\circ}$ C temperature using a platinum pan. The polymers and monomers were studied by differential scanning calorimetry.

Phase transition temperatures and LC phase identification were also studied by Hot Stage Microscopy (Linkam HFS 91, Nikon) fitted with a Linkam THMS-600 heating stage.

X-Ray Diffraction analysis was performed on a Bruker-AXS model D8 diffractometer using copper K α radiation ($\lambda = 1.542$ Å).

Ultraviolet-Visible spectra were recorded using a CARY 100 Scan UV-Visible spectrophotometer and Cary Win UV Scan Application, 2002 Version: 3.00 (182) Software.

ATR Infra-Red spectra were recorded using a Thermo Scientific diamond crystal spectrometer, Nicolet iS5 iD5.

Cyclic Voltammetry was used to study the study the redox properties of the polymers and the instrument used was a Uniscan Potentiostat-Galvanostat P580.

Photoluminescence studies were recorded at room temperature using a Varian Cary Eclipse fluorescence spectrophotometer with a 300W Xe lamp as the excitation source. The spectrometer was calibrated using the fluorescent emission of Rhodamine-B and appropriate correction curves.

Quantum Cache (Scigress) modelling software was used to predict the molecular structure of the monomers and polymers.

2.3 Organic Synthesis:



Figure 34: Reaction scheme for the preparation 3-bromo-2-[(E)-2-{4-[(E)-2-(3bromothiophen-2-yl)ethenyl]phenyl}ethenyl]thiophene and 3-bromo-2,5-bis[(E)-2-(thiophen-2-yl)ethenyl]thiophene (C 4, C 5)

2.3.4 Synthesis of 3-bromo-2-(bromomethyl)thiophene and 3-bromo-2,5-

bis(bromomethyl)thiophene (C1):

Materials: Paraformaldehyde, 3-bromothiophene, 33% aqueous HBr, anhydrous MgSO₄.

Paraformaldehyde (3.6 g, 0.12 mol) and 3-bromothiophene (9.78 g, 0.06 mol) were placed in a flask, 4ml HBr 33% (9.6 g, 0.12 mol) was added and the mixture was stirred and refluxed at 30 to 70°C. A clear solution was produced. The product was extracted with ether and dried with MgSO₄. Starting materials were removed by kugelrohr distillation at 90-115°C. A brown liquid was obtained.



GCMS results for C1 (MS:m/z=256)

2.3.5 Synthesis of diethyl [(3-bromothiophen-2-yl)methyl] phosphonate and diethyl ({3-bromo-5-[(diethoxyphosphoryl)methyl]thiophen-2-yl}methyl) phosphonate (C2 and C3):

Materials:3-bromo-2-(bromomethyl)thiophene,3-bromo-2,5-bis(bromomethyl)thiophene, triethyl phosphite, ethyl acetate, hexane.

The compounds were prepared through the procedure of Jorgensen et al 75 . 3-bromo-2-(bromomethyl)thiophene (4 g, 0.016 mol), 3-bromo-2,5-bis(bromomethyl)thiophene and triethyl phosphite (2.66 g, 0.16 mol) were mixed and refluxed at 100-120°C. The product was a mixture of mono (2.59 g, 51%) and disubstituted (1.86 g, 25%) compounds, which were separated by column chromatography (ethyl acetate and hexane 2:1). The disubstituted compound stuck to the base line and was flushed out by methanol.

MS:m/z=312, MS:m/z=464

2.3.6 Synthesis of 3-bromo-2-[(E)-2-{4-[(E)-2-(3-bromothiophen-2yl)ethenyl]phenyl}ethenyl]thiophene (C4):

Materials: Diethyl [(3-bromothiophen-2-yl)methyl] phosphonate, benzene-1,4dicarbaldehyde, potassium *t*-butoxide. The solvent used was dry THF.

Mono substituted diethyl [(3-bromothiophen-2-yl)methyl] phosphonate (1 g, 3.2 mmol) was added to benzene-1,4-dicarboxaldehyde (0.21g, 1.6 mmol) and potassium *t*-butoxide (0.727g, 6.4 mmol) in 30 ml dry THF and the solution turned dark red – purple. A dark tar or viscous liquid was obtained which couldn't be characterised.

2.3.7 Synthesis of 3-bromo-2,5-bis[(E)-2-(thiophen-2-yl)ethenyl]thiophene (C5):

Materials: Diethyl ({3-bromo-5-[(diethoxyphosphoryl)methyl]thiophen-2-yl}methyl) phosphonate, thiophene-2-carboxaldehyde, potassium *t*-butoxide. The solvent used was dry THF.

Disubstituted diethyl ({3-bromo-5-[(diethoxyphosphoryl)methyl]thiophen-2yl}methyl) phosphonate (1.86 g, 4.08 mmol) was added to thiophene-2carboxaldehyde (0.918g, 8.2 mmol) potassium *t*-butoxide (1.37g, 12.24) in 30 ml THF and the solution turned black. A dark tar or viscous liquid was obtained which couldn't be characterised.

2.3.8 Synthesis of 3-(6-bromohexyloxy)methylthiophene (compound I):



Materials: Potassium *tert*-butoxide, 18-crown-6, thiophene-3-methanol, 1,6dibromohexane, anhydrous MgSO₄. The solvent was anhydrous diethyl ether.

The compound was prepared by the method of Brown et al ⁵⁴. Potassium *tert*-butoxide (3.34 g, 0.03 mol) was added to a solution of 18-crown-6 (0.8 g, 0.003 mol) in anhydrous diethyl ether (100 ml). The mixture was stirred at room temperature and thiophene-3-methanol (2.0 g, 0.018 mol) was added. A calcium chloride guard tube was fitted, and stirring was continued for 15 min. 1,6-dibromohexane (30 g, 0.12 mol) was then added drop-wise over a period of 10 minutes and the mixture was stirred for 72 h. The reaction was quenched with water (100 ml) and the mixture was extracted with ether. The combined organic layers were washed with saturated NaCl solution (50 ml), then with water (50 ml) and dried with anhydrous MgSO₄. The solvent was removed under reduced pressure and the product purified by distillation (Kugelrohr). The purity was established by GC-MS analysis (3 g, 60%).

MS: m/z = 278



¹H NMR (400 MHz, CDCl₃, ppm) CI: 7.3-7.0: (3H, thiophene ring), 4.5: (2H, thiophene-CH₂-O), 3.5-3.3: (4H, Br-CH₂, O-CH₂), 1.3-1.5 (8H, aliphatic protons).

2.3.9 Synthesis of diethyl (4-cyanobenzyl)phosphonate (Compound II)



Materials: 4-bromomethyl benzonitrile, triethyl phosphite,

The compound was prepared through the procedure of Jorgensen et al 75 . A mixture of 4-bromomethyl benzonitrile (25.5 mmol, 5 g) and triethyl phosphite (43.5 mmol, 7.2 g) was heated under refluxed for 24 h. The product was purified by Kugelrohr distillation at 165 ° C (5.1 g, 79%).

MS: m/z = 253

2.3.10 Synthesis of 4-[(E)-2-(4-hydroxyphenyl)ethenyl]benzonitrile (Compound





Materials: *Para*-hydroxybenzaldehyde, diethyl (4-cyanobenzyl)phosphonate, and potassium *t*-butoxide, The solvents used were dry THF and IMS.

The compound was prepared through the procedure of Jorgensen et al ⁷⁵. *Para*-hydroxybenzaldehyde (25 mmol, 3.053 g) was added to a solution of diethyl (4cyanobenzyl)phosphonate (CII) (25 mmol, 6.35 g) and potassium *t*-butoxide (6.28 g, 56 mmol) in 100 ml of dry THF under nitrogen, with stirring. The solution was stirred at room temperature for 30 min; it was then refluxed for 12 h. 40 ml of 6 N HCl was added and the mixture was refluxed for another 20 min, and then added to 300 ml of cold water. The yellowish solid obtained was vacuum filtered and recrystallized from IMS (4.2 g, 76%).

MS:m/z=220

¹H NMR (400 MHz, CDCl₃, ppm) CIII: 9.68 (s, 1H, phenoxide proton), 8.9-6.7: (d, 8H, Aromatic proton), (d, 2H, ethylene proton).

2.3.11 Synthesis of Monomer 1:



Materials: 4-[(E)-2-(4-hydroxyphenyl)ethenyl]benzonitrile (Compound III), 3-(6bromohexyloxy)methylthiophene (Compound I), anhydrous potassium carbonate. The solvent used was N,N-dimethylformamide (DMF).

The compound was prepared by the method of Brown et al ⁵⁴. 4-[(E)-2-(4hydroxyphenyl)ethenyl]benzonitrile (Compound III) (0.0045 mol, 0.994 g) was added to a solution of 3-(6-bromohexyloxy)methylthiophene (Compound I) (0.004mol, 1.109 g) and anhydrous potassium carbonate (0.84 g, 0.006 mol) in DMF (50 ml); the mixture was refluxed for 12h. The reaction mixture was transferred into 200 ml water and filtered. The residue was recrystallized from methylated spirit and purified by flash column chromatography (CHCl₃ on silica) (0.85 g, 50%)

MS:m/z=417

¹H NMR (400 MHz, CDCl₃, ppm) M1: 6.9-7.9: (8H, Aromatic proton), (3H, thiophene ring), (2H, ethylene proton), 4.5: (2H, Ar-O-CH₂), 4, 3.5: (4H, O-CH₂), 1.8-1.5 (8H, aliphatic protons).

2.3.12 Synthesis of diethyl benzylphosphonate (Compound IV)



Materials: benzyl bromide, triethyl phosphite

A mixture of benzyl bromide (29.2 mmol, 5 g) and triethyl phosphite (43.5mmol, 7.2 g) was refluxed for 24 h. The product was purified by Kugelrohr at 165 ° C (4 g, 60%). MS:m/z=228

2.3.13 Synthesis of 4-[(E)-2-phenylethenyl]phenol (Compound V)



Materials: *Para*-hydroxybenzaldehyde, diethyl benzylphosphonate and potassium *t*-butoxide. The solvents used were dry THF and IMS.

Para-hydroxybenzaldehyde (3,42 g, 28 mmol) was added to a solution of Compound IV (28 mmol, 6.35 g) and potassium *t*-butoxide (6.28 g, 56 mmol) in 100 ml of THF under nitrogen with stirring. The solution was stirred at room temperature for 30 min; it was then refluxed for 12 h. 40 ml of 6 N HCl was added and the mixture was refluxed for another 20 min, and then poured into 300 ml of cold water. The yellowish solid obtained was vacuum-filtered and crystallized from IMS (3.1 g, 56%).

2.3.14 Synthesis of Monomer 2:



Materials: Compound I, Compound V, anhydrous potassium carbonate. The solvent used was DMF.

Compound V (0.0045 mol, 0.883 g) was added to a solution of Compound I (0.004mol, 1.109 g) and anhydrous potassium carbonate (0.84 g, 0.006 mol) in DMF (50 ml); the mixture was refluxed for 12h. The reaction mixture was transferred into 200 ml water and filtered. The residue was recrystallised from methylated spirit and purified by flash column chromatography (CHCl₃ on silica) (0.98 g, 62%).



¹H NMR (400 MHz, CDCl₃, ppm) M2: 6.8-7.4: (9H, Aromatic proton), (3H, thiophene ring), (2H, ethylene proton), 4.5: (2H, Ar-O-CH₂), 4, 3.5: (4H, O-CH₂), 1.8-1.5 (8H, aliphatic protons).

2.3.15 Synthesis of 4-{(E)-[(4-hydroxyphenyl)imino]methyl}benzonitrile





Materials: Para-aminophenol, para-cyanobenzaldehyde. The solvent used was methanol.

Para-aminophenol (1.64 g, 0.015 mol) and cyanobenzaldehyde (2 g, 0.015 mol) were dissolved in 50 ml methanol and refluxed for 12 hours; a yellowish solid was obtained and recrystallized (2.1 g, 63%).

MS:m/z=222

¹H NMR (400 MHz, CDCl₃, ppm) CVI: 9.6 (s, 1H, phenoxide proton), 8.7-68: (s, 1H, CH=N), (d, 8H, aromatic proton).

2.3.16 Synthesis of Monomer 3:



Materials: Compound I, Compound VI, anhydrous potassium carbonate. The solvent used was DMF.

Compound VI (0.0045 mol, 1.00 g) was added to a solution of Compound I (0.004mol, 1.109 g) and anhydrous potassium carbonate (0.84 g, 0.006 mol) in DMF (50 ml); the mixture was refluxed for 12h. The reaction mixture was transferred into 200 ml water and filtered. The residue was recrystallised from methylated spirit and purified by flash column chromatography (CHCl₃ on silica) (1.1 g, 66%).

MS:m/z=418

¹H NMR (400 MHz, CDCl₃, ppm) M3: 6.9-7.9: (8H, Aromatic proton), (3H, thiophene ring), (1H, imine proton), 4.5: (2H, Ar-O-CH₂), 4, 3.5: (4H, O-CH₂), 1.8-1.5 (8H, aliphatic protons).

2.4 Polymerisation

2.4.1 Chemical Polymerisation

Materials: Monomers 1,2,3, anhydrous FeCl₃, sodium EDTA, dried MgSO₄. The solvent was dichloromethane (DCM).

The polymerisation of compound M1 was carried out by chemical oxidation under nitrogen atmosphere. M1 (0.5 g, 0.0012 mol) was added to a filtered solution of FeCl₃ (0.324 g, 0.002 mol) in anhydrous DCM (50 cm³). The solution was heated at room temperature for 4h and the oxidant residues were removed by extraction with 0.1 M sodium EDTA solution. The organic phase was washed with water (2×50 cm³), dried with anhydrous MgSO₄, and the solvent removed by rotary evaporation under reduced pressure. The polymerisation of compounds M2 (0.57 g, 0.0015 mol) and M3 (0.5 g, 0.0012 mol) were carried out via the same procedure.

2.4.2 Solid-state Polymerisation on ITO glass substrate and silicon wafer:

Materials: Monomers 1, 2, 3, anhydrous FeCl₃. The solvent used was 1, 1, 2, 2-tetrachloroethane.

The monomers were dissolved in 1,1,2,2-tetrachloroethane and spin-coated onto ITO glass or silicon wafer substrates at a speed of 1500 RPM. These films were exposed to the vapour of FeCl₃ on a hotplate at 200°C.



Figure 35: Vapour-phase polymerisation on hotplate

2.4.3 Electrochemical Polymerisation

Electrochemical polymerisation of monomers was studied by cyclic voltammetry technique (Uniscan Potentiostat-Galvanostat P580) on an ITO glass substrate in a solution containing the monomer in tetrabutylammonium tetrafluoroborate (TBAF) (1 mmol) in chloroform.

The solutions had previously been deoxygenated by nitrogen bubbling. A saturated KCI-calomel electrode (SCE) was used as the reference electrode and a stainless steel sheet as the counter electrode. (The stainless steel had previously been shown to be unreactive with the electrolyte under the potential conditions used in the experiments.)
2.4.3.1 Electrochemical Polymerisation of M1:

Materials: M1 and tetrabutylammonium tetrafluoroborate. The solvent used was chloroform.

M1 was electrochemically polymerised from an electrolyte solution containing TBAF (0.33 g, 1 mmol) and the monomer (0.5 g, 0.0012 mol) dissolved in 50 ml of chloroform (N₂ purged). The cell consisted of a stainless steel counter electrode, an indium-tin oxide (ITO) glass working electrode and a self-contained saturated calomel reference electrode. The working electrode potential was cycled 10 times from -0.3 V to +1.8 V vs. SCE, at a scan rate of 50 mVs⁻¹.

2.4.3.2 Electrochemical Polymerisation of M2:

Materials: M2 and tetrabutylammonium tetrafluoroborate. The solvent used was chloroform.

M2 was electrochemically polymerised from an electrolyte solution containing TBAF (0.33 g, 1 mmol) and the monomer (0.57 g, 0.0015 mol) dissolved in 50 ml of chloroform (N₂ purged). The cell consisted of a stainless steel counter electrode, an indium-tin oxide (ITO) glass working electrode and a self-contained saturated calomel reference electrode. The working electrode potential was cycled 10 times from -0.3 V to +1.8 V vs. SCE, at a scan rate of 50 mVs⁻¹.

2.4.3.3 Electrochemical Polymerisation of M3:

Materials: M3 and tetrabutylammonium tetrafluoroborate. The solvent used was chloroform.

M3 was electrochemically polymerised from an electrolyte solution containing TBAF (0.33 g, 1 mmol) and the monomer (0.5 g, 0.0012 mol), dissolved in 50 ml of chloroform (N₂ purged). The cell consisted of a stainless steel counter electrode, an ITO glass working electrode and a self-contained saturated calomel reference electrode. The working electrode potential was cycled 10 times from -0.3 V to +1.8 V vs. SCE, at a scan rate of 50 mVs⁻¹.

2.5 Hot-Stage Polarising Microscopy

2.5.1 Hot-Stage Polarising Microscopy of monomers

A film of each monomer was prepared on an ITO glass substrate via spin coating from a solution of monomer in 1,1,2,2-tetrachloroethane. These films were placed inside a hot-stage fitted onto a polarising microscope stage, heated at a constant rate of 10°C per minute until they reached their melting point and then finally cooled down to ambient temperature. The phase transitions observed were recorded through a camera mounted on the polarising microscope with magnification of 10X.

In the next stage the samples were heated until they reached their melting point and were then cooled down in the presence of a magnetic field (0.2 Tesla) applied perpendicularly to the glass substrate. The phase transitions were recorded by observing the microscopic images under crossed polarizers.

2.5.2 Hot-Stage Polarising Microscopy of polymers

The monomer films were prepared on the ITO glass substrate as described above, and then polymerised by exposure to the vapour of FeCl₃. These polymer films were heated to 270°C and then cooled down to RT. The phase transitions observed were recorded through a camera mounted on the polarising microscope. In the next stage, the polymer films were heated to 270°C and were then cooled down in the presence of a perpendicular magnetic field (0.2 Tesla). The phase transitions were recorded by observing the microscopic images under crossed polarizers.

2.6 Fluorescence Spectrometry

2.6.1 Fluorescence Spectrometry of the monomers

A film of each monomer was prepared by dissolving the monomer in 1,1,2,2tetrachloroethane onto and spin coating an ITO glass substrate. These monomer films were excited at 350nm and the fluorescent emission was recorded. In the next stage, the monomer films were heated on a hot-stage at a constant rate up to their melting points and then cooled down to room temperature in the presence of a magnetic field. The emission characteristics were recorded again.

2.6.2 Fluorescence Spectrometry of the polymers

The monomer films were prepared on an ITO glass substrate as above and polymerised by exposure to the vapour of FeCl₃. The polymer films were examined by fluorescence spectroscopy and the emission recorded. In the next stage, the polymer films were heated to 270°C, and then cooled down to room temperature in the presence of a perpendicular magnetic field (0.2 T). The polymer films were again examined by fluorescent emission spectroscopy.

2.7 Electrical Conductivity

In order to measure the conductivity of polymer films, 5 mm diameter pellets of the polymers with a uniform thickness were prepared from the powder samples by using a force of 2 tons after evacuating the air from the die with a vacuum pump. The polymers were doped by exposure to saturated iodine vapour (40 Pascal or 0.3 torr) for 24 hours at room temperature. The conductivities of polymer pellets (doped and undoped) were measured by a standard 2-probe method. The two-probe method is a commonly used technique for samples of fairly low conductivity; it characterises a

sample of semiconducting material and can be effectively carried out with a controlled current source and a voltmeter. In order to use this method, the sample thickness must be uniform, and it is assumed that the sample is isotropic. A Keithley type 617 electrometer was used to record electrical resistance measurements. The relationship between the measured resistance R (ohms) and the conductivity σ (Siemens per metre) is presented in the following equation:

$$\sigma = \frac{L}{AR}$$

where L= pellet thickness (m) (measured with a micrometer), and A= cross-sectional area of disk surface (m^2) .

2.8 X-Ray Diffraction (XRD)

2.8.1 XRD of monomers

A film of each monomer was prepared via spin coating (1500 RPM) onto a silicon wafer after dissolving the monomer in 1,1,2,2-tetrachloroethane. These films were heated up to their melting point and then cooled down to room temperature at a constant rate of 5°C per minute. After cooling, the films were analysed on the X ray diffractometer. In the next stage the monomer films were heated up again to their melting point and then cooled down to ambient temperature in the presence of a magnetic field of 0.2 T.

2.8.2 XRD experiments on the polymers

The monomer films were prepared as described above on a silicon wafer and polymerised by exposure to the vapour of FeCl₃. The resulting polymer films were heated up to 270°C then cooled down to room temperature at a constant rate of 5°C per minute. After cooling, the films were analysed by X-ray diffractometry. In the next stage the polymer films were heated up to 270°C and then cooled down to room temperature in the presence of a magnetic field of 0.2 T before using X-ray diffractometry.

Chapter III:

Results & Discussion

3.1 Synthesis and Characterisation

3.1.4 Synthesis of 3-bromo-2-(bromomethyl)thiophene and 3-bromo-2,5bis(bromomethyl)thiophene

Attachment of bromomethyl group to 3-bromothiophene was carried out through the condensation with an aldehyde and the resulting hydroxyalkyl thiophene was unstable under the reaction conditions; in the presence of hydrogen bromide, bromoalkylation of thiophene can however be achieved (Figure 41). There is a possibility for the formation of either monosubstituted or disubstituted ⁷³ products.



Figure 36: Reaction scheme for the preparation of C4 and C5

3.1.5 Synthesis of diethyl [(3-bromothiophen-2-yl)methyl]phosphonate (C2) and diethyl ({3-bromo-5-[(diethoxyphosphoryl)methyl]thiophen-2-

yl}methyl)phosphonate (C 3)

C 2 and *C* 3 (Figure 41) were prepared through the Arbuzov reaction ⁷⁴, which is initiated by the $S_N 2$ reaction of the nucleophilic phosphite with the electrophilic bromomethyl group to give a phosphonium intermediate. The displaced bromide anion reacts via another $S_N 2$ reaction with the phosphonium intermediate to give the desired phosphonate and another bromoalkane.



Figure 37: Reaction scheme for Arbuzov reaction⁷⁴

The syntheses of C_2 and C_3 were successful, and the spectroscopic results have been summarised in the last Chapter (see also Appendices).

3.1.6 Synthesis of 3-bromo-2-[(E)-2-{4-[(E)-2-(3-bromothiophen-2-

yl)ethenyl]phenyl}ethenyl]thiophene(C 4)

3.1.7 Synthesis of 3-bromo-2,5-bis[(E)-2-(thiophen-2-yl)ethenyl]thiophene (C5)

The preparations of C4 and C5 (Figure 41) were attempted through the Horner-Wadsworth-Emmons reaction $^{75-77}$, which is similar in mechanism to the Wittig Reaction. The approach of the carbanion to the carbon of the carbonyl group is preferred when the smaller aldehydic hydrogen eclipses the bulky phosphoranyl moiety. This process places the ester group *syn* to the aldehyde R group, but the developing alkene assumes an E-orientation of these groups after rotation to form the oxaphosphetane. The syntheses of *C4* and *C5* were unsuccessful. A dark tar or viscous liquid was obtained which couldn't be characterised. Work on these two products was therefore not continued any further.



Figure 38: Reaction scheme for Horner-Wadsworth-Emmons reaction 75



Figure 39: Reaction scheme for the preparation of mesogens C III, CV and CVI

As mentioned earlier, a structure of two benzene rings was considered as the rigid core of the mesogen. The benzene rings were connected through an ethylene or an imine group which could increase the conjugation in the mesogen unit and add to the stability of the structure.



Figure 40: Reaction scheme for the preparation of P1, P2 and P3



Figure 41: Reaction scheme for the preparation of compound I

3.1.8 Synthesis of 3-(6-bromohexyloxy)methylthiophene (CI)

The reaction (Figure 46) starts with the displacement of bromine (leaving group) by a nucleophile. The mechanism most often happens at an aliphatic sp³ carbon centre with an electronegative, stable leaving group attached to it. The leaving group is expelled from the opposite side and the product is formed (S_N 2 mechanism). Weakly polar solvents such as ethers and ketones are employed. 18-crown-6 was used to enhance the solubility of the alkoxide as it exhibits an affinity for potassium ions.

The synthesis of 3-(6-bromohexyloxy)methylthiophene (CI) was successful, and the spectroscopic results have been summarised in the last Chapter (see Appendices).



Figure 42: Reaction scheme for the preparation of Compound II and Compound III

3.1.9 Synthesis of diethyl (4-cyanobenzyl)phosphonate (Compound II)

C II was prepared through an Arbuzov reaction, which is initiated by the $S_N 2$ reaction of the nucleophilic phosphite with the electrophilic bromoalkane to give a phosphonium intermediate. The displaced bromide anion reacts via another $S_N 2$ reaction with the phosphonium intermediate to give the desired phosphonate and another bromoalkane.

3.1.10 Synthesis of 4-[(E)-2-(4-hydroxyphenyl)ethenyl]benzonitrile (Compound III)

The preparation of C *III* was carried out through the Horner-Wadsworth-Emmons reaction is similar to the mechanism of the Wittig Reaction. The approach of the carbanion to the carbon of the carbonyl group is preferred when the smaller aldehydic hydrogen eclipses the bulky phosphoranyl moiety. This places the ester group *syn* to the aldehyde R group, but the developing alkene assumes an E-orientation of these groups after rotation to form the oxaphosphetane ⁷⁷.



¹H NMR (400 MHz, CDCl₃, ppm) CIII: 9.68 (s, 1H, phenoxide proton), 8.9-6.7: (d, 8H, Aromatic proton), (d, 2H, ethylene proton).



Figure 43: Reaction scheme for the preparation of Monomer 1

3.1.11 Synthesis of Monomer 1

In the presence of potassium carbonate, compound *III* is converted to the phenolate anion. This phenolate anion can undergo O-alkylation via the normal S_N2 reaction to yield the product monomer 1. The O-alkylated product is formed by an analogue process to the reaction in a Williamson Ether Synthesis.



Figure 44: Reaction scheme for the preparation of Compound IV and Compound V

3.1.12 Synthesis of diethyl benzylphosphonate (Compound IV)

C IV was prepared through an Arbuzov reaction, which is initiated by the $S_N 2$ reaction of the nucleophilic phosphite with the electrophilic bromomethane to give a phosphonium intermediate. The displaced bromide anion reacts via another $S_N 2$ reaction with the phosphonium intermediate to give the desired phosphonate and another bromoalkane.

3.1.13 Synthesis of 4-[(E)-2-phenylethenyl]phenol (Compound V)

The preparation of C IV and C V reaction was carried out through the Horner-Wadsworth-Emmons reaction, which is similar in mechanism to the Wittig Reaction. The approach of the carbanion to the carbon of the carbonyl group is preferred when the smaller aldehydic hydrogen eclipses the bulky phosphoranyl moiety. This process places the ester group *syn* to the aldehyde R group, but the developing alkene assumes an E-orientation of these groups after rotation to form the oxaphosphetane.



Figure 45: Reaction scheme for the preparation of monomer 2

3.1.14 Synthesis of Monomer 2

In the presence of potassium carbonate, compound V gets converted to the phenolate anion. This phenolate anion can undergo O-alkylation via the normal S_N2 reaction to yield the product monomer 2. The O-alkylated product is similar to those seen in Williamson Ether Syntheses.



Figure 46: Reaction scheme for the preparation of Compound VI

3.1.15 Synthesis of 4-{(E)-[(4-hydroxyphenyl)imino]methyl}benzonitrile (Compound VI)

The formation of an imine involves two steps. First, the amine nitrogen acts as a nucleophile, attacking the carbonyl carbon. In the next step, nitrogen is deprotonated, and the electrons from the N-H bond 'push' the oxygen off the carbon, leaving a C=N double bond (an imine) and a displaced water molecule ⁷⁸.



Figure 47: Reaction scheme for Schiff base reaction 78



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¹H NMR (400 MHz, CDCl₃, ppm) CVI: 9.6 (s, 1H, phenoxide proton), 8.7-68: (s, 1H, CH=N), (d, 8H, aromatic proton).



Figure 48: Reaction scheme for the preparation of monomer 3

3.1.16 Synthesis of Monomer 3

In the presence of potassium carbonate, compound VI is partially converted to the phenolate anion, which can undergo O-alkylation via the normal S_N2 reaction to yield the product, Monomer 3. The O-alkylation is similar to the reaction seen in Williamson Ether Synthesis.

3.2 UV-Visible and Fluorescence Spectroscopy results

UV-Visible Spectroscopy

The UV-visible absorption spectral data of polymers in the absence and presence of a magnetic field are presented in Figure 54. The π - π * transitions of the polymers occur at shorter wavelengths than for unsubstituted polythiophenes (350-390 nm) and this range of values are comparable to the results of Brown et al ⁷⁹ for poly{3-[6-(4-cyanobipheny]-4'-yloxy)hexyloxy] methylthiophene-2,5-diyl} (λ_{max} =385).

The bulky 3-substituents could have resulted in a blue shift of the absorption edge. However, in the presence of a magnetic field, the liquid crystal alignment might be expected to increase the conjugation and cause decreases in the transition energies, so the absorption peaks may shift to longer wavelengths.

Since the absorption of light is related to the band gap, the absorption spectra from UV-Visible spectroscopy enable us to calculate the band gap through Planck's equation ⁸⁰: $E=hc/\lambda$

For the units used in this thesis, Planck's equation becomes:

Band gap(eV)=1240/Absorption Edge (nm)

The energy gap of undoped polymer films was estimated through the Tauc equations. The direct-allowed transition relationship $[(EA)^2 \text{ versus } E]$ gave the best linearity ⁸¹.



Figure 49: Tauc plots for band gap of P1 (A) and P2, P3 (B) on ITO substrate before and after applying magnetic field

Analysis of the absorption edges of P1, P2 and P3 by solid-state UV-visible spectroscopy showed fairly similar band gap values. The band-gap energies of the polymers were considerably higher than those of poly(3-hexylthiophene)-poly(3-hexyloxythiophene) random copolymers (E_g =1.58 eV) and poly(3-hexylthiophene) (E_g =1.94 eV)⁸².

A significant property of poly(alkylthiophene)s is the regioregularity of the polymer, which strongly affects the geometry of the polymer chain. In a fully regioregular polymer, the adjacent monomer units are connected in a head-to-tail (H-T) arrangement, facilitating a coplanar structure. The full regioregularity of the polymer backbone results in a small band gap ⁸³. The larger energy gaps observed in un-aligned P1, P2 and P3 (2-2.7 eV) could be due to the lack of regioregularity and bulky substituents, which can produce conformational defects and generally poor π -overlap.

Polymers	Energy gap values (eV)
P1	2.98
P1 M	2.90
P2	2.85
P2 M	2.71
Р3	2.58
РЗ М	2.36

Table 3.1: Energy gaps of the polymers extrapolated from UV-Visible spectra Table 3.1 shows the band gap (E_g) energies for the polymers, calculated from the extrapolations of the data in Figure 54. A decrease in the E_g has been observed after exposure to the external magnetic field in each case. Introducing an external magnetic field to the LC polymers is likely to have caused a reorientation of the mesogenic groups, and as a result, affected the alignment of the polymer backbones. P1 and P3 showed the highest and lowest band gaps respectively. A decrease of 0.54 eV in the energy gap of P3 could be due to the introduction of a more polar group (Schiff base linkage) in that polymer, making the effect of the mesogen more powerful.

Fluorescence Spectroscopy

Photoluminescent properties of the polymers were investigated in the solid phase by means of a spectrofluorimeter. Due to the low solubility of the polymers it was not possible to study the samples in solution; therefore a film of each polymer on an ITO glass substrate was prepared by spin coating as explained in the previous chapter.

Figure 55 presents the solid-state fluorescence emission spectra. The emission spectra exhibited very similar shapes and spectral peaks for the polymers examined. The differences in the peak wavelengths were in all cases less than 10 nm. The fluorescent spectrum for the ITO glass substrate showed no major peak within this region. Therefore it was deduced that the similarities of the spectra were due to the common feature of the thiophene backbone in each polymer.

Major peaks in emission spectra	
λ(nm)	E (eV)
496	2.50
523	2.37
555	2.23
595	2.08

Table 3.2: Wavelengths and thecorresponding transitionenergies from the fluorescentspectrum of P3.

The samples were excited at a wavelength of 350 nm and the fluorescence spectra showed emission maxima in the region 475-625 nm due to the π - π * transition into the

excited state which has been reported in the literature for polythiophenes⁸³. The polymer films' emission spectra were well resolved, with a few quite sharp peaks.

Table 3.2 shows the major peaks in the emission spectrum of P3, and the strongest peaks at 523 nm (2.37 eV) and 555 nm (2.23 eV) are comparable to the energy gap of P3 extrapolated from Figure 54.







В

С

Figure 50: Solid state emission spectra of P1 (A), P2 (B) and P3 (C)

The individual sharp peaks suggest that for all the polymers the same isolated short conjugated sections of the polymers were excited; hence similar spectra were seen in all cases. The mesogenic groups of each polymer are different, and therefore we can say that the peaks correspond to the polymer backbone (which is unchanged in all three).

The most intense peak is found at 550nm, and the presence of smaller peaks appears in a patterned way on both sides of this central peak. Although there are only about five major peaks found in the spectra, it can be proposed that these spectra are vibronic in nature due to the fairly regular spacings of these peaks (a transition from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly). All the main peaks could correspond to transition to different vibrational states in the vibrational manifold of the π energy level from the ground vibrational state of the π^* energy level ⁸⁴⁻⁸⁶.



In support of this analysis, it may be pointed out that the energy differences between the main peaks are approximately 0.14 eV, which is similar to one of the strongest peaks in the polymer IR spectra.

3.3 Hot-Stage Polarising Microscopy

Hot-stage polarising microscopy is often used to observe the thermotropic behaviour of liquid crystals and polymeric samples. In the initial heating stage, samples are placed between microscope slides. As the temperature is increased, by viewing through crossed polars it is possible to study the behaviour of a sample and its phase changes as a function of temperature by the observation of characteristic liquid crystal patterns or optical textures ⁸⁷.

The transition temperatures for all monomers were determined by hot-stage polarising microscopy and verified by DSC, as these are discussed and presented in section 3.4. The distinct phases observed in the samples were smectic (S), nematic (N) and isotropic (I). Due to the combination of crystalline and glassy regions in the polymers, the phase transition temperatures were difficult to measure. All the monomers were heated at a constant rate (5 °C /min) on a glass slide until melting occurred, and then the samples were cooled to room temperature.

3.3.1 Hot-stage polarising optical microscopy results for M1

The optical micrographs of M1 show several phase transitions upon heating and cooling the sample film. The optical polarising microscope photographs of the textures of M1 (Figure 56) were recorded in the heating and cooling cycles. Initially, M1 exhibited optical anisotropy when observed by optical polarising microscopy, suggesting that the mesogens provided the compound with thermotropic liquid crystalline behaviour. The first phase transition from isotropic to a liquid crystal nematic phase was seen about 190 °C to 210 °C. The other main change in the texture happened about 60 °C to 80 °C. When the monomer was cooled from its isotropic state, many goldish textures appeared from the dark background and grew to form bigger domains.







Figure 51: Optical micrographs of M1

3.3.2 Hot-stage polarising optical microscopy results for M2

The optical micrographs of M2 (with no nitrile group) show only one phase transition upon heating and cooling the sample film. When the monomer was heated, the optical polarising micrographs of the textures of M2 (Figure 57) exhibited the first phase transition from smectic to isotropic phase at about 220 °C. When the monomer was cooled from its isotropic state, a smectic-like texture appeared from the dark background and developed into brighter domains at about 210 °C. As can be seen in Figure 57, this phase is stable all the way down to room temperature.



Figure 52: Optical micrographs of M2

3.3.3 Hot-stage polarising optical microscopy study of M3



Figure 53: Optical micrographs of M3

The observation for M3 (upon heating) was quite different from M1 and M2 and the monomer texture showed a clear smectic to isotropic phase transition at 165 °C. When the monomer was cooled from its isotropic state, a smectic texture appeared at about 150 °C. The presence of the Schiff base linkage in the centre of the mesogenic group may have increased the positional interaction between the molecules.

3.3.4 Hot-stage microscopy results of monomers in the presence of a magnetic field

In the present study, hot-stage microscopy was used to observe signs of molecular order after thermal treatment under the influence of a magnetic field of 0.2 T (or 2 K Gauss).

In order to study the effect of an applied magnetic field on the monomers' structures, they were heated in the hot-stage to reach the isotropic phase and then cooled down to room temperature at a constant rate. The samples were investigated by polarising optical microscopy. In the second stage, the samples were heated to the isotropic phase and cooled down to room temperature in the presence of the magnetic field under identical conditions.

Most liquid crystalline organic molecules are diamagnetic; hence induced, rather than permanent magnetic dipoles are responsible for the reorientation of the LC molecules in a magnetic field ⁸⁸. The liquid crystalline molecules tend to orientate themselves parallel to the magnetic field, decreasing the distortion of the magnetic flux when they are perpendicular to the magnetic field.



Figure 54: Liquid crystal molecule in magnetic field

M 1 showed a polycrystalline texture before and after applying magnetic field. As can be seen in Figure 60, the sample showed more alignment and a brighter colour distribution.



Figure 55: Hot stage polarising microscopy photos of M1 at RT after cooling from an isotropic liquid (A) in the absence, and (B) in the presence of magnetic field.

On the other hand, as can be seen in Figure 61, M2 was less responsive to the magnetic field; this may be due to the lack of a nitrile group in M2. The nitrile electronwithdrawing group would help in polarising the molecule and increase the intermolecular interactions.



Figure 56: Hot stage polarising microscopy photos of M2 at RT after cooling from an isotropic liquid (A) in the absence, and (B) in the presence of magnetic field.

A

B


A

В

Figure 57: Hot stage polarising microscopy photos of M3 at RT after cooling from an isotropic liquid (A) in the absence, and (B) in the presence of magnetic field.

With the magnetic field applied to the films during the domain growth, uniform planar alignment occurred in the bulk of the nematic phase, and remained after cooling and switching off the field. These changes are more distinct in M3. The orientation appeared stable against external magnetic fields applied afterwards at room temperature. Parshin et al ⁸⁹ investigated electric and magnetic field effects on the orientation of domains in a nematic liquid crystal on a polymer surface. When they applied a magnetic field to a sandwich parallel to the substrate during the domain growth, uniform planar alignment occurred in the bulk of the nematic phase.

3.3.4 Hot-stage microscopy results for polymers cooled from 300 °C to room temperature in the presence of a magnetic field



Α

В

Figure 58: Hot stage polarising microscopy photos of P1 cooled (A) in the absence, and (B) in the presence of magnetic field.

Slight changes in the textures of the polymer films were observed during the study by HSM; however, the colour, the high melting point and the infusibility of the resulting polymers made it difficult to observe the phase transitions by HSM in detail. Therefore the polymer films were further investigated by the X-ray diffraction technique.

В



Figure 59: Hot stage polarising microscopy photos of P2 cooled (A) in the absence, and (B) in the presence of magnetic field.

A

The polymers showed dark textures during heating and cooling, which made it difficult to observe the phase transitions. However, with the aid of XRD analysis, the textures can probably be attributed to the presence of smectic phases, which indicates that P1 and P2 show some liquid crystallinity. This suggests that the spacer provides polythiophene backbones and the mesogens with the flexibility to move and pack in a regular fashion.



A

В



The polymer films showed a brighter colour (higher transmission) after treating with magnetic field, which is likely to be an indication of an increase in the liquid crystalline alignment, since it is caused by the presence of optical anisotropy in the samples. The spacer gives the mesogens the flexibility to rearrange themselves after exposure to the external field.

3.4 Differential Scanning Calorimetry (DSC)

DSC is used to observe thermal changes involved in glass transitions, liquid crystalline phase transitions and melting points, as well as chemical reactions ⁹⁰. Using DSC, it is possible to observe the small thermal energy changes that occur as matter changes from a solid to a liquid crystal and from a liquid crystal to an isotropic liquid ⁹¹. In this study, the effects of heating and cooling on monomer samples were investigated. The results can be seen in Table 3.3.

Polymers	Transition temperature (°C)						
or Monomers	C→S	S→C	S→N	N→S	N→I	I→N	
M1	60		154	167	185		<u></u>
М2	85	76	112		194	183	
М3	64				165(S	→I) 142(I→S)
P1							177
P2							180
P3							179

Table 3.3. The distinct phases observed in the samples by DSC analysis. Crystalline (C), Smectic (S), Nematic (N), and isotropic (I).



Figure 61: DSC thermogram of M1

The DSC thermogram of M1 shows the first sharp endothermic peak at 60 °C and it could be considered as a crystalline to smectic transition. The HSM results for this monomer showed a phase change at this temperature. Another (broad) peak can be seen from 80 °C to 105 °C and it could be considered as the glass transition. The third phase transition happens at 154 °C. The HSM micrographs indicate the presence of a phase change from smectic to nematic liquid crystallinity at this temperature. Upon cooling the sample, only one sharp exothermic peak around 167 °C was observed, and the nematic to isotropic phase change occurs around 190 °C.



Figure 62: DSC thermogram of M2

In DSC thermograms of M2, three transitions can be seen between 80 °C and 130 °C. As can be seen from the DSC thermogram for M2, the first endothermic phase change can be observed at 85 °C, however the HSM micrographs did not show any phase change at this temperature. The second significant peak appearing around 112°C can be related to a smectic to nematic transition, and there appears to be a small nematic to isotropic change around 200 °C. Two peaks at 183 °C and 76 °C were observed during cooling the sample which could correspond to isotropic to nematic and smectic to crystalline phase transitions respectively.



Figure 63: DSC thermogram of M3

Two characteristic phase changes can be seen in the DSC thermograms of M3. The first phase change was around 64°C, and according to HSM micrographs it belongs to a crystal to smectic phase transition. In the HSM studies, no nematic phase was observed and the second endothermic phase transition seen at around 165°C can be considered as a smectic to isotropic transition. Upon cooling a peak was observed at 142 °C which could correspond to isotropic to smectic phase transion.

Some factors such as the combination of crystalline and glassy material in the polymers, the high melting points and the infusibility of the resulting polymers made it difficult to measure the phase transition temperatures by DSC. For the polymers we could only observe phase changes during the heating scan (The thermograms are provided in the Appendices).

Phase transitions were observed between 160 °C to 180 °C for P1, P2 and P3, which can be considered as glassy to nematic transitions. These results can be compared with results obtained by Brown et al. Their DSC results showed a glassy to nematic transition for 3-[6-(4-cyanobiphenyl-4"-yloxy)hexyloxy]methylthiophene at 176 °C.

3.5 The thermal stabilities of the polymers investigated by TGA

The TGA thermograms show the weight loss behaviour ⁹² of P1, P2, P3 and P4 in a nitrogen atmosphere, which occurred at temperatures around 250° C and 570° C. Minor weight losses starting at low temperature can be considered as being due to the release of water or other volatile residues. For P4, the initial degradation step from 220° C to 350° C, probably involves the degradation of the attached mesogenic groups. A significant amount of residue (70%) was left from the initial mass, which suggests that the residue mostly contains the polymer backbone. P1 and P2 showed almost identical behaviour. Both polymers were stable up to 380° C. Due to the imine linkage in P3, its thermal stability is lower than P1 and P2.



Figure 64: TGA thermograms of polymers under nitrogen atmosphere.

3.6 Electrical Conductivity:

A pellet of each polymer (with and without treatment by an axial magnetic field) was lightly doped by exposure to the mild oxidant, iodine vapour, for 24 hours at ambient temperature. The electrical conductivities of slightly doped P1, P2 and P3, were measured in the in-plane and axial direction after equilibrating for 72 hours, and can be seen in Table 3.4. These results are comparable with the measured conductivity of $9x10^{-8}$ Sm⁻¹ by Soto et al ⁹³ for poly(3-alkyloxymethylthiophene)s.

Compound	Conductivity (σ)/Sm ^{.1} Before MF	Axial Conductivity MF (72 hours) (σ)/Sm ⁻¹	In-plane Conductivity MF (σ)/Sm ⁻¹
Pl	3.4x10 ⁻⁷	1.46x10 ⁻¹⁰	1.5x10 ⁻⁷
P2	9.2x10 ⁻⁷	6.8x10 ⁻⁸	3.9x10 ⁻⁷
Р3	2.4x10 ⁻⁶	7.5×10 ⁻⁷	1.8×10 ⁻⁶

Table 3.4: Measured conductivities of P1, P2 and P3 pellets before and after treatment with a magnetic field (MF).

The relatively low conductivities of these polymers may be due to the conformational structures of the polymer chains. The presence of the alkyl chain in position 3 of the thiophene rings could cause a distortion in the dihedral planarity between the neighbouring rings of the chain, and as a result the conductivity would decrease, due to not being able to achieve the quinoid structures that allow the movement of electric

charges. Since terminal bulky groups were added, the steric interactions among these would increase the distortion in the chain.

The polymers showed large decreases in their axial conductivities (parallel to the MF), but the conductivities remained high in the plane of the pellets. This is proposed to be due to the fact that the polymers were more aligned in the plane of the disk (perpendicular to the magnetic field). It is reasonable to envisage that, in the LC state, the mesogenic units align with the applied magnetic field. The thiophene backbone units, being roughly perpendicular to the mesogens, would then be constrained to align themselves approximately parallel to the flat disk surfaces. Hence the conductivity (after doping) is expected to be high within the disk plane, and lower along the disk axis.

3.7 Cyclic Voltammetry

Voltammograms of the P1, P2 and P3 films doped with tetrabutylammonium tetrafluoroborate showed one oxidation peak between 1.3 V and 1.9 V, which is a typical redox behaviour of conducting polymers ⁹⁴. In the literature, peaks around 0.6 and 1.9 V are sometimes attributed to the generation of polarons and bipolarons, respectively.



Figure 65: Cyclic voltammetry behaviour of M1. Scan rate is 50 mV/s.



Figure 66: Cyclic voltammetry behaviour of M2. Scan rate is 50 mV/s.

The oxidation potentials of the monomers were determined by cyclic voltammetry. M2 and M3 exhibited two anodic peaks, the first peaks being due to oxidative doping of the polymer chain (accompanied by a balancing counteranion) and the second ones are due to oxidation of the thiophene monomers to form radical cations.



Figure 67: Cyclic voltammetry behaviour of M3. Scan rate is 50 mV/s.

As can be seen in the voltammograms, the peak currents increased as the cycle numbers increased, indicating the formation and growth of a polymer as reported earlier for other thiophene polymers ⁷⁷. However no solid polymeric film was observed on the ITO substrate, and the reason for that is unknown.

Monomers	Monomer Oxidation	Polymer Doping	Polymer Dedoping
	Potential	Potential	Potential
M1	1.59 V		
M2	1.99 V	1.1 V	0.3 V
М3	1.99 V	1.1 V	0.2 V

3.8 X Ray Diffraction

To investigate further the behaviour of monomers and polymers revealed by hot-stage microscopy and DSC, X-Ray diffractometry measurements were carried out to give a better understanding of molecular packing and structure of the monomers and polymers. Due to the high melting point and low solubility of the bulk solid polymers, it was not possible to study them in the presence of a magnetic field; eventually however, the problem was overcome by preparation of polymer films on a silicon wafer substrate through solid-state polymerisation.

3.8.1 XRD of monomers

In the present work X-ray diffractometry was used to observe any signs of microscopic structural changes under the influence of a magnetic field of 0.2 T. In order to study the effect of a magnetic field on the monomers' structures, they were studied by XRD before and after applying the magnetic field under identical conditions. X-ray diffraction patterns showed that the monomer films had higher crystallinity than the powder samples. The powder XRD data could not be analysed fully to enable the crystal structures to be determined, but an attempt was made to see whether any major features of the XRD patterns could be correlated with reasonable structures modelled by the Scigress software.



Figure 68: M1 structure modelling by Scigress

Under ideal conditions, XRD analysis can deliver useful information about molecular orientation and packing in mesophases in liquid crystalline polymers ^{95,96}. The structures of the monomers 1,2 and 3 films and powders were studied using X-ray diffraction at room temperature. Figure 74 shows that the XRD pattern of M1 displays quite sharp Bragg reflections at various angles. In the film sample of M1, the first reflection at low angle corresponds to a long d-spacing of 14.8 A°, which is less than the molecular length modelled by Scigress (Figure 73); this may indicate a smectic mesophase with displaced bilayer arrangement, where the mesogens are integrated in an stacking fashion.



The geometry was optimised by Scigress to simulate the possible layer structure, which contains the d-spacing found in XRD. The peak at about 6 A° may be due to the distance between the molecules within the same plane and the peak at 4 A° may correlate with the interlayer distance. The lack of a comparable peak in the powder sample indicates that the smectic mesophase developed after applying heat to the M1 film.



Figure 69: XRD pattern of M1 film on silicon wafer



Figure 70: XRD pattern of M1 film on silicon wafer after applying a magnetic field



Figure 71: XRD pattern of M1 film on silicon wafer before and after applying magnetic field

After treating M1 with the magnetic field, a peak at 2.70 A° appeared; however the peak could not be reproduced. The rest of the d-spacings had a very close similarity and some small changes can be observed.



Figure 72: M2 structure modelling by Scigress

The XRD pattern of M2 (Figure 79) shows high crystallinity in the monomer film. The d-spacing of 25.2 A° is greater than the molecular length of M2 and may be an indication of a π -stacking mode of the benzene rings. If the benzene rings are in a sandwich mode, the d-spacing can be bigger than in a parallel-displaced mode.

As can be seen in Figure 80, after treating M2 film with a magnetic field, no distinctive changes can be found in the d-spacing, although the intensities of the peaks increased. This may be due to an increase of the molecular organisation caused by the external field.



Figure 73: XRD pattern crystal structure modelling of M2 by Scigress



Figure 74: XRD pattern of M2 film on a silicon wafer



Figure 75: XRD pattern of M2 film on a silicon wafer after applying a magnetic field



Figure 76: XRD pattern of M2 film on a silicon wafer before and after applying a magnetic field



Figure 77: M3 structure modelling by Scigress

Figure 83 shows that the XRD pattern of M3 exhibits Bragg reflections at low angles. In the film sample of the M3 the first reflection at low angle corresponds to long dspacings of 13.8 A° and 14.7 A°, which are less than the molecular length (Figure 82); this may indicate a smectic mesophase with bilayer arrangement, where the mesogens are in a parallel-displaced stacked conformation. These results are in agreement with the smectic features observed by HSM. M3 showed a significant change by a broad peak appearing at 5.98 A° (Figure 84). This peak was easily reproduced by re-heating the sample to its isotropic phase and cooling down again in a magnetic field.



Figure 78: XRD pattern of M3 film on a silicon wafer



Figure 79: XRD pattern of M3 film on a silicon wafer after applying a magnetic field

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Figure 80: XRD pattern of M3 film on a silicon wafer after reheating

Figure 87 shows that the M3 film was investigated in four stages. In the first and third stages the XRD diffractograms were studied after cooling down slowly from the isotropic state to room temperature. In the second and fourth stages the film was exposed to a magnetic field and the reappearance of a peak with a d-spacing of 5.98 A° each time appears to be an indication of the influence of the external field on the sample molecules.



Figure 81: XRD pattern of M3 film on a silicon wafer after reapplying magnetic field for a second time



Figure 82: XRD pattern of M3 film on a silicon wafer after repeatedly reapplying a magnetic field after annealing cycles

3.8.2 XRD of polymers

Under ideal conditions, XRD analysis can provide valuable information about molecular arrangement, mode of packing and type of order in a mesophase of a polymeric liquid crystal ⁹⁷. The polymer thin films were studied using XRD at room temperature after the samples had been quenched from their liquid-crystal states.



Figure 83: Suggested chain packing in P2



Figure 84: XRD pattern of P1 film on a silicon wafer

P1 showed some strong peaks at low and high angles. As can be seen from Figures 89 and 90, no significant change can be found in the XRD pattern of P1 before and after applying the magnetic field (some of the relative intensities changed for example peak at d=5.8 A° became weaker but the peak at d=1.5 A° became stronger). This effect on the polymeric structures could be attributed to the lack of free volume. The peak at low angle from which a d-spacing of 5.87 A° is derived from Bragg's law, is consistent with a lateral packing arrangement of the mesogenic groups, as modelled by Scigress.



Figure 85: XRD pattern of P1 film on a silicon wafer after applying magnetic field



Figure 86: XRD pattern of P2 film on a silicon wafer



Figure 87: XRD pattern of P2 film on a silicon wafer after applying magnetic field

P2 similarly showed some strong peaks at low and high angles. As can be seen from Figures 91 and 92, some peaks at 13.88 A°, 9.0 A°, 6.79 A°, 5.46 A° and 4.56 A° disappeared after treating the P2 film with the magnetic field, indicating that a change in the alignment of the LC domains had occurred.

The peak at low angle with a d-spacing of 5.87 A ° observed for P1 and P2 was attributed to the lateral packing arrangement of the mesogenic groups. These results can be compared with the XRD results of Chen et al ⁹⁸ for poly[3-(6-(4-cyanobiphenyloxy) hexyl) thiophene].

The diffractogram of poly[3-(6-(4-cyanobiphenyloxy) hexyl) thiophene] quenched from liquid crystal states exhibited a broad peak with a d-spacing of 4.4 A° occurring in the lateral packing arrangement of the mesogenic pendants ^{98,101}.



Proposed 3D packing arrangement of polymer P3HbpT with the smectogens interdigitating in antiparallel fashion ⁹⁸.

The XRD patterns of P3 exhibited a small degree of crystallinity in the polymer film. Only one significant peak could be observed at low angle ($2\Theta = 9.0^{\circ}$). This was rather surprising, in view of the good crystallinity of M3 films, but it was not possible to obtain sufficiently thick films of P3 to produce satisfactory XRD data.

Chapter IV

Conclusion &

Recommendations for

Future Work

Conclusion

The work discussed in this thesis involved the synthesis of liquid crystalline conjugated polythiophenes, chemical and physical characterisations of the monomers and the polymers. Amongst all the monomers and intermediates synthesised, the research concentrated on monomers 1, 2 and 3 with terminally-attached mesogens, and the corresponding polymers. The synthetic steps and structures are reprised in the scheme below. The polymerisation was studied by cyclic voltammetry, but the most successful polymerisations were achieved by chemical, rather than electrochemical means.



A decrease in the E_g values (calculated from the extrapolations of UV-visible data) was observed after exposure to the external magnetic field. The applied magnetic field is thought to have affected the orientation of the mesogenic groups, and as a result, increased the planarity of the polymer backbones.

Polymers	Energy gap values (eV)
P1	2.98
P1 M	2.90
P2	2.85
P2 M	2.71
Р3	2.58
РЗ М	2.36

The photoluminescent properties of the polymers were investigated in the solid phase by means of a spectrofluorimeter. The emission spectra exhibited very similar shapes and spectral peaks for the polymers examined, The peaks appeared in a regular patterned way on both sides of the main peak. It was proposed that these spectra were vibronic in nature due to the spacings of these peaks. Therefore these peaks could correspond to transitions from the ground state of the π^* energy level to different vibrational energies in the vibrational manifold of the π energy level. Under HSM, the monomers exhibited liquid crystalline phases. In this study, the effects of heating and cooling programmes on monomer and polymer samples were investigated, and the distinct phases observed in the samples by DSC analysis are shown in the table below.

Polymers	Transition temperature (°C)						
or Monomers	C→S	S→C	S→N	N→S	N→I	I→N	
M1	60	· · · · ·	154	167	185		
M2	85	76	112		194	183	
М3	64				165(S→I)	142(I→S))
P1							177
P2							180
Р3							179

The DSC thermograms also exhibited phase transitions upon heating and cooling the monomers. Monomers 1 and 2 showed the presence of smectic to nematic and nematic to isotropic phase transitions whereas monomer 3 only showed the smectic to isotropic phase transition.

The monomers and polymers were exposed to a magnetic field and the effect of the field was studied by HSM and XRD. Some rearrangements in the molecular organisation of the monomers and polymers were observed by HSM and these changes were further studied by XRD.

XRD provided a good understanding of molecular packing and structure of the monomers and polymers. The action of the magnetic field on the monomers showed

some distinctive and small changes in the XRD spectra. The influence of the external field on M3 was confirmed by the reappearance of a peak with a d-spacing of 5.98 A° each time after applying a magnetic field.

The dc electrical conductivities of slightly iodine-doped P1, P2 and P3 were measured at room temperature. The electrical conductivities of polymer pellets after applying a magnetic field and slightly doped was measured in the axial and the in-plane directions.

Compound	Conductivity (σ)/Sm ⁻¹ Before MF	Axial Conductivity MF (72 hours) (σ)/Sm ⁻¹	In-plane Conductivity MF (σ)/Sm ⁻¹
PI	3.4x10 ⁻⁷	1.46x10 ⁻¹⁰	1.5x10 ⁻⁷
Р2	9.2x10 ⁻⁷	6.8x10 ⁻⁸	3.9x10 ⁻⁷
Р3	2.4x10 ⁻⁶	7.5x10 ⁻⁷	1.8x10 ⁻⁶

Polymers showed a large decrease in their axial conductivities, while the conductivities remained high in the plane of the pellets. This is thought to be due to the fact that the polymers were more aligned in the plane of the disks, which were perpendicular to the magnetic field.

It is noteworthy that the polymer (P3) that showed the strongest liquid crystallinity also exhibited the smallest band-gap energy and the highest electrical conductivity. The combination of evidence from different techniques strongly supports the proposition that the mesogenic groups can be used to influence the electronic properties of polythiophenes.

Recommendations for Future Work

For areas in the project where the preparation of some of the compounds such as CIV and CV was unsuccessful, it would be useful to try another route to reach the target compounds.



The resulting polymers had poor solubilities in most organic solvents and reacting the monomers with 3-hexylthiophene in order to make a copolymer might help to overcome this difficulty. It could also lower the T_g of the polymers, so that LC effects might be observed at low temperatures.

The magnetic field was perpendicular to the surfaces of the film samples, and it would be interesting to study the samples by XRD while they are parallel to the field. It might also have a beneficial effect on the electrosynthesis of thin films.
It would be informative to study the effects of applied electric fields on the monomer and polymer samples. Applying an electric field to the compounds sandwiched between ITO electrodes might help us to investigate the rearrangement of molecular packing in the samples.

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Appendices

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GCMS results for CI





GSMS results for C2 and C3



GCMS results for CII, MS: m/z= 253



GCMS results for CIII, MS:m/z=220



ATR results for CIII





GCMS results for C2

```
File :D:\MSDChem\1\DATA\DAN-21MAY13-3.D
Operator :
Acquired : 22 May 2013 4:56 using AcqMethod DEFAULTAUTO.M
Instrument : Instrument 1
Sample Name:
Misc Info :
Vial Number: 13
```



GCMS results for C3





GCMS results for CVI





GCMS results for M3

3



DSC results for P4



¹H NMR results for CIII



GCMS results for CIV

:D:\MSDChem\1\DATA\DAN-2MAY13SECOND.D





GCMS results for M1



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

¹H NMR results for CVI

WU50648/Desktop/OPEGH/OPEGH 010.esp

and Se



ATR results for CVI











¹H NMR results for M1



¹H NMR results for M3



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

¹H NMR results for CI

4



P2



Ρ3



DSC results for P1



DSC results for P2



DSC results for P3



monomer CN HS MF Line (CDs) BCS 7-0 M1 2 4933 #2.70k ar 1882 d=2.079 d=2.147 k 10 30 40 50 3 2-Theta - Scale

Construction of the second sec



















nemer schill base hs - File monomer schill base hs new - Type: 2Th/Th locked - Start 3.000 * - End: 60.000 * - Step: 0.100 * - Step time: 2, s - Temp.: 25 *C (Reem) - Time Started: 1400080344 s - 2-Th endions: Import





PCN spin mf reheat 2 - File: PCN spin mf reheat 2 saw - Type: ZTN/Th locked - Start 5.000* - End: 65.000* - Step: 0.100* - Step time: 1. s - Temp: 25 *C (Room) - Time Started: 1423246080 s - 2-Theta: 5.000* - Constituent import



ED/PCH spin netword 3 - File: PCH spin netword 3 zww - Type: 21%/Th locked - Start 5 000 * - End: 65 000 * - Step: 0.100 * - Step line: 1. s - Temp: 25 *C (Room) - Time Started: 1423658176 s - 2-Theta: 5 000 * - Theta: Operations: Import



PCN Spin wafer 1D MF reheated

PCN Spin wafer 1D MF


PCN Spin wafer 1D





XRD pattern of M1 loose powder







XRD pattern of M3 loose powder



XRD pattern of P3 film on silicon wafer



XRD pattern of P2 film on silicon wafer



UV-visible spectra of the P1, P2 and P3 films on ITO substrate after applying magnetic field



UV-visible spectra of the P1, P2 and P3 films on ITO substrate.



Solid state emission spectra of M2 (A) and M3 (B)



DSC thermogram of P1



DSC thermogram of P2



DSC thermogram of P3

CONDUCTIVITIES (IN-PLANE) OF POLYMER SAMPLES AFTER EXPOSURE TO MAGNETIC FIELD & RE-DOPING

For the 4-probe contact configuration:

Conductivity $\sigma = I / [V.l.G]$

where: I = current

V = voltage

l =sample thickness

G = geometric factor $\simeq 4.3$

Sample	I (A)	V (V)	Conductivity/Sm ⁻¹
P1	2.5 x 10 ⁻⁸	38.8 ± 0.5	1.5 x 10 ⁻⁷
P2	1.0 x 10 ⁻⁸	5.96 ± 0.02	3.9 x 10 ⁻⁷
P3	5.0 x 10 ⁻⁸	6.55 ± 0.03	1.8 x 10 ⁻⁶

Compound	Resistance (R) Ω	Cross sectional area (A) m ²	Thickness (L) m	Conductivity (ơ)/Sm ⁻¹
Pl	2.2x10 ⁷	1.33x10 ⁻⁴	1x10 ⁻³	3.4x10 ^{.7}
P2	8.2x10 ⁶	1.33x10 ⁻⁴	1x10 ⁻³	9.2x10 ⁻⁷
Р3	3.1x10 ⁶	1.33x10 ⁻⁴	1x10 ⁻³	2.4x10 ⁻⁶

Compound	Resistance (R) Ω	Cross sectional area (A) m ²	Thickness (L) m	Conductivity MF(doped 48 H) (σ)/Sm ⁻¹
Pl	1.8x10 ¹¹	1.33x10 ⁻⁴	1x10 ⁻³	4x10 ⁻¹¹
P2	2.2x10 ⁸	1.33x10 ⁻⁴	1x10 ⁻³	3.4x10 ⁻⁸
Р3	2.6x10 ⁸	1.33x10 ⁻⁴	1x10 ⁻³	2.9x10 ⁻⁸

Compound	Resistance (R) Ω	Cross sectional area (A) m ²	Thickness (L) m	Conductivity MF(doped 72 H) (σ)/Sm ⁻¹
Pl	5.2x10 ¹⁰	1.33x10 ⁻⁴	1x10 ⁻³	1.46x10 ⁻¹⁰
P2	1.1x10 ⁸	1.33x10 ⁻⁴	1x10 ⁻³	6.8x10 ⁻⁸
Р3	1.0x10 ⁷	1.33x10 ⁻⁴	1x10 ⁻³	7.5x10 ⁻⁷

Conductivity measurements