KINGSTON UNIVERSITY

Intrinsically-Conducting Polymers

A Thesis Submitted in Partial Fulfilment of the Requirements of Kingston University for the Degree of Doctor of Philosophy

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Abstract

The synthesis, properties optimisation and blending of two intrinsically conducting polymer families have been investigated. Electron rich polymers, based on polythiophene derivatives, and electron deficient polymers, based on polypyridine derivatives, were successfully synthesised and characterised. Poly (3,4-ethylenedioxythiophene) [PEDOT] was synthesised by controlled oxidative polymerisation. Hexyl-substituted EDOT, which is commercially unavailable, was successfully synthesised via an eight step reaction. Poly (3-nitropyridine) [PPy-3-NO_2] was produced following a revised literature method. The synthesised polymers were then blended together in a 1:1 monomer ratio.

A search for evidence of charge transfer between the blended polymers was carried out using several techniques. UV-Visible spectroscopy showed signs of an increase in the extent of conjugation due to charge transfer. ESR measurements showed a large increase in the concentration of unpaired electrons in the blends. Cyclic voltammetry was employed to study the electrochemical behaviour, and revealed that the charge transfer caused the polymers in the blend to oxidise and reduce differently from the pure polymers. Finally, electrical conductivity measurements indicated an increase in the bulk conductivity when blending the polymers together reaching, in some cases, up to two orders of magnitude.

Acknowledgment

The completion of this research would not have been possible without the support and encouragement of several people, all of whom deserve special mention.

Firstly, I would like to thank my supervisor, Professor Peter Foot, for his invaluable support and guidance throughout the research project. His thought-provoking suggestions and comments have been influential in shaping the final product of the research.

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Finally, I would like to dedicate this dissertation to my beloved Mum, Salwa, and Dad, Issam, for their principled support and pearls of wisdom. I also offer special thanks to my brother, Aeyad, for his financial and moral support. I am grateful for the opportunity to put into print my love and thanks to my sisters, Lina, Noora and their families, for their endless moral support.

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1 Introduction

These days, polymers are an important part of our daily life to the extent that almost everything we use involves them. Plastics, fibres, rubbers, coatings etc; all these are terms we use in our modern vocabulary. Whatever the method one chooses to demonstrate its applications and uses, a fundamental factor is that a particular polymer is used because it does the job better than other materials, either for its unique properties or its economy[1].

Polymer is a term used to describe a very large molecule consisting of structural units and repeating units connected by covalent chemical bonds. The term is derived from the Greek words: 'poly' meaning many, and 'meros' meaning parts[2]. The key feature that distinguishes polymers from other molecules is the repetition of many identical, similar, or complementary molecular subunits in these chains. These subunits, known as monomers, are small molecules of low to moderate molecular weight, and are linked to each other during a chemical reaction called polymerization.

Instead of being identical, similar monomers can have various chemical substituents. The differences between monomers can affect properties such as solubility, flexibility and strength. In proteins, these differences give the polymer the ability to adopt a biologically-active role in preference to others. Identical monomers with non-reactive side groups result in a polymer chain that will tend to adopt a random coil conformation, as described by an ideal chain mathematical model. Although most polymers are organic, with carbon-based monomers, there are also inorganic polymers; for example, the silicones, with a backbone of alternating silicon and oxygen atoms.

1.1 Polymer Classification

Polymers are typically classified according to four main groups:

- Thermoplastics (linear or branched chains)
- Thermosets (cross linked chains)
- Elastomers
- Coordination polymers

The term polymer covers a large, diverse group of molecules, which ranges from substances such as proteins to stiff, high-strength Kevlar fibres. For example, the formation of polyethene (also called polyethylene) involves thousands of ethene molecules bonded together to form a straight (or branched) chain of repeating $-CH_2-CH_2-$ units, normally with a $-CH_3$ at each terminal (depending on the termination mechanism).

Polymers are often named in terms of the monomer from which they are made. Polyethylene has a saturated structure because it is synthesized from ethene in a process during which all the double bonds in the vinyl monomers are lost.

Synthetic polymer formation is governed by random assembly from the constituent monomers; as a result, polymer chains within a solution or substance are generally not of equal length. This is unlike smaller molecules in which every atom is stoichiometrically accounted for, and each molecule has a set molecular mass. An ensemble of differing chain lengths, often obeying a normal (Gaussian) distribution, occurs because polymer chains terminate during polymerization after random amounts of chain lengthening (propagation).

1.2 Plastics... from Insulators to Conductors...

Polymers, in general, are a combination of (σ-sigma) bonds and (π-pi) bonds forming immobile covalent bonds between the carbon atoms[3]. The electrons in a conjugated double bond system are also relatively localised. Before a current can flow along the molecule, one or more electrons have to be removed or inserted to produce a charge imbalance. If an electrical field is then applied, the electrons constituting the conjugated bonds can move rapidly along the molecule chain. The bulk conductivity of the polymer will still be limited by the fact that the electrons have to "jump" from one molecule to the next[4]. Hence, the chains preferably have to be well packed in ordered systems, in order to minimise the energy barriers for the inter-chain transport.

1.3 Conducting Polymers, a Historical Review

Polymers can be found in almost all products in our everyday life: clothes, furniture, home appliances, cars, electronics, etc. because of their excellent properties; they are lightweight, relatively cheap and easy to fabricate, modify and process. The concept of polymers did not achieve general acceptance until the early years of the 20th Century. Popularly known as "plastics," polymers are large molecules constructed from smaller structural units (monomers) covalently bonded together in any conceivable pattern Most of polymers are treated as insulators because of their high resistivity.

The term 'electrical conductor' is usually assigned to metals or alloys. The discovery of conducting polymers has opened a new branch in materials research by modifying the monomer building block and bonding scheme, the mechanical and thermal properties of the polymer can be controlled.

Today, organic polymers can be made to conduct electric currents and, in future, they may also exhibit useful magnetic properties. Research and development in properties of plastics have already brought them very close to metals in terms of their mechanical properties, strength, elasticity and moulding etc.

In 1910[5], the electrical conductivity of a form of polyaniline (Pani) was reported. The conductivity was improved when the polymer was treated with acetic acid; however, this new discovery was forgotten. In the succeeding decades, chemists repeatedly tried to make polymers with metallic conductivity. In the late 1950s and early 1960s, Natta *et al* and Luttinger synthesised polyacetylene but the product did not exhibit significant conductive properties. Dall'Olio *et al*[6] prepared polypyrrole from aqueous sulphuric acid in 1969, but the product had poor mechanical and electrical properties. In 1979, Diaz and co-workers at IBM in San Jose reported that polypyrrole (Ppy) could be obtained as a free-standing film by electrochemical oxidation of pyrrole in acetonitrile[7,8].

The discovery of conducting polymers via doping in 1977[9] opened new doors for many researchers at the time. The motivation for further research was primarily the need to develop materials with important electronic and optical properties. Figure 1 shows the location of conducting polymers among classes of material from insulators to conductors.

The fast-moving progress has provided a greater understanding of conducting polymers, leading to various methods of synthesising new generations of conducting polymers. Advanced research has shown the possibility of obtaining new materials with novel characteristics. The current range of applications is remarkably wide.

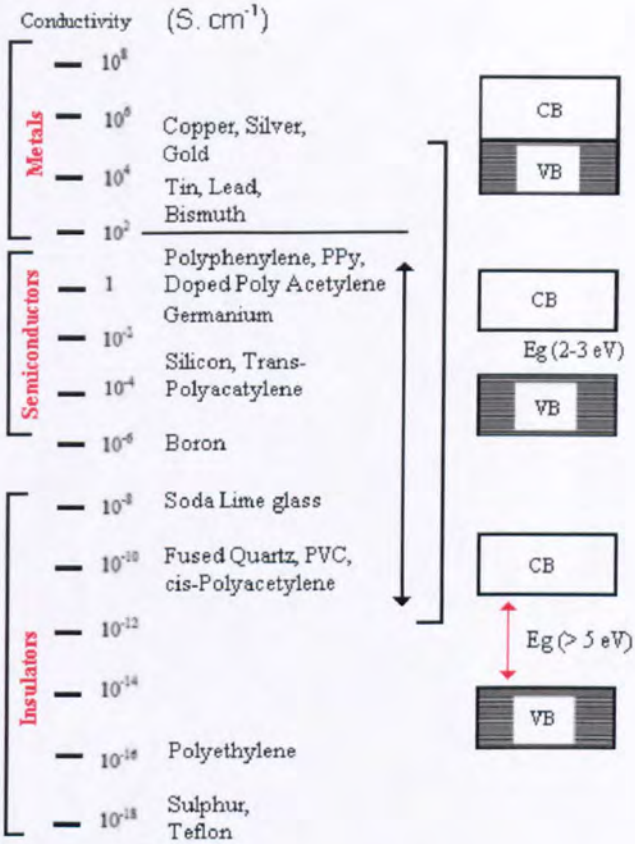


Figure 1 Classification of materials over a range of 24 orders of magnitude from insulators to conductors (Valence Band = VB; Conduction Band = CB; Band Gap = Eg)

1.4 Basic Characteristics of Conducting Polymers

Electro-active polymers are generally classified into two main groups based on their electric transport process. The first group includes ionic conducting polymers; they are often called 'polymer electrolytes' or 'polymer ionics'. Polyethylene oxide, in which lithium ion is mobile, is a typical example.

The second group of intrinsically conducting polymers or conjugated polymers is electronic conductors[10]. This type of polymeric material is the subject of this research. Polypyridines (Ppy), Polypyrrole (Ppyr) and Polythiophene (Pth) are examples of this class of materials.

Chapter Two

Literature Review

2 Literature Review

2.1 Intrinsically Conducting Polymers

Intrinsically conducting polymers (ICPs) are an exciting new class of electronic materials, which have attracted rapidly increasing interest since their discovery[11]. ICPs have the potential of combining the high conductivities of pure metals with the processability, corrosion resistance and low density of polymers[12] and are beginning to find applications in the fields of battery materials[13], electrochromic displays[14], electromagnetic shielding[15], sensor technology[16], non-linear optics[17]and molecular electronics[18] .

Nevertheless, their properties require further adaptation, improvement and optimisation. The use of substituted monomers and post-treatment has brought considerable benefits in terms of better processability. Unfortunately, limitations on the production of useful and stable conductivity by conventional means can arise for diverse reasons. At low concentrations, small ions located between the chains tend to immobilise the charge carriers in the polymer by means of their strong Coulombic attraction, although this becomes less noticeable at higher concentrations, when charges are more efficiently screened from each other. Conversely, bulky counter ions have a weaker Coulombic effect but a greater tendency to disrupt the structural perfection of polymer chains; this can enormously reduce the effective delocalisation of the π-electron states, and again paralyse the charge carriers.

2.2 Synthesis of π-Conjugated Polymers

2.2.1 Polyacetylene

Polyacetylene is considered a prototype as the simplest conjugated organic polymer[19]. The current interest in conductive polymers began in the 1970's, when it was found that the

electrical conductivity of polyacetylene, a semi-conductor when pristine, could be increased by over fifteen orders of magnitude by treatment with oxidising agents such as iodine.

Polyacetylene has been the most theoretically[20] and experimentally studied conducting polymer, owing to its simple conjugated structure and high conductivity (10^4-10^6 S cm^{-1}), comparable to that of metals[21].

Synthesis of Polyacetylene

Polyacetylene was originally prepared by two main synthetic routes, the Shirakawa and the Luttinger[22] one. Both materials were insoluble and unprocessable. Edwards and Feast[23] developed an alternative route for the preparation of polyacetylene via a soluble precursor polymer.

Shirakawa Route

Most research on polyacetylene has been performed by this route, which involves via the Ziegler-Natta polymerisation of acetylene[24,25] (Figure 2). By varying the catalyst concentration in the solvent, it is possible to obtain polyacetylene as a gel, powder or thin film.[26].

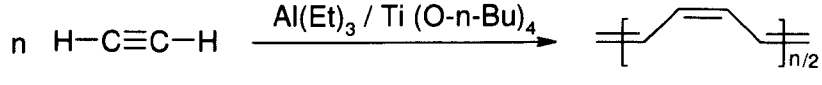


Figure 2 Shirakawa's route to polyacetylene

Increasing the temperature and the aging time of the catalyst improves the conductivity[27],whereas the concentration and the aluminium-titanium ratio determine the morphology[28,29].

Absolute trans-polyacetylene is synthesised in the absence of the aging step, and the use of a titanium-aluminium ratio of one[30]. The use of silicone oil as an alternative solvent to toluene is claimed to yield a polymer containing an equal amount of cis and trans moieties and a much lower concentration of sp^3 carbon atoms[31]. A so called "reducing agent" method was developed by Naarmann et al[32], where the addition of a reducing agent to the catalyst prior to the polymerisation affords stretchable polyacetylene with conductivities of up to $10^5 S.cm^{-1}$. Tsukamoto[33] has prepared materials exhibiting equal or even higher conductivities by treating the catalyst in a high-boiling solvent, such as decalin, at temperatures around 200°C.

Polyacetylene produced by the Shirakawa route has two main disadvantages, however: the electrical conductivity decays rapidly upon exposure to air and the polymer is entirely intractable. Exposure to air results in the formation of carbonyl, hydroxyl and epoxide groups, which lead to the destruction of the conjugated structure. The Naarmann process yields materials with the highest known electrical conductivity per unit weight, with the exception of superconductors, although the reasons for these effects are unclear. A number of approaches have been developed to resolve the intractability problem inherent with the Shirakawa method. One such approach has been the use of copolymerisation, with the potential of combining the high conductivity of polyacetylene with the processability normally associated with conventional polymers. In practice, however, the properties of these copolymers tend to be significantly different from those of the constituent polymers and, while some of the intractability problems have been overcome, this is at the expense of high conductivity.

The Luttinger Route:

Using group VIII metals and a hydride reducing agent as catalyst, Luttinger[22] discovered in the early sixties that polymerisation of acetylene yields polyacetylene powders. The significance of this route has been established by Enkelmann et al.[34] who discovered that these powders can be processed into films, either from suspension or by moulding the powders. These films exhibit properties similar to the material synthesised by the Shirakawa route. The main advantage over the latter is that it allows the polymerisation to be performed in the presence of water and oxygen.

"Durham" Precursor Route:

The processability of polyacetylene can be significantly improved using soluble precursor polymers that are easily converted into insoluble polyacetylene. Feast *et al* [35] at Durham University developed a method where the initial polymer is converted to polyacetylene by the application of heat (Figure 3). The monomer is polymerised by Ring Opening Metathesis Polymerisation (ROMP) to give a high molecular weight precursor polymer.

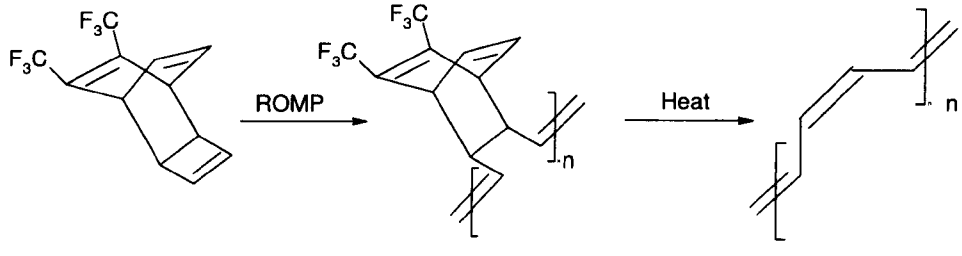


Figure 3 Synthesis of polyacetylene; The Durham Precursor Route

The precursor polymer is soluble in common organic solvents and easily transformed into "amorphous" polyacetylene at slightly elevated temperatures. To improve the stability of the precursor polymer, the original monomer has been photochemically converted into

pentacyclic isomer by UV irradiation[36]. Polymerisation of this indeed yields a stable precursor polymer, but the great exothermicity of the subsequent conversion reaction limits the applicability.

Aligned Soluble Polyacetylenes

An extension of this approach has been the spatially-oriented synthesis of polyacetylene, where polymer chains become aligned, thereby facilitating charge transfer between the chains and thus improving dc conductivity. Soluble materials have been produced, exhibiting high dc electrical conductivities of the order of 10^4 Scm^{-1}.[23,37].

When chemically doped using a variety of oxidising agents, such as bromine, iodine or arsenic pentafluoride, Durham polyacetylene exhibits electrical conductivities similar to that obtained by Shirakawa. The main advantage this material, however, is the ability to apply a stress to the precursor during heat treatment to produce dense, highly oriented films, which allow detailed studies of the anisotropic conduction of polyacetylene. In addition to chemical doping, polyacetylene can also be doped electrochemically, with electro-oxidation resulting in p-doping and reduction leading to n-doping[38].

2.2.2 Poly (Heterocycles)

From the first moment, it was realized that the applicability of polyacetylene was very limited because of its processing difficulty and the rapid decrease in conductivity upon exposure to air. Therefore, other ICPs that are more environmentally stable and can be polymerized in an (electro)chemical synthesis process have been developed; such as polypyrrole (PPy)[39], polyaniline (PANI)[40], polythiophenes[41], and polypyridine (Figure 4).

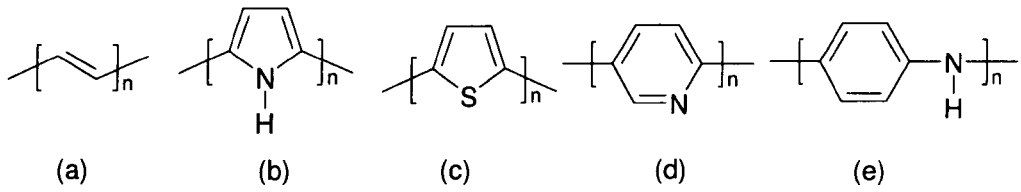


Figure 4 Intrinsically Conducting Polymers: (a) polyacetylene, (b) polypyrrole, (c) polythiophenes, (d) polypyridine and (e) polyaniline

The synthesis of polyacetylene in the highly conducting doped form was a starting point for a considerable number of studies. Electrodeposition of freestanding films of polypyrrole from organic media[42] opened the way to intensive research into polyheterocyclic and polyaromatic conducting polymers[43].

The electrochemical oxidation of these resonance-stabilised aromatic molecules has become one of the principal methods of preparing conjugated, electronically conducting polymers. Since the first reports of the oxidation of pyrrole, many other aromatic systems have been found to undergo electro polymerisation to produce conducting polymers. These include: thiophene, furan, aniline, and para-phenylene [44, 45, 46, 47], as well as many substituted, multi-ring and polynuclear aromatic hydrocarbon systems. All the resulting polymers have a conjugated backbone, which is required for electroactivity.

In addition, the polymers are electrochemically oxidised to their doped states as they are formed. This oxidation necessitates the incorporation of charge compensating anions, also known as dopants, into the oxidised film to maintain electro neutrality

Poly (heterocycles) can be viewed as a sp^2p_z carbon chain, in which the structure analogous to that in cis $(CH)_x$ is stabilised by the heteroatom[48]. These conducting polymers differ from polyacetylene due to the following:

- Their non degenerate ground state, related to the non energetic equivalence of their two limiting mesomeric forms: aromatic and quinoid.
- Their higher environmental stability.
- Their structural versatility, which allows the modulation of their electronic electrochemical properties by manipulation of monomer structure.

Highly conducting and homogeneous free standing films of polypyrrole (produced by oxidative electro-polymerisation of pyrrole[49]) formed a significant step in the development of conjugated poly (heterocycles).

Before discussing the properties of polyheterocyclic conducting polymers further, the mechanisms for the electronic conductivity and the nature of charge carriers in conjugated polymers are first considered.

Synthesis of Poly(heterocycles) – Polythiophene:

Polythiophene was synthesised for the first time in 1883[50]. The polymer was made by the washing of impure benzene with sulphuric acid. A black insoluble solid resulted, after further processing with sulphuric acid.

A well-defined synthesis of polythiophene did not see the light until the early 1980's. Following Yamamoto's first syntheses[51], employing Grignard-type coupling of 2,5-dibromothiophene, an extensive number of articles relating to the synthesis and properties of polythiophenes has been published. Polythiophenes exhibit promising properties, such as stability in both the neutral and the oxidized state under ambient conditions. Overall, the preparation of polythiophene and its derivatives was the result of several studies as a consequence of the synthetic knowledge[52].

The synthesis of polythiophenes is achieved through three major synthetic methods, specifically: organometallic coupling, oxidative coupling and electrochemical synthesis. These will be discussed in sections below.

Organometallic Coupling:

Nickel and palladium catalyzed cross-coupling of an organometallic compound with an organo-halide is a well-known method for the coupling of heterocycles[53]. Organomagnesium derivatives are most widely employed in the polythiophene synthesis, despite the availability of a large number of other organometallic reagents[54]. The earliest reports of the chemical preparation of unsubstituted polythiophene were produced in 1980 by two groups[55, 56]. They prepared polythiophene by a metal-catalyzed polycondensation polymerization of 2,5-dibromothiophene (Figure 5).

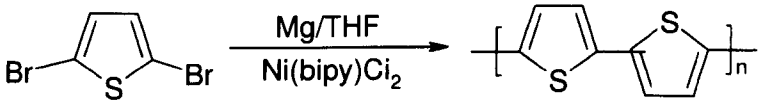


Figure 5 Yamamoto's Synthesis of Polythiophene

Yamamoto's synthesis reacts 2,5-dibromothiophene with Mg in tetrahydrofuran (THF) in the presence of nickel (bipyridine) dichloride. The Mg reacts with bromide to form either 2-bromo-5-magnesiobromothiophene or 2-magnesiobromo-5-bromothiophene (the same compound), which is self-coupled with the aid of the Ni^{II} catalyst to form a thiophene dimer, carrying an MgBr group at one end and a Br at the other. This reaction yields polythiophene at 40 to 60% based on dibromothiophene[56]. The molecular weight of the formed polythiophene is low, yet it is insoluble in THF causing the polymer to precipitate and preventing the formation of a higher molecular weight polymer.

Analogous outcomes were found by Lin and Dudek[55]. Polymerization of 2,5-dibromothiophene in the presence of Mg in THF using palladium(acac)2 (acac = acetylacetonate) or $Ni(acac)_2$ or $Co(acac)_2$ or $Fe(acac)_3$ catalysts yields low molecular weight polythiophene (Figure 6).

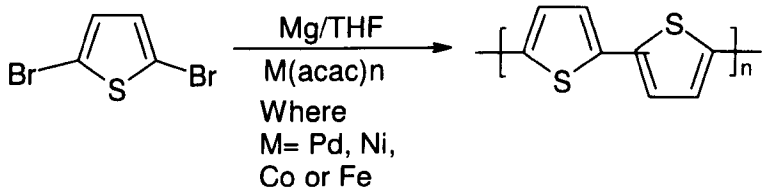


Figure 6 Synthesis of Polythiophene (Lin & Dudek)

Yields are improved up to 93% by the use of 2,5-diiodothiophene and $Ni(dppp)Cl_2$ as a catalyst[57]. First 2,5-diiodothiophene is reacted with Mg in ether under reflux (Figure 7).

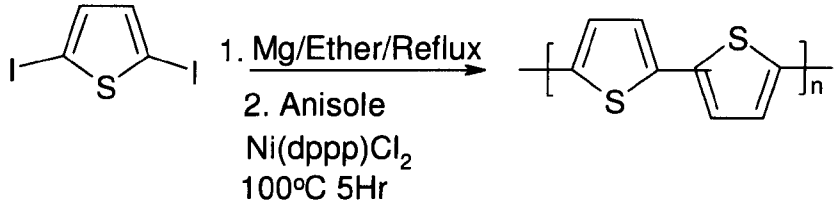


Figure 7 Wudl's Synthesis of Polythiophene

The formed iodomagnesioiodothiophene is isolated as a residue and redissolved in hot anisole, whereupon $Ni(dppp)Cl_2$ is added and the mixture heated at 100°C for 5h to induce polymerization. Extensive washing of the isolated PT with methanol, chloroform, THF, and chlorobenzene leads to the isolation of polythiophene with high purity.

Another interesting route was followed by Yamamoto *et al.*[58]on the polycondensation polymerization of 2,5-dihalothiophenes. Basically, a quantitative yield of polythiophene can be obtained from reacting 2,5-dibromothiophene, in the presence of zerovalent $Ni(COD)_2$ (COD = cyclooctadiene) as a catalyst making up the ligand consisting of triphenylphosphine (PPh_3) and bipyridine (Bpy) at 60-80°C in anhydrous dimethylformamide (DMF) as a solvent (Figure 8).

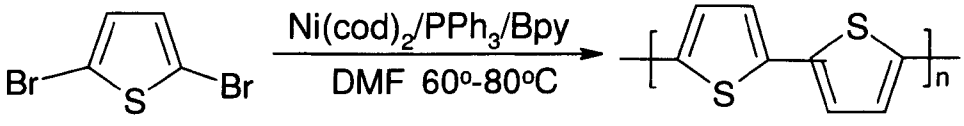


Figure 8 Synthesis of Polythiophene Ni(cod)/PPh3 method

Yamamoto reported that the percentage of Br end groups decreased as the reaction time was increased from 8h to 16h, indicating (unusually) that it was possible that some insoluble polythiophene continues to grow.

The limited solubility of polythiophene started the quest to develop a soluble and processable thiophene based polymer. The first environmentally stable and soluble poly (3-alkyl-substituted-thiophene) was synthesized analogously to the magnesium route of polythiophene synthesis, although the structures obtained all are regiorandom (Figure 9).

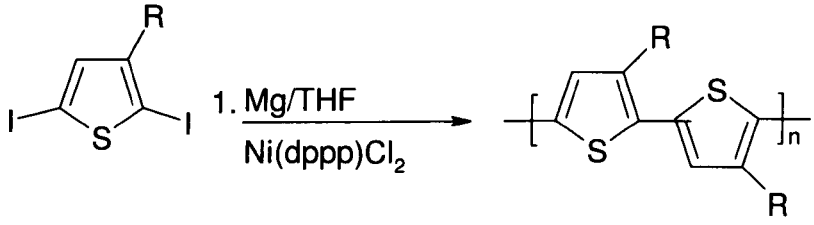


Figure 9 Synthesis of poly(3-alkylthiophene)

This was explained as a result of the heterogeneity of the Grignard iodide mixture, consisting of the diiodo-, the bis-Grignard and two mono-iodo-mono-Grignard compounds[59].

Electrochemical Synthesis

The synthesis of polythiophenes by electrochemical oxidation has been widely used since it was first described by Diaz[60]. The electrochemical synthesis of conducting polymers has several advantages over chemical polymerisation. Firstly, in-situ deposition of the polymer at the surface of the electrode eliminates processability challenges, as the polymer is in the pure form. Secondly, further flexibility in the preparation is achieved by means of control of the thickness, morphology and degree of polymer doping by the quantity of charge passed. In addition, the polymers are simultaneously oxidised to their doped conducting forms during polymer growth.

Electropolymerisation is achieved by the electro-oxidation of thiophene in an inert organic solvent containing supporting electrolyte[61]. The mechanism of the electropolymerisation of five-membered heterocycles[62] is illustrated in Figure 10.

Initiation of electrochemical polymerisation begins in step (E) with a one electron oxidation of the monomer to develop its radical cation. A high concentration of these species is sustained at the anode surface, as the rate of electron transfer significantly exceeds the monomer diffusion rate to the electrode surface. Propagation occurs at the following step, a chemical reaction (C), and involves the spin-pairing of two radical cations to form a dihydro dimer dication, which subsequently undertakes the loss of two protons and rearomatisation to form the dimer. Aromatisation is the driving force of the chemical step (C).

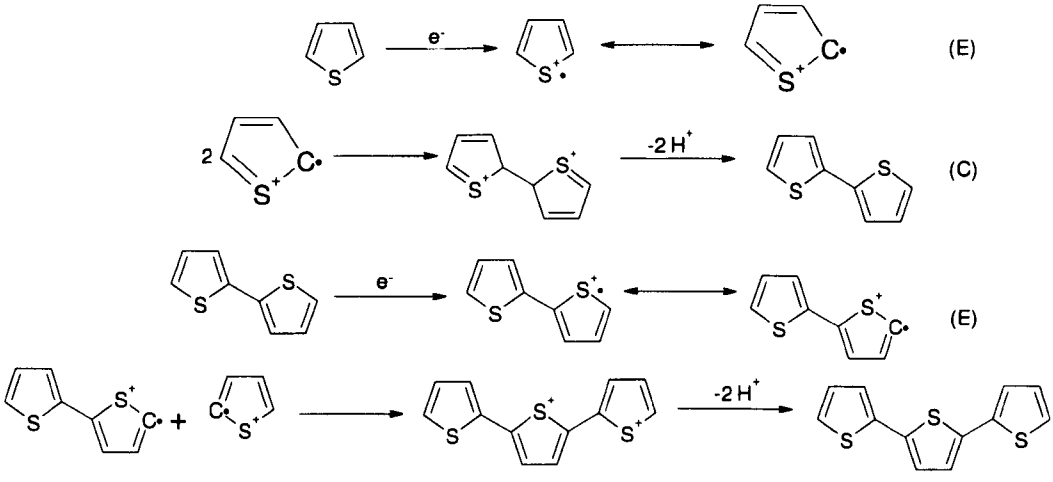


Figure 10 Proposed mechanism for the electropolymerisation of thiophene.

Coupling occurs predominantly through the α-carbon atoms of the heterocyclic ring, since these are the positions of highest unpaired electron π-spin density, therefore greater reactivity. At the applied potential, the dimer, which is more easily oxidised than the

monomer, exists in a radical cation form and undergoes further coupling reactions with other radical cations. This electropolymerisation process continues until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the anode surface[63]. Spectroscopic measurements[64] have shown that, initially, short oligomers are produced with longer chains emerging afterwards and that the electrical properties of the bulk material only become apparent when the growth centres have overlapped to form an unbroken film.

Nevertheless, this mechanism for electropolymerisation is significantly simplified, with the nature of the 'rate limiting' step and the exact role of oligomers in the initial deposition step remaining unresolved.[65]

Since the oxidation of the conjugated oligomers occurred at less positive potentials than their corresponding monomer, polymer oxidation occurs simultaneously with electrodeposition. Usually, one electron is removed from the polymeric backbone for every three-four monomer units to form polar configurations. Conductive polymers can be cycled between the oxidised conducting state and the neutral insulating state[66], this process being controlled by the diffusion of counter ions into and out of the film.

2.3 Conductivity Process in Intrinsically Conducting Polymers

2.3.1 Band Theory

The conduction band[67] in a covalent solid is the upper band of allowed electron states Ec. The lowest possible energy state in the conduction band is denoted by Ec. This band is usually empty, since energy is required for the electrons to be promoted from the valence band. Electrons in the conduction band are free to move about the lattice.

The valence band is the lower band of allowed states, and Ev represents the highest energy state in the valence band. Since electrons have the tendency to fill the lowest available energy states, the valence band is always nearly full, especially as the temperature falls towards 0°K. As the temperature is rises or a source of energy (shining a light) is introduced, electrons can absorb the energy and leave the valence band to reach the conduction band.

Band theory has been used to explain the conductivity of inorganic crystalline materials. The existence of electrons in the conduction band is crucial to the conduction process. In insulators, the electrons in the valence band are separated by a large gap from the conduction band; in metals, the valence band overlaps the conduction band.

On the other hand, in semiconductors there is a small enough gap between the valence band and the conduction band (Figure 11) that, with the presence of a suitable doping agent, the material can become conducting.

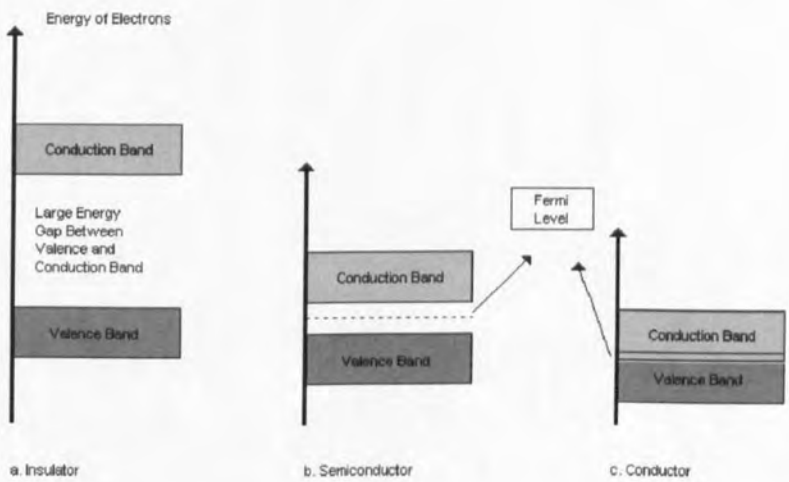


Figure 11 Energy Bands for Solids.

In a conjugated polymer, such as polyacetylene, the structural simplicity provides a convenient entry into the band gap discussion[68]. PA is composed of a chain of sp^2 hybridized carbon atoms linked by alternating single and double bond, where resonance causes these bonds to have almost the same length and there is extensive delocalization along a chain. The communication along the main chain of the polymer is due to the overlapping p-orbitals forming π bonds. When the electrons are added in, there should be no energy difference between the full VB arising from the HOMO of polyacetylene and the unfilled CB from the LUMO. This explains the expected high conductivity which requires a partially filled band.

For this hypothetical PA, the continuous delocalised π systems might be expected to form a half-filled valence band which, in fact, would be an ideal condition for conduction of electrical current. Nevertheless, this polymer can efficiently lower its energy by retaining some degree of bond alternation, which introduces a band gap of 1.5 eV, making it a high energy gap semiconductor.

2.3.2 Mechanism of Conductivity in Conjugated Polymers

Orbitals of successive carbon atoms overlapped along the backbone leads to electron delocalisation that provides the pathway for charge mobility along the backbone of the polymer. The essential characteristic of all conjugated polymers is their quasi-infinite π electron system extending over a large number of recurring monomer units[69]. This feature results in a material with anisotropic conductivity, strongest along the axis of the chain.

Polarons - Doped Carbon Chains

Conducting polymers are slightly conducting intrinsically; however this can be greatly enhanced by doping. Electron conduction in polymers, such as polyheterocyclics, is a result

of the free-to-move charge carriers known as polarons and bi-polarons (Figure 12), formed when an electron-acceptor or dopant (A) is added.

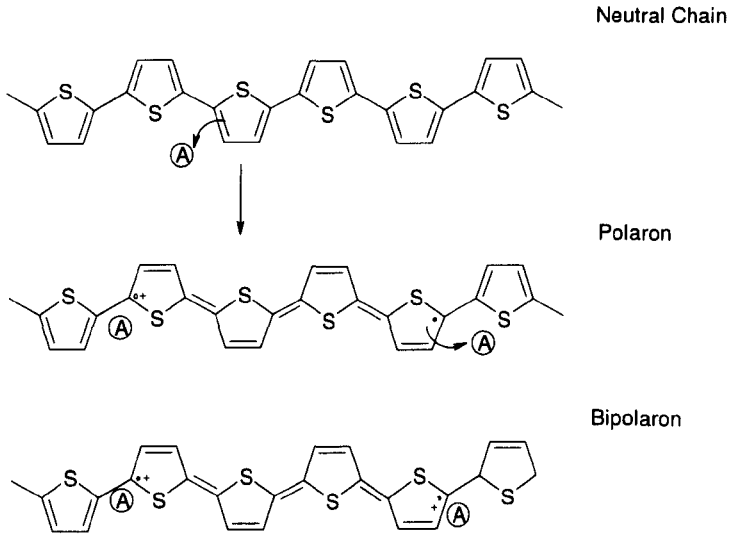


Figure 12 Formation of Polarons

The movement of these charged species along a polymer chain is accommodated with significant regional distortions, in which electron hopping is involved. Applying an electric field will cause the polaron to move along the chain and conduct a current, since the activation energy for hopping is of the order of millielectron-volts (meV) [comparable with the thermal vibrational energy available at room temperature].

Types of Doping

The polymer may store charge in two ways[70]. In an oxidation process, it could either lose an electron from one of the bands or it could localise the resulting positive charge over a small section of the chain. In "P-Type" doping for example[71], the electron-accepting dopant molecule attracts an electron from the polymer chain and becomes negatively charged. The positively charged part of the chain is termed a 'radical cation', or polaron. The electron of

the double bond is mobile and can move easily. As a consequence, the unpaired spin successively moves along the molecule. The positive charge, on the other hand, is fixed by electrostatic attraction to the negatively charged molecule, which does not move so readily.

If the polymer chain is slightly more strongly doped, polarons condense pair-wise into so-called solitons[72] (Figure 13). These solitons are then responsible, in complicated ways, for the transport of charges along the polymer chains, as well as from chain to chain on a macroscopic scale.

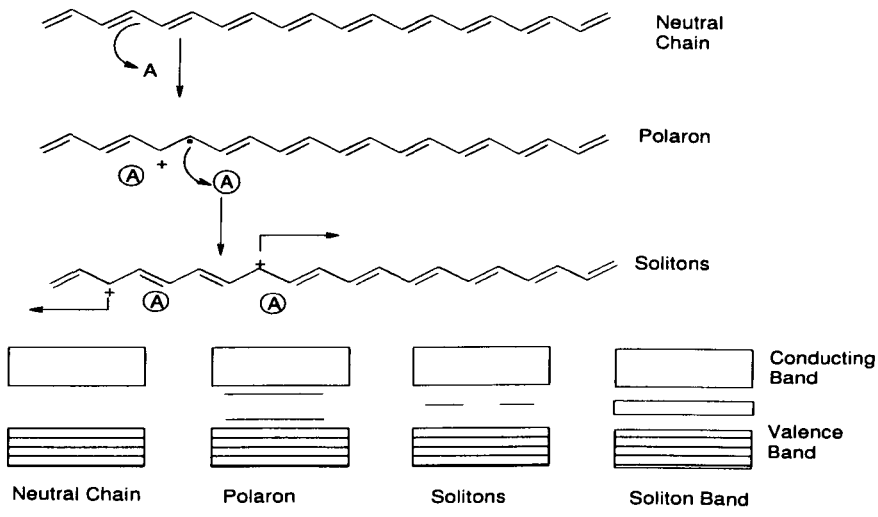


Figure 13 Band Structure of Charged Species in Polyacetylene.

Charge Transport

Although polarons and bipolarons are known to be the main source of charge carriers, the precise mechanism of the conductivity is not yet fully understood. The problem lies in attempting to trace the path of the charge carriers through the polymer. All of these polymers are highly disordered, containing a mixture of crystalline and amorphous regions (Figure 14).

It is necessary to consider the transport along and between the polymer chains and also the complex boundaries established by the multiple numbers of phases. This has been studied by examining the dependence of conductivity on doping, temperature, magnetic field and the frequency of the current used. These tests show that a variety of conduction mechanisms are possible.

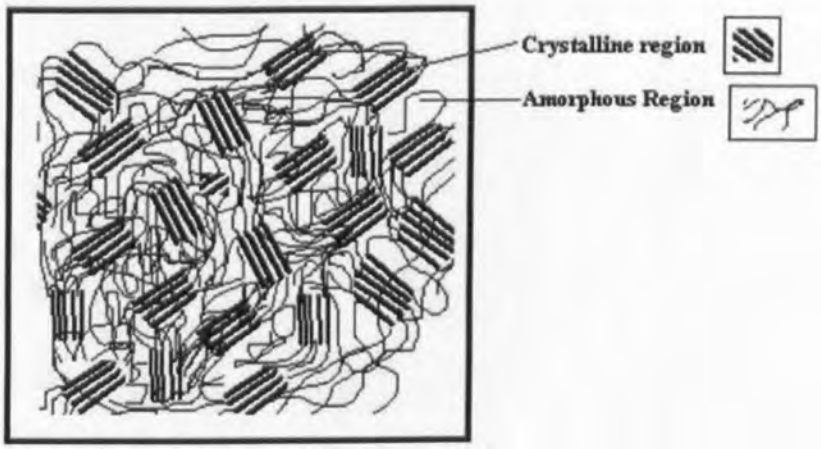


Figure 14 Mixed Amorphous and Crystalline Polymer Structure

The main step is often the movement of charge carriers between highly conducting domains. Charge transfer between these conducting domains can occur by thermally activated hopping or tunnelling. This is consistent with conductivity increasing exponentially with temperature.

2.4 Factors Affecting Conductivity in Conjugated Polymers

2.4.1 Matrix Effect

An organic semiconductor matrix, in essence[74], is far less strongly coordinated than a typical inorganic one. Molecules are bound by weak van der Waals (vdW) forces, instead of strong inter-atomic covalent bonds. Doping occurs by a direct movement of electrons from host to dopant in p-type and the opposite for n-type doping, rather than by incorporation of the

dopant via formation of covalent bonds and release of excess charge to a band, as occurs in inorganic semiconductors.

By virtue of the vdW forces and anisotropic bonds, the organic matrix is much softer and will suffer more distortion than the inorganic matrix upon the insertion of dopant atoms or molecules (up to concentration of a few percent)[73]. Because of increased localisation, dopant-dopant interaction is weaker and doping concentrations can be pushed significantly higher than in inorganic semiconductors, without leading to effects like 'dopant banding'; however, there is often a threshold concentration which must be reached before there is a significant decrease in resistivity.

2.4.2 Localisation and Polarisation

The physics of charge transport in molecular films is dominated by localisation and polarisation[74]. The intermolecular overlap of wave functions is small and transport often occurs via thermally activated hopping. The charge released by the dopant to the host molecule is far less delocalised than in inorganic semiconductors, and charge-dopant separation does not occur as readily; hence, the conductivity may often be described effectively by Polaron Theory[75].

2.4.3 The Band Gap

The band gap of conjugated polymers is usually fairly large, since structural distortion opens an energy gap at the Fermi level[76]. Consequently, conjugated polymers are considered as insulators (or at most semi-conductors) in their neutral state. The role of dopants in a conducting polymer is either to remove or add electrons to the polymer, e.g. for p-type doping, I_2 will abstract an electron forming an I_3^- ion. If an electron is removed from the top

of the valence band of a semi-conducting polymer, the vacancy created does not delocalise completely; a radical ion is obtained. The radical cation (polaron) is somewhat localised, partly due to Coulomb attraction to its counter ion, which normally has a very low mobility, and partly because of the local change in equilibrium geometry of the radical cation relative to the neutral molecule. That change is a lattice distortion, which could be described as a deviation from the ideal three-dimensional regularity of the polymer crystal structure. This is evident in the solid form of many small organic molecules; for example the ground state of biphenyl is benzenoid, but the geometry of its radical cation is quinoidal[77].

2.4.4 Counter Ion & Lattice Distortion

Since the counter ion is not mobile, a high concentration of counter ions is required, so that the polaron can move in the field of the closest counter ion[76]. If a second charge is removed from an already oxidised section of the polymer, either a second independent polaron may be created or, if the charge removed is the unpaired electron of the first polaron that is removed, a bipolaron is formed. Since the radical cation has a spin of ½, the spins of bipolarons sum to S=0. The two charges of the bipolaron are not independent, but move as a pair, rather like the Cooper pair in superconductivity theory.

The formation of polarons and bipolarons is associated with local lattice distortion, their presence might be expected to be delocalised over the entire polymer chain. However, the species is localised, with an associated lattice distortion creating a localised electronic state.

2.5 Applications of Intrinsically Conducting Polymers

2.5.1 Electromagnetic Shielding of Electronic Circuits

Intrinsically conducting polymers are excellent candidates for electronic and electromagnetic applications. Amongst these polymers, polyaniline has become known as one of the most promising materials, due to the easiness of its synthesis, its environmental stability and the possibility to blend it with thermoplastics[78]. Polyaniline can have high levels of conductivity and permittivity[79] and these properties can be tuned easily and precisely by blending with conventional polymers and rubbers. So in developing high performance materials for electromagnetic shielding or radar absorption with good processability, low density and low cost become possible.

The electromagnetic shielding effectiveness and absorption depend on the level of conductivity and permittivity of the materials and their variations with frequency[80].

2.5.2 Corrosion Inhibition of Metals by Electrically Conductive Polymers

Conducting polymers are remarkable in that they can be doped to highly conductive states approaching the conductivities of metals; their ability to store and transport charge is seen as a key element in their reported ability to anodically protect metals against rapid rates of corrosion[81]. Conducting polymers such as polypyrrole and polythiophene have already been found to be very effective at stabilising photoactive materials, such as cadmium sulfide and gallium arsenide, by providing a corrosion-resistant coating which improves the life-time of these materials[82]

It has been found [83] that stainless steel electrodes coated with thin layers of PAni remain passive in acid solutions. PAni ensures an effective protection, i.e. the corrosion potential of stainless steel is shifted in the direction of noble metals, and corrosion current decreases.

2.5.3 Use of Conducting Polymers as Antistatic Materials

Plastics have a tendency to undergo static charging in dry air as a result of friction. Walking over synthetic carpeting can create a potential of up to several thousand volts, which is discharged when, for instance, a door handle is touched. The same effect is observed in the production and processing of photographic films during fast winding if these have not received antistatic treatment[84]. The discharges occur with a flash of light, pre-exposing the film and rendering it unusable. Another field in which static charging must be avoided is the packaging of electronic components, since present-day transistors and integrated circuits are irreversibly damaged by voltages in excess of 100V.

In order to prevent these effects from occurring in practice, photographic films and packaging films for electronic components are given an antistatic treatment by increasing the conductivity of the plastic, so that charge can be eliminated more readily or does not build up in the first place.

Chemical polymerization of ethylenedioxythiophene (EDOT) in the presence of aqueous polystyrenesulfonate (PSS) yields a colloidal poly(3,4-ethylenedioxythiophene) (PEDOT) solution that is directly suitable for aqueous processing[85]. When PEDOT/PSS is deposited on a polyethylene terephthalate film, the surface resistance becomes relatively independent of the atmospheric humidity. Stability tests show that PEDOT/PSS is considerably more stable to hydrolysis, light, and temperature than other conducting polymers.

These properties effectively meet the requirements for an antistatic layer for photographic film and have led to an annual multi-ton production of PEDOT/PSS by Bayer AG. More than 100 million square metres of photographic film are coated in this way every year*.

It should be noted that, apart from the antistatic treatment of photographic or packaging films, PEDOT/PSS coatings can also be used for the antistatic treatment of other plastics[86], as well as glass. Through the addition of appropriate binders, suitably coordinated with the particular substrate used, it is possible to achieve transparent to slightly grey coatings, suggesting that this material may prove useful in many other applications.

2.5.4 Organic Conducting Polymers in Thin-film transistors

Organic thin-film transistors (OTFTs) based on conjugated polymers, oligomers, or other molecules have been considered as a viable substitute for conventional thin-film transistors (TFTs) based on inorganic materials. Due to the relatively low carrier mobility of the organic semiconductor layers, OTFTs cannot rival the speed of field-effect transistors based on single-crystalline inorganic semiconductors, such as Si and Ge, which have charge carrier mobilities about three orders of magnitude higher[87]. Subsequently, OTFTs are not yet suitable for applications requiring very high switching speeds; nevertheless, the processing characteristics and demonstrated performance of OTFTs imply that they can be competitive for existing or novel thin-film-transistor applications requiring large-area coverage, structural flexibility, low-temperature processing, and, especially, low cost. Such applications include switching devices for active-matrix flat-panel displays, based on either liquid crystal pixels or organic light-emitting diodes[88]. OTFTs could also be used in active-matrix backplanes for "electronic paper" displays[89] based on pixels comprising either electrophoretic ink-

* Source: www.bayer.com

containing microcapsules or "twisting balls"[90] . Other applications of OTFTs include low-end smart cards and electronic identification tags.

2.5.5 Conducting Polymers in Light-Emitting Diodes (LED)

Polymer based light-emitting diodes (LED) were first demonstrated in the 1980s. The first polymer LEDs used polyparaphenylene (PPP) or poly(phenylenevinylene) (PPV) as the emitting layer. Since 1990 many different polymers have been shown to emit light under the application of an electric field (electroluminescence, EL). PPV and its derivatives are still the most commonly used materials, but polythiophenes, polypyridines, poly(pyridylvinylenes), polyphenylenes and copolymers of these materials are now being used.

A large effort in industry and academia to improve stability, lifetime, and efficiency has prompted the study of a vast number of novel configurations in polymer devices. Poly(phenylenevinylene), used instead of gallium arsenide or small organic molecules (electroluminescence), has lower manufacturing costs but, until recently, it offered too short a lifetime.

2.5.6 Conducting Polymers and Rechargeable Batteries

There is a considerable interest in the research of conductive polymers and their use as active materials in rechargeable batteries. Due to their low densities, it was considered that batteries with power densities much higher than those of the ordinary lead/acid battery could be easily achieved. Since charge on a polymer backbone is distributed over three or four repeating units, the charge capacity per unit weight for conducting polymers is marginally better than that of metal oxides.

Polyaniline (PAni) is the most investigated electro-active polymer in battery applications[91,92]. Its first important commercial application has been the button cell batteries of Bridge-stone Seiko[93]. The manufacturing cost for other conducting polymers, apart from polyaniline, is expensive. The main characteristics of Li-PAni secondary batteries, in contrast with conventional Li secondary batteries, were the longer cyclic life, lower self-discharge rate, endurance to over-discharge, low production cost, and the shape flexibility for making thin films. Since the specific capacity of Li-conducting polymer secondary batteries is small, these are used as back-up power sources for small electronic devices[94].

2.6 A New Approach...

A novel approach intended to overcome the previously mentioned challenges is the backbone of this research. Hence, the "ideal" counter ion for a stable conducting polymer would have a well-distributed compensating charge to diminish the Coulomb effect on the charge on the polymer, while being highly compatible with the crystal structure of the polymer to avoid disorder or torsion of the polymer backbone.

The present project relies upon the synthesis, optimisation and blending of complementary conducting polymer backbones[95], chosen to be structurally compatible with each other, both being chemically substituted in order to favour charge-transfer doping between the two polymers. This is clearly distinguished from simple organic charge-transfer salts, in which the conducting "pathway" comprises a co-facial assembly of planar or discotic molecules in segregated stacks. The salts are essentially brittle ionic solids, whereas polymers are mechanically superior and (in certain cases) thermoplastic and processable. Another distinction is that the nature of long-range electron delocalisation is different in the two types

of material: in the proposed complementary polymers it occurs primarily via covalent conjugative overlap of the orbitals within each long polymer molecule.

2.6.1 Research Aims

This research will investigate this new approach and it is proposed to use the following sequence of steps to achieve this:-

1. Synthesis of monomers for donor and acceptor polymers;

2. Separate polymerisation to form the component polymers;

3. Purification of the polymers via re-precipitation: this is very important in order to remove harmful, electrically-active impurities;

4. Preparation of a series of "dopant-free" conducting polymer blends with a range of potential degrees of charge-transfer

5. Investigation of the nature and extent of charge-transfer by cyclic voltammetry and by UV-Visible, and ESR spectroscopy;

6. To study the temperature dependence of electrical conductivity and carrier mobility, in order to characterise the mechanism of conduction.

Chapter Three:

Methodology

3 Methodology

3.1 Synthesis of Conducting Polymers

Conducting polymers can be synthesised via chemical or electrochemical routes; however, many polymers, most notably polyacetylene, are still only accessible via chemical synthesis. The reason for choosing the chemical polymerisation route in this research is due to the fact that electropolymerisation will only produce polymers that could be studied as thin films. Moreover, in many cases, polymers made via electrochemical polymerisation are doped with the oxidant used for the polymerisation, which often proves to be almost impossible to remove totally .

3.2 Nominated Polymers

3.2.1 Electron Rich Polymers: Polythiophene and its Derivatives

Among the numerous linear π-conjugated conducting polymers, polythiophene and its derivatives have been investigated intensively because of their attractive electrical and optical properties [96,97,98,99]. From a theoretical point of view, polythiophene has often been considered as a model for the study of charge transport in conducting polymers with a non-degenerate ground state; on the other hand, the high environmental stability of both its doped and undoped states, together with its structural versatility, have led to numerous developments aimed at practical applications.

Poly (3-Methoxythiophene)

The incorporation of an alkoxy group at the 3-position of the thiophene ring yields polymers with an optical absorption maximum of 475-530nm or higher, comparable with those of P3AT's. This can be attributed to both the electron donating effect of the alkoxy group and

the more planar conformation of poly (3-alkoxythiophene) 'P3AOT' compared to that of P3ATs[100].

The existence of the electron-donating alkoxy group significantly decreases the oxidation potential of these polymers and stabilises the conducting state[101]. It was observed that P3AOTs have a lower conductivity of about 10^{-4}-10^{-2} Scm^{-1} after electrochemical doping, due to low molecular weight and irregular structure. P3AOT's are soluble in organic solvents, even after doping up to 20%.

In order to gain a better knowledge of the influence of the introduction of alkoxy groups on the thermal and optical properties of the conducting polythiophene derivatives, poly(3-methoxythiophene) has been chemically polymerised using iron(III) chloride as an oxidising agent under low temperature with controlled addition of monomer[102].

Poly (3,4-Ethylenedioxythiophene) PEDOT

The well-known polymers of thiophene[103] are based mainly on a 2,5-linkage. Cross-linking in the 3 and/or 4-position gives networks which, in addition to chain rigidity, is one reason for the insolubility and infusibility of these polymers. Cross-linking is impossible if the 3 & 4 positions in the monomer are already occupied. One possibility is to incorporate stabilising substituents; since polymers such as polythiophene normally carry a positive charge when doped, substituents with +M-effect should stabilise the positive charge and hence the doped polymer.

In 1991, poly(ethylenedioxythiophene) was first reported[104]. 3,4-ethylenedioxythiophene is produced from thiodiacetic acid in a five step synthesis[105]. Poly(3,4-ethylenedioxythiophene) (PEDOT) exhibits an electronic band gap (defined as the onset of the first π-π^* absorption)

of 1.6-1.7eV and a λ_{max} of ca. 610nm, making it deep blue in colour[106]. Due to its low oxidation potential, thin films of neutral PEDOT must be handled carefully, as they oxidise rapidly in air.

PEDOT-based polymers are currently, and will in the future be, used in many applications. Examples are: through-hole plating of printed circuit boards, antistatic coating, hole-injection layers on ITO substrates for organic electroluminescent devices, sensors and rechargeable batteries, etc..

Chemical Synthesis of Poly (Ethylenedioxythiophene) PEDOT

This very stable conducting polymer was initially chemically synthesised by BASF as a thin film coating for antistatic plastic[107]; the material showed excellent stability in the conductive state.

Alkoxy substituents in the 3- and 4- positions of thiophene prevent the occurrence of α, β coupling during electropolymerisation[108]. Normally, α, β coupling interrupts the conjugation along the polymer chain, lowers the conductivity of the resulting material and may be the cause of over-oxidation at higher potentials.

Polythiophenes with substituents other than alkyl groups have been investigated, among which those with electron-donating alkoxy groups have displayed promising electrical and optical properties.[109]The polymers so obtained had a fairly high molecular weight, fewer defects and increased crystallinity. The extent of conjugation in these polymers is higher than that in poly(3-alkylthiophene)s. PEDOT was initially found to be an insoluble polymer, yet it exhibits some very interesting properties. In addition to a very high conductivity (ca. 300Scm^{-1}), PEDOT was found to be almost transparent in thin, oxidised films.

Neutral PEDOT: Preparation by Organometallic Polycondensation.

Neutral and non-doped PEDOT have been prepared by organometallic dehalogenation polycondensation of 2,5-dichloro-3,4-ethylenedioxythiophene with a zerovalent nickel complex[110] in accordance with the following equation:

Figure 15 Organometallic Dehalogenation Polycondensation of heterocycles

This method in the above reaction is expected to provide a versatile means for molecular design and synthesis of electrically conducting π-conjugated polymers. Polycondensation of 2,5-dichloro-3,4-ethylenedioxythiophene affords π-conjugated polymers with well-defined linkages between the monomer units. The dichloro substituted monomer is synthesised by chlorination of 3,4-ethylenedioxythiophene with N-chlorosuccinimide in THF at 0°C.

PEDOT Nanoparticles Prepared in Aqueous Solutions

PEDOT nanoparticles[111] with enhanced conductivity and processability have been prepared by oxidative polymerisation in dodecylbenzenesulfonic acid (DBSA) micellar solutions. DBSA was used as a surfactant to form micelles and as a doping agent. Monomers of EDOT, which has extremely low solubility in water, were easily solubilised in aqueous DBSA micellar solution.

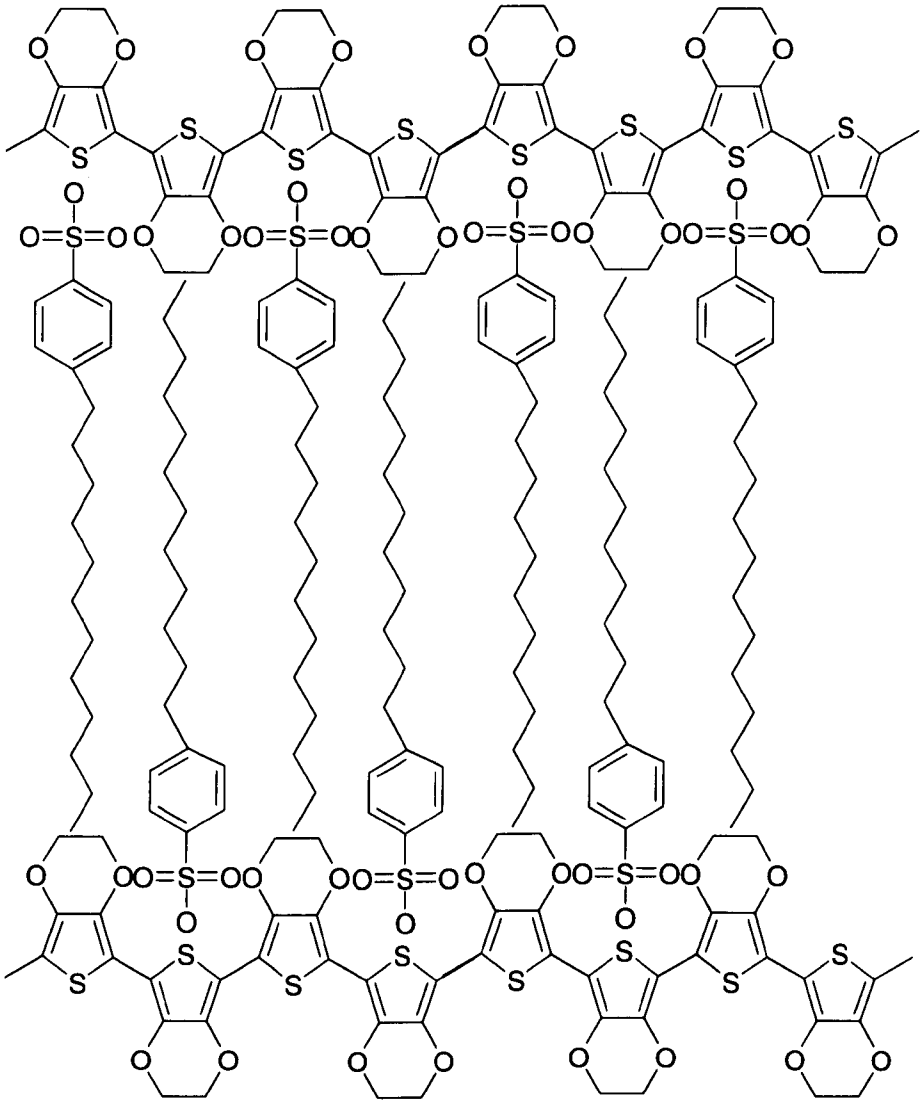


Figure 16 Proposed Structure of the PEDOT Nanoparticles Doped with DBSA

The electrical conductivity of the product varied with the polymerisation conditions, and was relatively high (up to $50Scm^{-1}$).

Synthesis of PEDOT in High Concentration Emulsion Polymerization

PEDOT with high electrical conductivity was prepared by oxidative polymerization of 3,4-ethylenedioxythiophene under high concentration emulsion conditions, in the presence of 2-

naphthalenesulfonic acid sodium salt acting as an emulsifier and a doping agent, and $Fe_2(SO_4)_3$ as an oxidant[112], which resulted in PEDOT (Figure 17) with high electrical conductivities and a good yield. This method uses a concentrated emulsion medium, which contains the emulsifier and the monomer in much higher concentrations; such a high-concentration emulsion polymerization has been applied for the preparation of non-conjugated polymers[113].

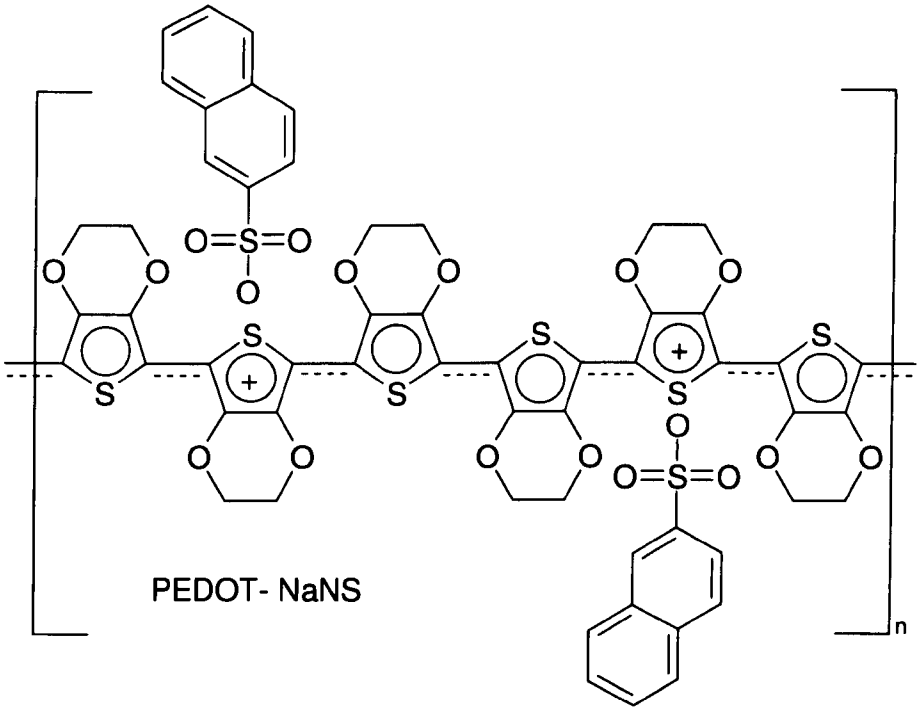


Figure 17 PEDOT Sodium Naphthalenesulphonate

Oxidation Polymerisation; Process for the Preparation of Neutral PEDOT

PEDOT (Figure 18) is prepared in the neutral, undoped form by oxidation polymerisation in chloroform with ferric chloride ($FeCl_3$) at room temperature under nitrogen[114]. An important feature of the process is the fact that the oxidant is used in less than the stoichiometric

amounts. For the polymerisation of a thiophene monomer, theoretically two equivalents of the oxidising agent are required per mole of the monomer.

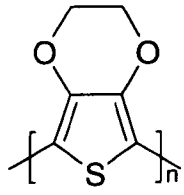


Figure 18 Neutral PEDOT

It is essential for the reaction that not more than 99% of the stoichiometrically required amount of oxidant is used.

Hexyl-Substituted Poly (3,4-Ethylenedioxythiophene) PEDOT-C_6

Although PEDOT shows remarkable stability as compared to other members of the thiophene family, the problem of limited solubility of the neutral undoped PEDOT was found to be resolved by substitution of the oxyethylene ring by a long alkyl group. The polymers were synthesised by chemical and electrochemical oxidative polymerisation of the corresponding substituted monomers.

Hexyl-substituted EDOT (or EDOT-C_6) was synthesised following a revision of the method of Kumar and Reynolds[115]. The monomer was made via an eight-stage synthesis from bulk chemicals (Figure 19).

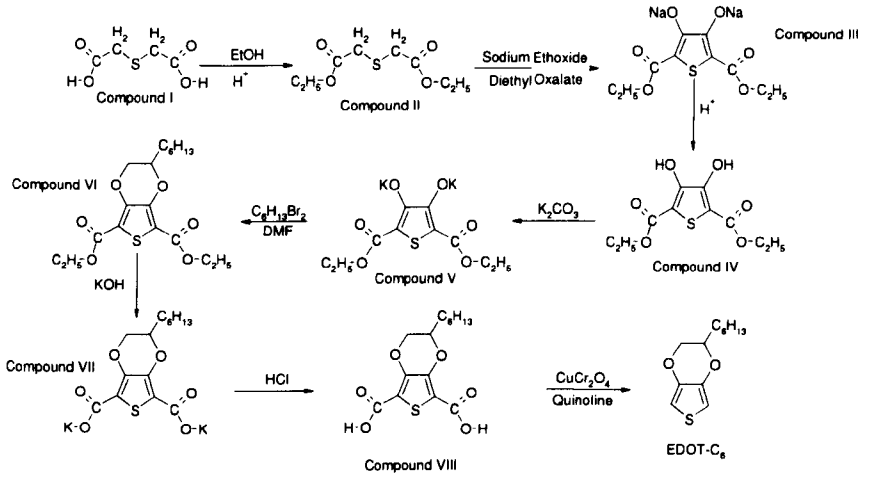


Figure 19 Eight Stage Synthesis of EDOT-C6

Thiodiglycolic acid (compound 1) undergoes an esterification reaction in the presence of sulphuric acid (as a catalyst) to diethyl thiodiglycolate (compound 2). The diester was then reacted with sodium ethoxide and diethyl oxalate in a ring-closing reaction with the diester.

The mechanism of the ring closing reaction is thought to be as illustrated in Figure 20:

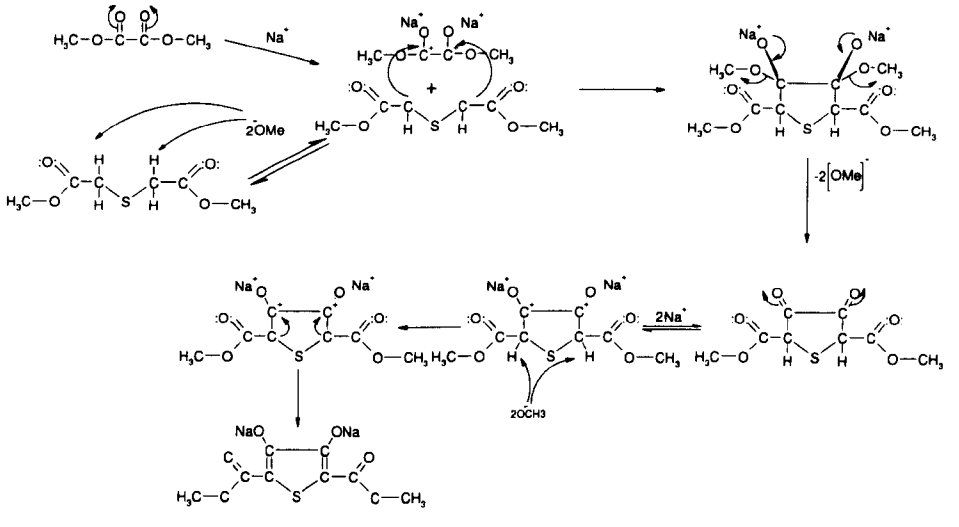


Figure 20 Illustration of a possible mechanism of ring closure in the preparation of EDOT-C6

The sodium salt of 3,4-dihydroxy-2,5-dicarbethoxythiophene (compound 3) was then hydrolysed with HCl to yield 3,4-dihydroxy-2,5-dicarbethoxythiophene (compound 4), which was found to be a very important intermediate compound†. Compound 4 was then reacted with potassium carbonate to produce the potassium salt of 3,4-dihydroxy-2,5-dicarbethoxythiophene (compound 5). A ring-closing reaction between compound 5 and 1,2-dibromooctane was performed in DMF to yield EDOT-C6 2,5-dicarbethoxy diester (compound 6); the diester underwent a saponification reaction with KOH to yield EDOT-C6-2,5-dicarbethoxy diester dipotassium salt (compound 7) which, in turn, was hydrolysed with HCl to yield EDOT-C6 2,5-dicarboxylic acid (compound 8). The diacid was then transformed into the monomer EDOT-C6 through a de-carboxylation reaction in the presence of copper chromite catalyst.

The EDOT-C_6 monomer was polymerised in a similar manner to EDOT by oxidative polymerisation with anhydrous $FeCl_3$ under nitrogen.

3.2.2 Electron Deficient Polymers: Polypyridine and its Derivatives

π-Conjugated poly(arylene)s attract much attention owing to their electronic and optical properties as well as their increasing applications[116]. Polypyridines are the most fundamental π-conjugated polymers possessing electron-deficient properties due to the presence of electron-withdrawing imine nitrogen in the monomer unit. As a result, polypyridines can serve as electron-transporting materials.

† This precursor is the cornerstone to major ethylenedioxythiophene derivatives, sold at £107.00 per 1g (Sigma-Aldrich)

Poly (Pyridine-2,5-diyl)

Polypyridine was found to be a unique conjugated polymer, in that it is a truly rigid-rod polymer whilst nevertheless being solution processable[117]. Unlike most heterocyclic monomers for conducting polymers[118], pyridine cannot be polymerised directly by oxidation; however, poly(pyridine-2,5-diyl) can be prepared by oxidative addition, disproportionation and reductive elimination of 2,5-dibromopyridine[119]. The polymerisation (Figure 21) is done using zerovalent nickel complex as the dehalogenation agent for 2,5-dibromopyridine, based on the coupling of aromatic halides with nickel complexes.

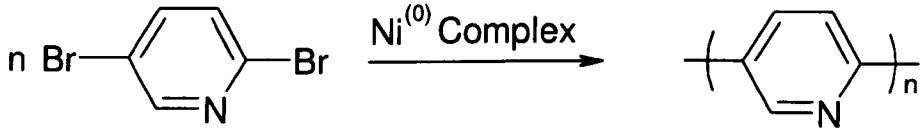


Figure 21 Dehalogenation polycondensation of 2,5-dibromopyridine

The mechanism of polymerisation[120] is illustrated in Figure 22; the disproportionation reaction is considered to be facilitated in polar solvents like DMF.

Polypyridine was found to be soluble in polar solvents such as formic acid and to be relatively electron accepting; hence it could be *n*-type doped more easily than *p*-type doped.

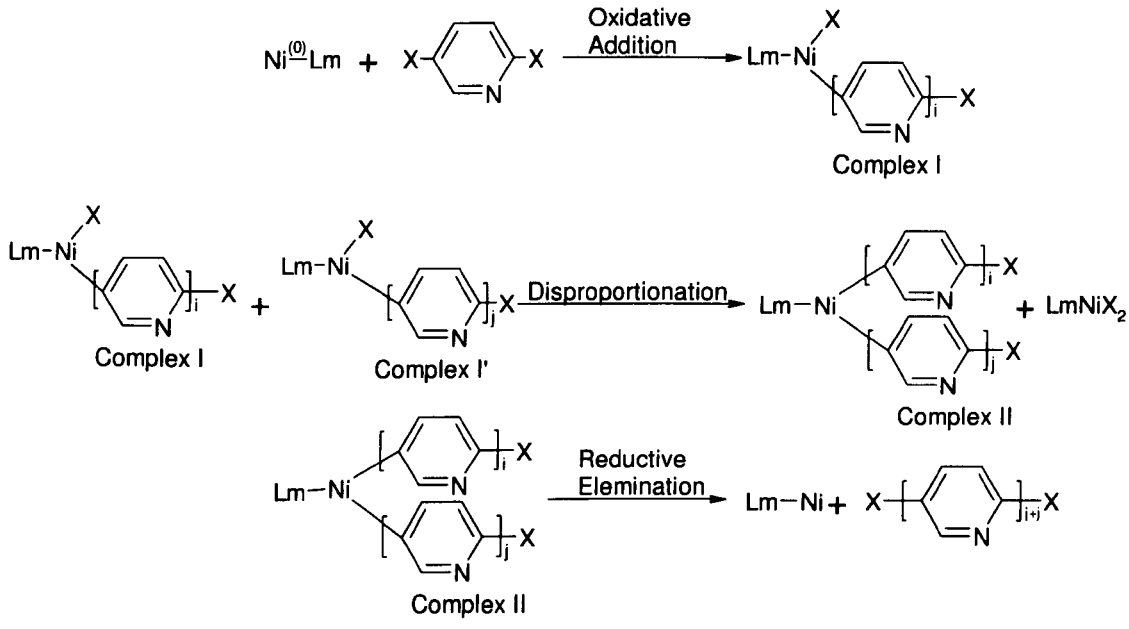


Figure 22 Mechanism of Dehalogenation Polycondensation Polymerisation

A similar route to zerovalent nickel dehalogenation was reported by Monkman *et al*[121], where the nickel complex was synthesised *in situ*, leading to a more economic preparation with 95% yields.

Poly (3-nitropyridine-2,5-diyl)

In order to enhance the electron withdrawing properties of polypyridine, the introduction of electron-withdrawing substituents such as nitro was considered in this project.

Polypyridine has been prepared by dehalogenation polycondensation polymerisation. This method is not suitable for the preparation of the nitrated polymer due to the presence of the nitro group, which often leads to side reactions in organometallic processes.

According to the literature[122], direct nitration of polypyridine with mixed acids was found to be unsuccessful. Copper-promoted Ulmann coupling of halogenated aromatic compounds

proceeds well, especially when these compounds have nitro substituents in the ortho- or para- positions with respect to the halogen atoms[123] . Poly (3-nitropyridine-2,5-diyl) was prepared by following a revised method by Chio *et al*[124]

The monomer was synthesised by the bromination of 2-hydroxy-5-bromo-3-nitropyridine in phosphorus oxybromide. The polymerisation of monomer 1 in DMF over activated copper yields poly (3-nitropyridine-2,5-diyl) (Figure 23).

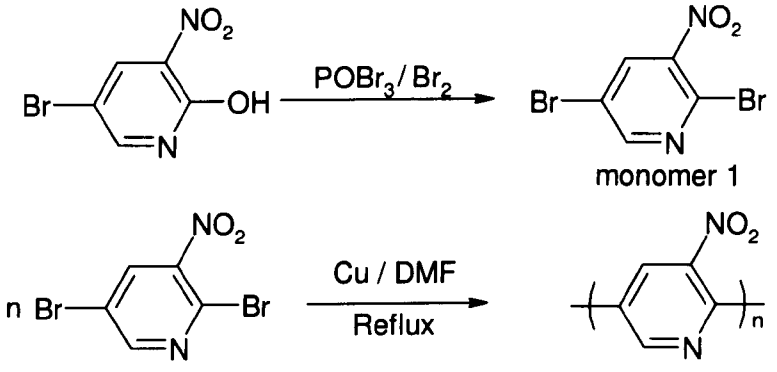


Figure 23 Preparation of Poly (3-nitropyridine-2,5-diyl)

Chapter Four:

Electron Donating Polymers; Experimental, Results and Discussion

4 Electron Donating Polymers

4.1 Experimental

4.1.1 Poly (3-methoxythiophene) Synthesised at Low Temperature

Materials

Iron (III) chloride, anhydrous chloroform and hydrazine monohydrate were purchased from Sigma-Aldrich. The monomer 3-methoxythiophene was purchased from Avocado Chemicals and was used without further purification.

Polymerisation

$FeCl_3$ (2.6 g, 16mmol) was quickly weighed into a three neck round bottomed flask, in and was kept under nitrogen. Anhydrous $CHCl_3$ (15 ml) was added into the vessel at 0°C followed by monomer (0.456g, 4mmol) in $CHCl_3$ (5 ml) drop-wise over a period of 30 min.

The mixture was then stirred for 2h. The polymer was washed with methanol, dedoped by stirring in 50% aqueous hydrazine monohydrate and washed with water and methanol, then dried under dynamic vacuum (0.3–0.4mbar). The neutral polymer, poly (3-methoxythiophene), was designated as P3MOT (Yield 0.25g, 55%).

4.1.2 Preparation of PEDOT by Organometallic Polycondensation

Materials

2,2'-bipyridyl, 1,5-cyclooctadiene, N-chlorosuccinimide, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), hydrazine monohydrate , bis(1,5-cyclooctadiene)nickel° and sodium dithionite were used as purchased. 3,4-ethylenedioxythiophene was purchased from Sigma-Aldrich and used without further purification.

Monomer Synthesis

3,4-Ethylenedioxythiophene, EDOT (2.82g, 20mmol) was dissolved in 100ml of THF under N_2 in a schlenk tube setup and cooled to 0°C. N-chlorosuccinimide (NCS, 5.87g, 44mmol) was added and the mixture was stirred for 5h.

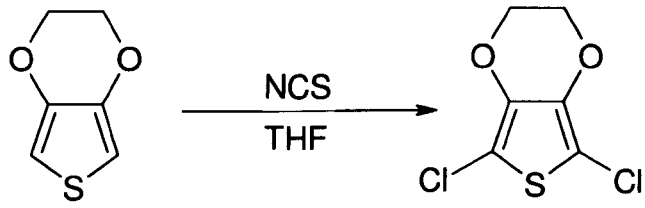


Figure 24 Preparation of 2,5-dichloro-3,4-ethlylenedioxythiophene

After the reaction was completed, sodium sulphite (2.00g) was added to the solution, and it was concentrated at room temperature by rotary evaporation. The product was extracted with an excess of hexane to remove the remaining THF and the solvent was removed at room temperature. The residue was dissolved in ethanol and crystallised at -20°C to give needles, which were collected by filtration under N_2 and dried under vacuum at 0°C to give 2,5-dichloro-3,4-ethylenedioxythiophene (Yield: 3.15g, 75%)

Polymerisation

Polymerisation was carried out under N_2 using the standard Schlenk technique. To a solution of $Ni(COD)_2$ (0.67g, 2.5mmol) in 10ml of dry DMF were added 0.2ml of 1.5-cyclooctadiene and 2,2'-bipyridyl (0.39g, 2.5mmol) at room temperature.

After the mixture was stirred for 1h, a solution of 2,5-dichloro-3,4-ethylenedioxythiophene (0.45g, 2.1mmol) in 10ml dry DMF was added to the reaction mixture. The solution was stirred for 5h at room temperature and then for 28h at 60°C. The black polymer obtained was

collected and worked-up by removing Ni compounds using hot toluene, warm aqueous solutions of EDTA (pH=3 & pH=7) and warm solution of NaOH (pH=11) then warm water and acetone. The work-up of the prepared PEDOT was carried out with N_2 purged solutions to avoid oxidation of the polymer with air.

Doping of Neutral Polymer with Iodine

The neutral PEDOT powder was exposed to iodine vapour under vacuum (about 1Pa) in a desiccator over iodine crystals at room temperature. After leaving for 3 days of exposure, excess I_2 was removed by leaving the sample under vacuum for 10h.

4.1.3 PEDOT Nanoparticles Prepared in Aqueous DBSA Solutions

Materials

EDOT (3,4-ethylenedioxythiophene) was obtained from Aldrich. Iron(III) chloride was purchased from Sigma and DBSA (dodecylbenzenesulfonic acid) from Fluka. The reagents were used as-received without further purification.

Polymerisation

An aqueous micellar dispersion was prepared by introducing a prescribed quantity of DBSA (Table 1) with stirring in 100 ml of deionised water in a 250 ml round flask. Then EDOT monomer was added to the DBSA micellar solution and solubilised with stirring for 1 h. the $FeCl_3$ was dissolved in 10 ml of deionised water and was syringed quickly and the mixtures were stirred for 20h at 30°C.

	DBSA	EDOT	$FeCl_3$
Batch 001	1.436g (44mmol)	0.50g (3.52mmol)	1.898g (11.70mmol)
Batch 002	2.448g (75mmol)	0.70g (4.92mmol)	1.898g (11.70mmol)
Batch 003	2.448g (75mmol)	0.71g (5.00mmol)	0.811g (5.00mmol)
Batch 004	2.448g (100mmol)	1.20g (8.44mmol)	0.811g (5.00mmol)

Table 1 Material Concentration for PEDOT Nanoparticles.

The resultant products were collected by filtration, washed with distilled water and methanol successively, then dried under vacuum at 40°C for 24 h.

Before drying the washed products, a small amount of each sample was re-dispersed in methanol by ultrasonication for 10 min to investigate solubility and perform UV-Visible analysis.

4.1.4 Synthesis of PEDOT in High Concentration Emulsion Polymerization

Materials

3,4-Ethylenedioxythiophene. Iron (III) sulfate pentahydrate and 2-sodium naphthalene sulfonate were purchased from Sigma-Aldrich. The reagents were used as received without further purification.

Polymerisation

To a 50ml round bottomed flask, 16ml of distilled water and 3.656g (0.0158mol) of 2-sodium naphthalene sulfonate were combined to form a micellar solution. Then 2.132g (0.0099mol) of EDOT was added to the solution and was stirred to obtain a high concentration emulsion. Iron (III) sulphate pentahydrate 4.52g (0.0092mol) in 8ml of

distilled water was added slowly drop-wise. The mixture was stirred for 20 hours at room temperature.

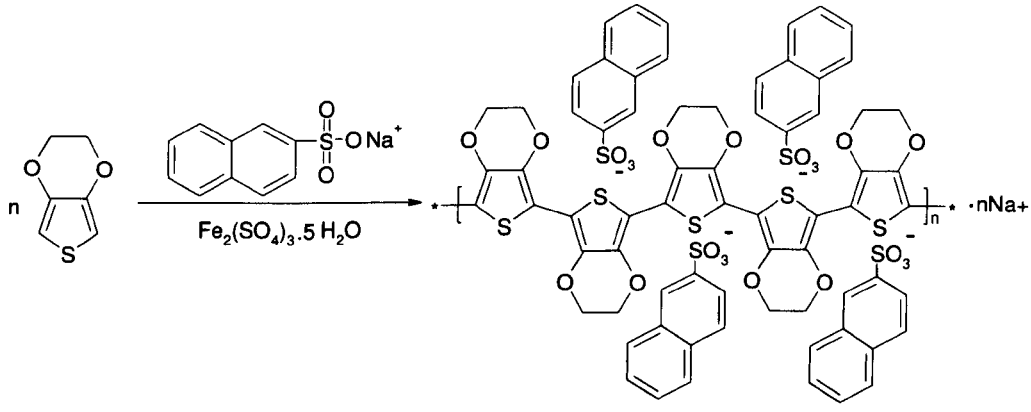


Figure 25 High Concentration Emulsion Polymerisation of EDOT

The polymer was collected by filtration, washed with distilled water and acetone and dried under vacuum at 40°C for about 1h. The product weight was 4.2g, so it was clear that there was still some humidity still trapped between the particles of the polymer. About 0.4g of the dried material was taken for conductivity analysis. The powder was ground and placed into the pellet maker and pressed for 15min under 50 ton load. The pellet weighed 0.385g.

A small sample of the polymer (PEDOT-NaNS) was then dedoped by stirring with 100ml hydrazine and the polymer was collected by filtration. Further dedoping was done by stirring the polymer with diethyl hydroxylamine. The polymer turned black and the ability to disperse in acetone was eliminated.

PEDOT-2NaNS Films

In order to prepare a film of this polymer, 0.1g of the polymer was dispersed into 10ml of acetone. The solution was stirred and ultrasonicated, then the polymer solution was evenly

spread over the glass substrate. The substrate was left to dry in the vacuum oven at 40°C overnight.

4.1.5 Oxidation Polymerisation; Process for the Preparation of Neutral PEDOT

Materials

3,4-Ethylenedioxythiophene, iron (III) chloride anhydrous and anhydrous chloroform were purchased from Sigma Aldrich. The reagents were used as received without further purification.

Polymerisation

1.422 g (10mmol) of 3,4-ethylenedioxythiophene (EDOT) were initially introduced in 100 ml of chloroform. 3.083 g (19mmol) of iron(III) chloride (anhydrous) was added in 10 portions in the course of 7.5 h while stirring at room temperature (23°C.).

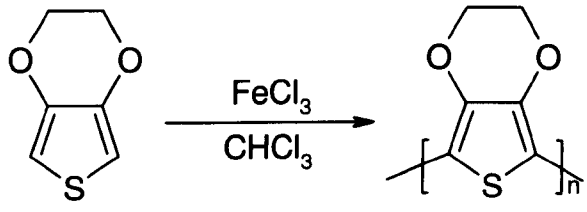


Figure 26 Oxidation Polymerisation of EDOT

After stirring for a further 16 h at room temperature, 50 ml of concentrated ammonia and 100 ml of methylene chloride were added and stirring continued for 1 h. After filtration, this process was repeated and the organic phase was then extracted by shaking three times with 100ml portions of 0.05 molar EDTA solution to remove remaining Fe ions. Thereafter, the dark red organic phase was washed several times with water, dried with sodium sulphate and

then evaporated to dryness in a rotary evaporator. The residue (0.7 g of crude product) was heated to reflux with ethanol for further purification. After cooling, 0.15 g (11% yield) of neutral PEDOT was isolated as a red-brown powder.

Neutral PEDOT Films & Polymer Solution

A neutral PEDOT solution was prepared by dissolving 0.025g of the polymer in 10ml chloroform. The solution was filtered through a 0.2μm polyamide filter paper to remove any undissolved impurities. The polymer solution was cast on quartz glass for UV-visible analysis. ITO glass substrate was used for the preparation of polymer films for cyclic voltammetry analysis.

4.1.6 Hexyl-Substituted Poly (3,4-Ethylenedioxythiophene) PEDOT-C_6

Materials

Thiodiglycolic acid, sodium methoxide, sodium ethoxide, dimethyl oxalate, diethyl oxalate, oct-1-ene, bromine, sodium bromide, sodium perborate tetrahydrate, potassium carbonate anhydrous, potassium hydroxide, DMF anhydrous, hydrochloric acid, and copper chromite were purchased from Sigma Aldrich. The reagents were used as received without further purification. Quinoline was purchased from Sigma Aldrich, purified by vacuum distillation and kept in the dark for future use.

Monomer Synthesis

Stage I

150g (1mol) of thiodiglycolic acid and 161ml (4mol) of ethanol and 4 drops of H_2SO_4 were placed in a 250ml round bottomed flask and the following reaction (Figure 27) was left to reflux at 140°C overnight:

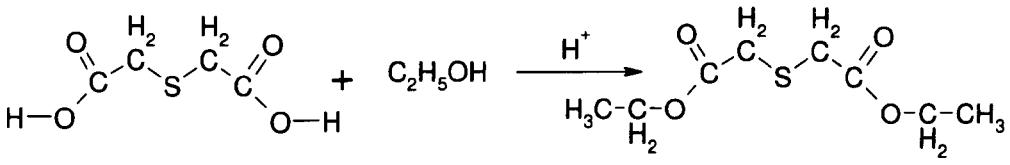


Figure 27 Stage I; Esterification of thiodiglycolic acid

The reaction mix was poured into 150ml of cold water and neutralised with a 10% aqueous solution of sodium hydrogen carbonate using indicator paper whilst stirring vigorously. The resultant mixture was left to stand for 5min. The aqueous phase was separated by decanting and the ester phase was extracted with 150ml chloroform in a separating funnel. The organic layer was separated and put into a flask and was put over magnesium sulphate to dry overnight. The mixture was filtered to remove the drying agent and the solvent was removed by rotary evaporation. The remaining product (compound II) was then purified twice by vacuum distillation [112g, 54% yield, *m/z* 206 (M+), bp. 122-126 at 40torr].

Stage II

57.5g (0.279mol) of dimethyl thiodiglycolate (compound II) and 41.75g (0.285mol) of diethyl oxalate were placed with 750ml of ethanol in a nitrogen purged 1000ml dry round bottom flask. 48.33g (0.7107mol) of sodium ethoxide was added to the stirred flask. The colour of the mixture turned yellow instantly, and the reaction (Figure 28) was left to run surrounded with ice for 5 hours while maintaining temperature below 5°C.

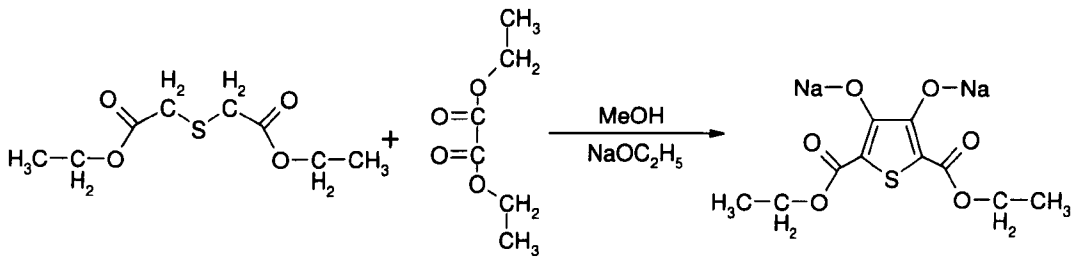


Figure 28 Stage II Preparation of 3,4-dihydroxythiophene-2,5-diethyl ester disodium Salt

The reaction was then brought to reflux for two hours, and then was left to cool to room temperature. The disodium salt (compound III) was collected by filtration and was washed with acetone and placed in the vacuum oven at 50°C to dry overnight (80.1g, 94% yield).

Stage III

3,4-Dihydroxythiophene-2,5-diethyl ester disodium salt (compound III) was dissolved in distilled water and 100ml of dilute HCl was added slowly. As the medium became acidic, a white precipitate dropped out of solution instantly (Figure 29).

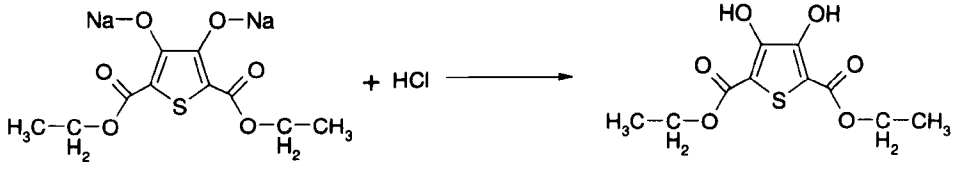


Figure 29 Stage III Formation of 3,4-dihydroxythiophene-2,5-diethyl ester

The precipitate was collected by filtration and was washed thoroughly with distilled water until the filtrate became neutral. The crude product (compound IV) was purified by co-solvent recrystallisation (ethyl acetate and ether) twice to yield shiny white needles.[58.48g, 86% yield *m/z* 260 (M+), m.p. 130-132°C] .

Stage IV

55g of 3,4-dihydroxythiophene-2,5-diethyl ester (compound IV) was dispersed in 500ml of ethanol in a 1000ml flask. A 10% KOH in ethanol solution was added slowly to the stirred solution. Instantly, the potassium salt started to form (Figure 30).

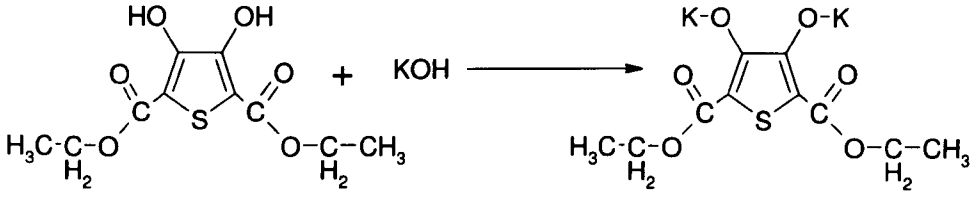


Figure 30 Stage IV; Formation of 3,4-dihydrocythiophene-2,5-diethyl ester dipotassium Salt

The product was finally obtained after stirring the solution for two hours and collection by filtration and washing with ethanol. The reaction yield a bright yellow compound (Compound V) and was left to dry in the vacuum oven overnight. [64g, 90% yield, m.p. >240°C, IR (KBr cm^{-1}): 2950, 2955, 2905 (C-H), 1665, 1635 (C=O)]

Preparation of 1,2-Dibromooctane (Avoiding the use of Bromine)

From the literature[125] it was found that a mixture of sodium bromide and sodium perborate in acetic acid provides a convenient method for preparing dibromoalkanes from alkenes.

Into a 250ml round bottom flask, 1.545g (13.5mmol) of 1-octene and 25ml of glacial acetic acid and sodium perborate tetrahydrate 2.29g (15mmol) were added, followed by 3.10g (30.0mmol) of sodium bromide. The reaction (Figure 31) was left to stir for two hours, then diluted with water and the product was extracted with 100ml of ether by shaking the solution in a separation funnel. The organic layer was washed with 100ml of a 10% sodium bicarbonate solution, 50ml of brine, 50ml of 10% sodium sulphite solution and was dried over anhydrous magnesium sulphate overnight. The solvent was eventually removed by

rotary evaporation. The resulting crude oil was purified by vacuum distillation. (29.1g, 80% yield)

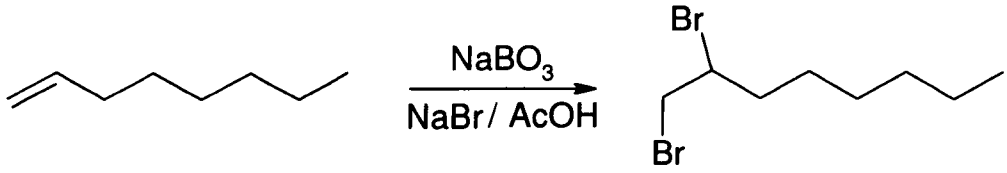


Figure 31 Preparation of 1,2-dibromooctane

Preparation of 1,2-dibromooctane by Direct Bromination

To a 250ml round bottomed flask, 15g (0.131mol) of 1-octene and 50ml of chloroform were added and the flask was surrounded with ice to control temperature. 21.42g (0.133mol) of bromine in 50ml of chloroform were placed in a dropping funnel, and was added dropwise to the stirred 1-octene solution. The final reaction mixture was coloured with a faint orange tint. The solution was washed with an aqueous solution of sodium sulphite and was separated using an extraction funnel and dried over magnesium sulphate. The solvent was removed by rotary evaporation. The compound was further purified by vacuum distillation. [32.4g, 89% yield, *m/z* 272 (M+)]

Stage V

13.72g (0.0431mol) of 3,4-dihydroxythiophene-2,5-diethyl ester dipotassium salt (compound V) were placed into a nitrogen flushed 120ml round bottom flask with 300ml of anhydrous DMF. 13g (0.0435mol) of freshly distilled 1,2-dibromooctane was added to the vessel and the reaction was left to stir under nitrogen at 120°C for 48 hours (Figure 32).

After the reaction had finished, it was brought to room temperature; the solution was filtered, the collected solid washed with 100ml warm ether and the organic solutions were

combined. The solvent was removed by rotary evaporation; the dark brown viscous residue was washed with hexane, then dissolved in acetone and reprecipitated by adding excess water to yield a cloudy brown dispersion.

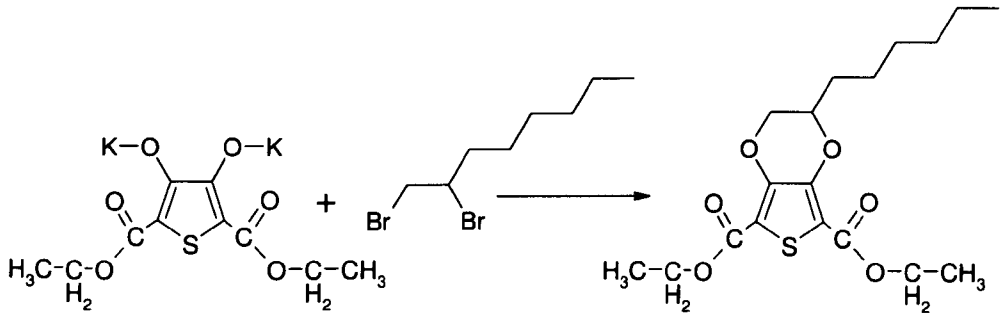


Figure 32 Stage V; Formation of EDOT-C_6 2,5-diethyl ester

The solid was collected by filtration and was left to dry in a vacuum desiccator overnight. The brownish white solid was purified by recrystallisation from ether. The precipitate (compound VI) was collected by filtration and washed with cold solvent. [Yield 7.2g, 48%, *m/z* 370 (M+)]

Stage VI

EDOT-C_6 diethyl ester (compound VI) was placed into a round bottom flask. 100ml of 10% potassium hydroxide solution was added and left to reflux for 6h (Figure 33).

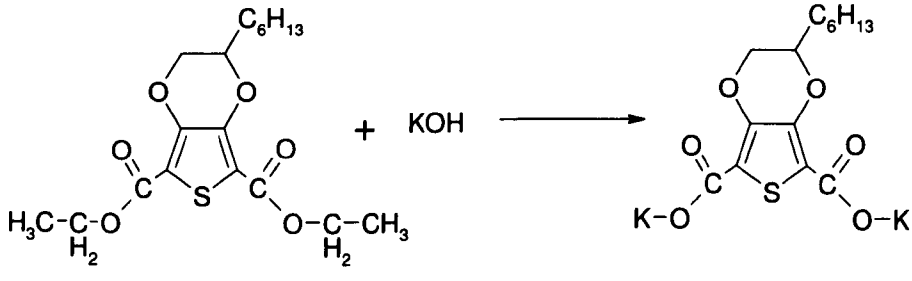


Figure 33 Stage VI; Saponification of EDOT-C_6 Diethyl Ester

After all the ester had dissolved, the reaction was completed and was cooled to room temperature. The solution was filtered to remove any insoluble impurities to yield a solution of the dipotassium salt (compound VII).

Stage VII

0.1M solution of hydrochloric acid was placed in a flask and the potassium salt of EDOT-C_6 diethyl ester solution (compound VII) was added slowly. Instantly a white precipitate was formed and fell out of solution. The reaction was left to stir for one hour.

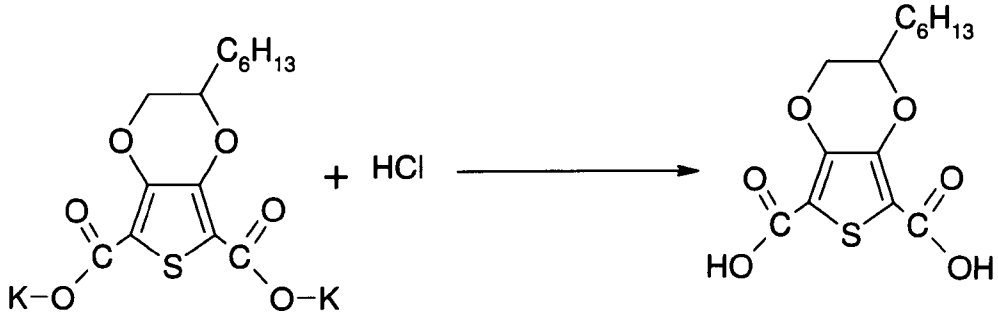


Figure 34 Stage VII, Hydrolysis with HCl

The product, EDOT-C_6 2,5-dicarboxylic acid (compound VIII) was collected by filtration and washed with water to remove excess acid. The compound was left to dry overnight in the vacuum oven. [4.4g, 68% yield, *m/z* 314 (M+)]

Stage VIII

1g of compound VIII was placed into a 250ml 1NRBF and 90ml of freshly distilled quinoline and 15% by mole (0.1483g) of copper chromite were added to the reaction vessel and the reaction was left to stir at 150°C for 24h (Figure 35).

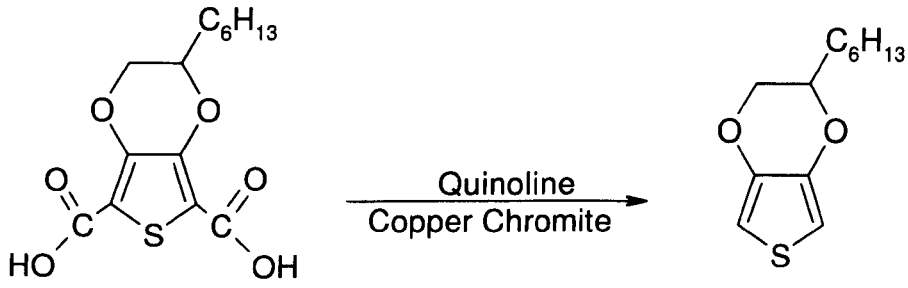


Figure 35 Stage VIII; Decarboxylation of the Diacid

The reaction was brought to room temperature. 100ml of pentane was added to the reaction and was left to stir for 5min. Quinoline was then removed by repeatedly washing with 1% HCl solution until the aqueous layer was acidic. The organic layer was then washed with sodium bicarbonate until aqueous layer was neutral. The organic layer was dried over magnesium sulphate and the solvent was removed by rotary evaporation. The resulting red brown liquid was further purified by flash chromatography (n-hexane) to yield EDOT-C_6 monomer [0.57g, yield 46%, *m/z* 226 (M+)].

Polymerisation

0.7138g (0.0032mol) of EDOT-C_6 was placed in a three neck round bottomed flask with 50ml of chloroform, and the reaction vessel was flushed with nitrogen. 0.973g (0.006mol) of $FeCl_3$ were dissolved in 100ml anhydrous dichloromethane and the oxidant solution was placed in a pressure- compensating dropping funnel and was added dropwise to the reaction vessel over a period of 7 hours. After addition of all oxidant solution, the reaction was left for a further 24 hours.

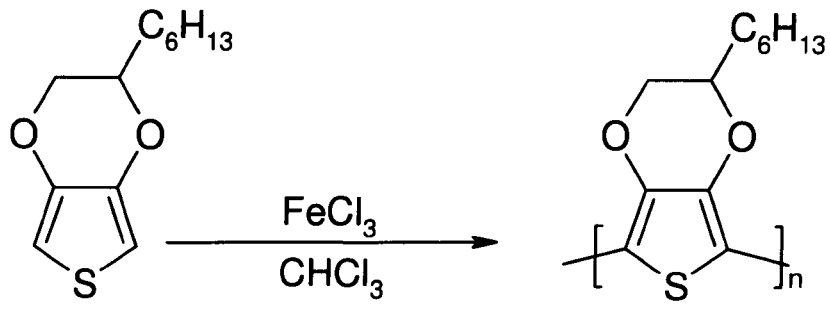


Figure 36 Chemical Polymerisation of EDOT-C_6

50ml of concentrated ammonia was added to the reaction vessel along with 100ml of DCM. The solution was left to stir for about one hour. The solution was then filtered to remove any insoluble impurities. The collected solution was then separated using a separation funnel. The deep purple organic layer was washed repeatedly with water and then with sodium bicarbonate. The solution was then dried over magnesium sulphate and the solvent was removed by rotary evaporation.

The residual polymer was further purified by refluxing with 100ml of methanol. The solution was filtered and the collected polymer was placed in the desiccator to dry under vacuum.(0.22g, 30% yield).

4.2 Results and Discussion

4.2.1 Poly (3-Methoxythiophene) Synthesised at Low Temperature

The polymerisation yielded a dark red powder after washing with methanol and subsequent reduction by chemical means using an aqueous solution of hydrazine.

P3MOT was found to be only partially soluble in chloroform, THF and methylene chloride; however, the films of the polymer on glass were not continuous and had many cracks. The polymer was stable, provided that it was stored in the dark.

Figure 37 depicts the FT-IR spectra of the polymer. The presence of the methoxy group is evident from a C-H stretching band at ca.2850 and 2950cm^{-1} due to $-CH_2-$ and $-CH_3-$ groups. Ring vibrational modes are seen at 1550, 1450 and 1350cm^{-1}. The band at 1069cm^{-1} is assigned to the C_{Ring}-O-C stretching. The vibrational band at 810cm^{-1} is attributed to a $C-H_{\beta}$ out-of-plane deformation mode of the thiophene rings. The absorption peak at 720cm^{-1} is ascribable to an equivalent $C-H_{\alpha}$ out-of-plane deformation.

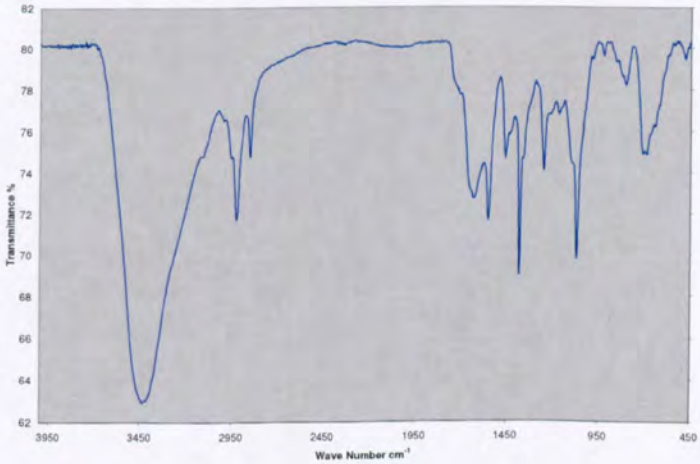


Figure 37 IR Spectrum of P3MOT

The C-H_β deformation band is weak in comparison with that of P3ATs, indicating that some β-defects exist in the polymer, which may be attributed to the strong electron-donating nature of the methoxy group making the β position more reactive.

The presence of two bands at ca. 2850 and 2950cm^{-1} suggests that the methoxy chain remains intact after polymerisation.

Table 2 below shows detailed IR band assignment:

Type of Vibration	Approximate Description of Vibrations	Experimental Frequency (cm^{-1})	Literature[102] Frequency (cm^{-1})
Thiophene in-plane modes	C=C stretching anti-symmetric	1552	1509
		1450	1468
	C-C stretching	1382	1350
		1249	1250
	C-H β out of plane deformation of ring	810	810
	C-S-C deformation	694	691
Methoxy group	CH_3. CH_2 asymmetric Stretching	2800-2926	2800-2950
	C-O-C stretching	1070	1070
	C-O-C deformation	440	440

Table 2 Comparison between the Observed Frequencies of P3MOT and Calculated Frequencies

Preliminary conductivity measurements have been preformed using the van der Pauw four probe technique. The sample did not show any conductivity in the dedoped state, and a very low conductivity around 10^{-7}S.cm^{-1} after doping with iodine. It is likely that the sample was not doped strongly enough, because of the relatively weak electron-accepting ability of the iodine; also, since the undoped polymer was insoluble in any solvent, preparation of polymeric solutions was not possible.

4.2.2 Preparation of PEDOT by Organometallic Polycondensation

The halogenation reaction of 3,4-ethylenedioxythiophene produced 2,5-dichloro-3,4-ethylenedioxythiophene with a good yield.

The crystals were characterised by FTIR spectroscopy as a KBr pellet (cm^{-1}) 2920 (C-H), 1078 (C-O-C), 1040 (C-Cl). IR peaks were nearly identical to those in the literature[110].

It was noted that leaving the product in the laboratory's lighting and temperature conditions caused some crystals to change colour to blackish grey, although further IR analysis did not reveal any change in the chemical structure.

Polymerisation was carried out under an inert atmosphere to prevent unwanted oxidation of the polymer by air. FTIR (Figure 38) analysis showed the following main peaks (KBr, cm^{-1}): C-H at 2923, skeletal vibration of the thiophene ring at 1445 and (C Ring-O-C) at 1097.

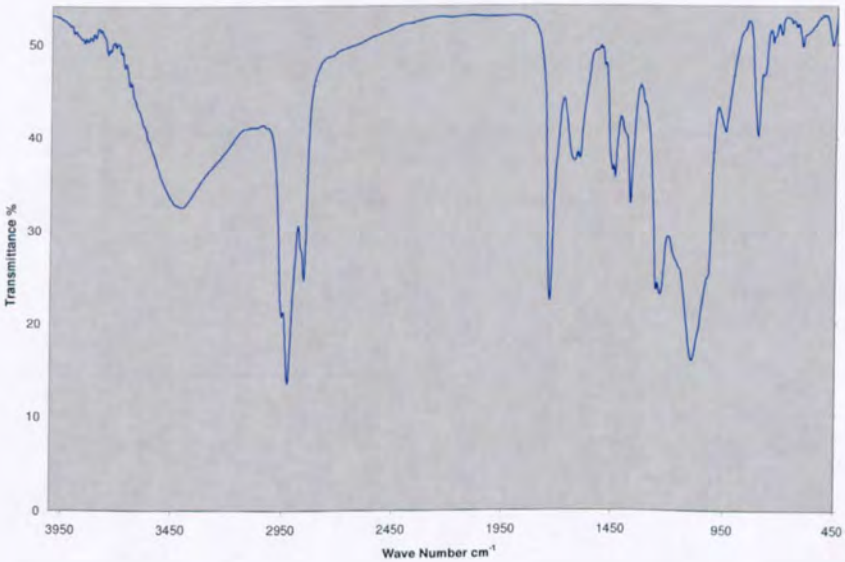


Figure 38 IR Spectrum of Neutral PEDOT

A broad peak at around 3400cm^{-1} reveals that the sample is still holding water molecules, and finally the peak at 1737cm^{-1} could be assigned to residual acetone used for polymer work-up. Full details of peak assignment and a comparison with values from the literature are listed in Table 3 below:

Type of Vibration	Approximate Description of Vibrations	Experimental Frequency (cm^{-1})	Litreature[126] Frequency (cm^{-1})
Thiophene in plane modes	C=C anti-symmetric	1581	1530
	C=C stretching	1445	1444
	C-C stretching	1376	1366
	C-C inter-ring stretching	1260	1267
	C-S-C deformation	684	691
Oxyethylene ring modes	CH_2 symmetric stretching	2972	-
	CH_2 asymmetric stretching	2923	2932
	CH_2 symmetric stretching	2854	-
	C-O stretching	1097	1070
		1020	1061
	Oxyethylene ring breathing	802	802
	C-O-C deformation	605	575
		470	440

Table 3 Comparison between the Observed Frequencies of Neutral PEDOT and the Calculated Frequencies

The dried product was doped using saturated iodine vapour. Due to the low yield of product recovered from the polymerisation process, it was not possible to prepare a 13mm pellet to perform four-probe conductivity measurement. Therefore, a 5mm pellet was prepared and was re-exposed to iodine vapour.

4.2.3 PEDOT Nanoparticles Prepared in Aqueous DBSA Solutions

The method that describes the preparation of PEDOT nanoparticles suggested 1.898g of oxidant $FeCl_3$ without mentioning the quantity of EDOT to be used. Theoretically, one mole of monomer needs two moles of oxidant; however this could cause over-oxidation and result in an insoluble polymer with high molecular weight; hence, a 1:1 molar ratio of oxidant: monomer was used. A value of 0.044M of DBSA was initially used as suggested by the

method outlined in the literature[111]. The colour of the collected polymer was black, although the expected colour of polymer was dark blue; this is thought to be a concentration effect, although it was noticed that changing the molar ratio of oxidant: monomer yielded a product with different colour, changing from blackish to dark blue.

IR analysis reveals that the product was nearly an exact match to the product synthesis by Choi et al[111]. Figure 39 shows the FT-IR spectra of PEDOT powder prepared with $FeCl_3$. Vibrations at around 1326 and 1518cm^{-1} are due to C-C or C=C stretching of the quinoidal form of the thiophene ring and due to ring stretching of benzenoid thiophene ring, respectively.

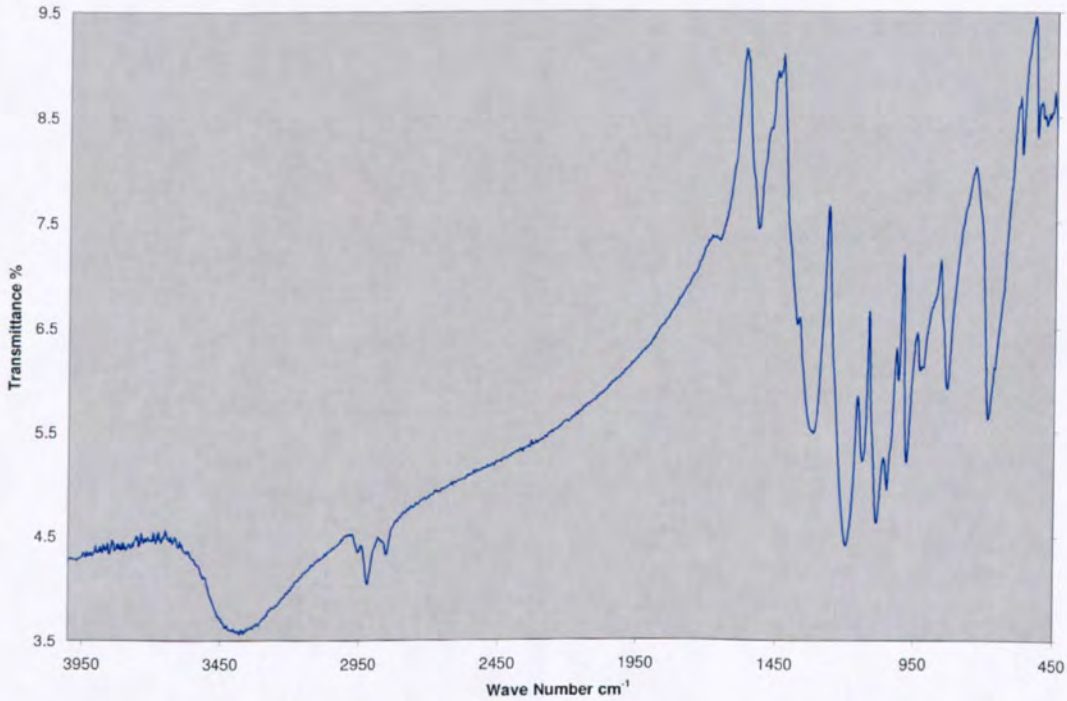


Figure 39 IR Spectrum of PEDOT Nanoparticles using DBSA-$FeCl_3$ System

Vibrations at 1195, 1139 and 1088cm^{-1} originated from C-O-C bond stretching in the ethylenedioxy group. C-S bond vibrations in the thiophene ring are also seen at 981, 837 and 688cm^{-1}.Table 4 below shows details of the peak assignments:

Type of Vibration	Approximate Description of Vibrations		Experimental Frequency (cm^{-1})	Literature[111] Frequency (cm^{-1})
Thiophene in plane modes	C=C C-C	Stretching of quinoidal structure	1518	1530
	Due to quinoid structure indicating well-doping		1326	-
	C-S stretching		980	962
	C-S-C deformation		688	691
Oxyethylene ring modes	CH_2 asymmetric stretching		2923	2932
	CH_2 symmetric stretching		2854	-
	C-O-C stretching		1195	1020-1275
			1131	
			1088	
	C-O-C deformation		605	575
			470	440

Table 4 Comparison between the Observed Frequencies of PEDOT Nanoparticles and Calculated Frequencies

The analysis of all batches was the same; hence IR was not able to explain the reason behind the colour change caused by changing the molar ratio. It is likely to be due to chain length variation (hence conjugation length).

Differing from results presented in literature[111], the DBSA-$FeCl_3$ system yielded PEDOT nanoparticles of low conductivities i.e. less than 1Scm^{-1}. That is due to possible dedoping occurring during the work-up process. The polymer was left for a prolonged period of time during filtration due to blockage of filter paper pores (a common incident when dealing with surfactants).

4.2.4 Synthesis of PEDOT in High Concentration Emulsion Polymerization

Oxidative polymerisation of PEDOT under high concentration emulsion conditions in the presence of 2-naphthalenesulphonic acid sodium salt proceeded well at room temperature. The doped polymer was found to be dispersible in acetone; however, treating the polymer with hydrazine as a reducing agent resulted in making the dedoped polymer insoluble.

Figure 40 exhibits FT-IR spectra of both doped and dedoped polymers, they give similar absorbing patterns; however, bands in the dedoped state have been shifted to a lower frequency for the doped polymer. The shifts may be due to a high degree of p-doping achieved in the high concentration emulsion polymerisation.

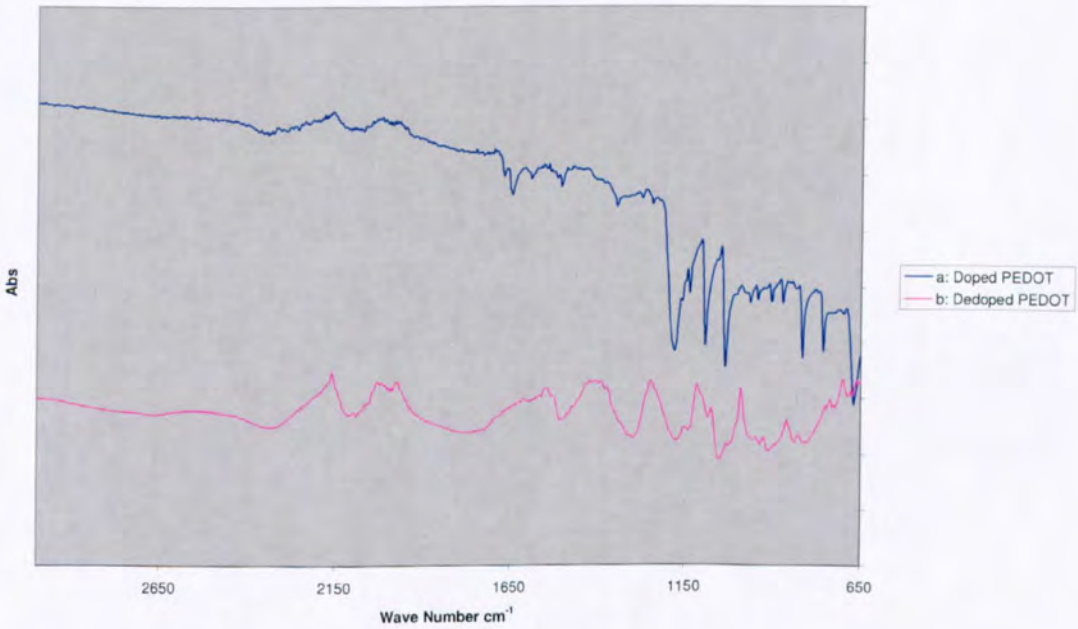


Figure 40 FT-IR Spectrum of PEDOT prepared by high concentration emulsion polymerisation. a=doped, b=dedoped.

The electrical conductivity of both pelletised doped and dedoped PEDOT was measured. The doped polymer exhibited a dc conductivity of 4.90S.cm^{-1} while the dedoped polymer drove the instrument outside its detection limits, indicating that the polymer had become completely dedoped. Since the solubility properties were eliminated by the dedoping process however, the polymer was found to be no longer suitable for solution blending with the electron deficient polymers.

4.2.5 Oxidative Polymerisation; Process for the Preparation of Neutral PEDOT

Controlled oxidative polymerisation of EDOT monomer proceeded well at room temperature. The use of excess concentrated ammonia was necessary to ensure that all doped polymer becomes dopant free and washed with the EDTA solution. The polymerisation yield was 18%. The neutral polymer was found to be soluble in common organic solvents, like chloroform and dichloromethane, to form a deep red solution. Elemental analysis was done by MEDAC Ltd. and returned the following results:

Element	Found	Calculated for $(C_6H_4O_2S)_n$
C %	51.78	51.45
S %	21.90	22.88
H %	4.08	3.88

Table 5 Elemental Analysis of PEDOT

A small sample of the neutral polymer was studied by ATR-IR spectroscopy (Figure 41).

The following peaks have been observed: 2974, 2870cm^{-1} (CH_2 symmetric stretching); 2925cm^{-1} ($CH_{aliphatic}$ asymmetric stretching); 1573cm^{-1} (CH_2 bending). 1487cm^{-1} (skeletal vibration of thiophene ring); 1467cm^{-1} (C=C antisymmetric stretching); 1434cm^{-1} (C=C

symmetric stretching); 1358cm^{-1} (CH_2 bending). Complete peak assignments are to be found in Table 6.

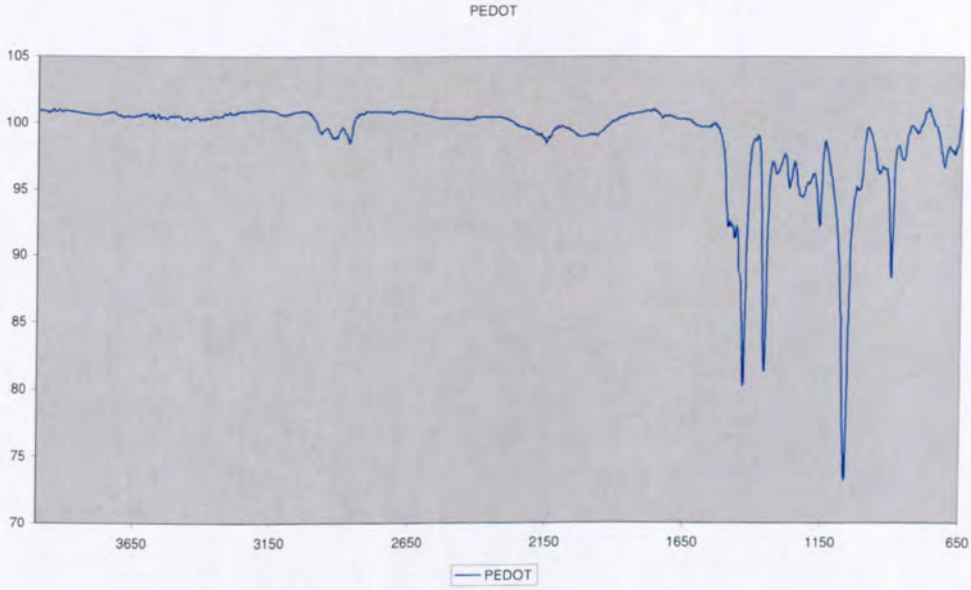


Figure 41 ATR-IR Spectrum of neutral undoped PEDOT

Type of Vibration	Experimental Frequency cm^{-1}	Literature Frequency	Approximate description of Vibrations
Thiophene in plane modes			
	1467	1468	C=C Stretching (antisym)
	1434	1408	C=C Stretching (sym)
	1358	1350	C-C Stretching
	1029	1015	Cycle deformation
	971	962	C-S Stretching
	926	911	S-C stretching
Oxyethylene ring modes			
	2974	-	CH_2 Symmetric Stretching
	2925	2932	CH_2 asymmetric Stretching
	2870	-	CH_2 Symmetric Stretching
	1358	-	CH_2 Bending
	1128	1110	C-C Stretching
	1059	1070	C-O Stretching
	1029	1061	C-O Stretching
	863	865	O-C-O deformation

	777	788	Oxyethelene ring deformation
	708	-	CH_2 Rocking
	589	565	-

Table 6 Comparison between the observed frequencies of the neutral PEDOT and literature[127] frequencies of reduced PEDOT.

A small quantity of the polymer was dissolved in chloroform and was evaporated on the inside wall of the quartz UV cell for UV-Visible spectroscopy. Figure 42 shows the UV spectrum for PEDOT,

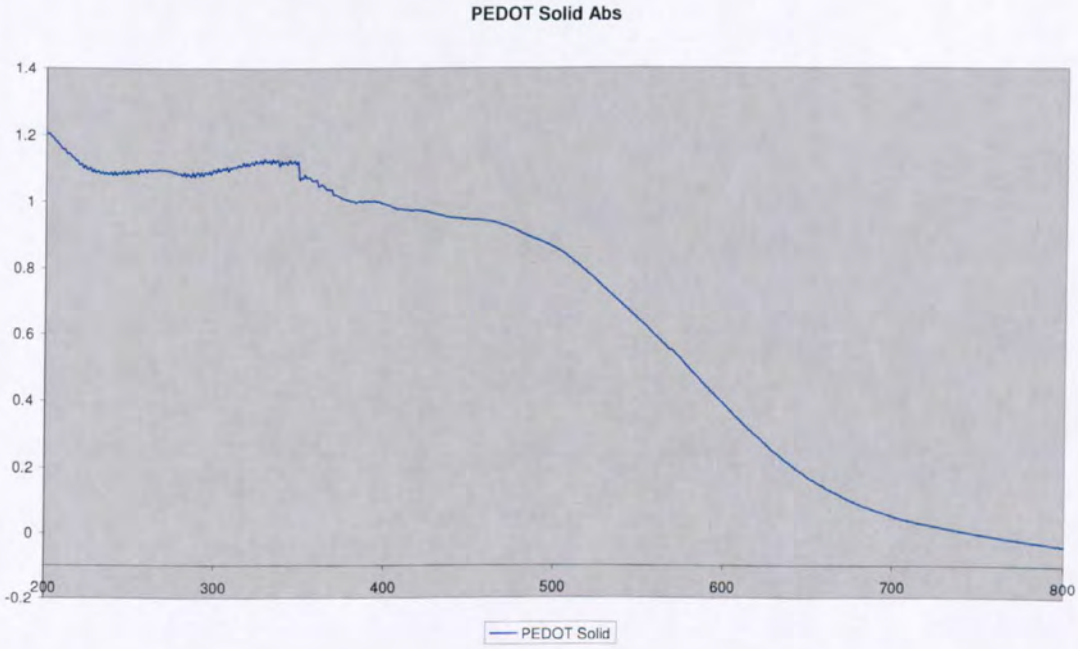


Figure 42 UV-Visible Spectrum of neutral undoped PEODT

Bulk conductivity measurement was performed on a 5mm pelletized sample. The polymer showed no signs of conductivity in the undoped form as the instrument was outside its resistance of limit. Thermoelectric testing was performed by placing the polymer pellet in between two copper electrodes in a manner similar to a thermocouple. By heating one side of the junction, the current generated was measured and was found to be positive. This shows

that the current was generated by holes (p-type), which is what we would expect from an electron-donating polymer.

Cyclic voltammetry (Figure 43) of a polymer film was performed in a 0.1M solution of tetrabutylammonium tetrafluoroborate in anhydrous acetonitrile. The polymer showed p-type oxidation and corresponding dedoping reduction at: 800mV and -200mV respectively.

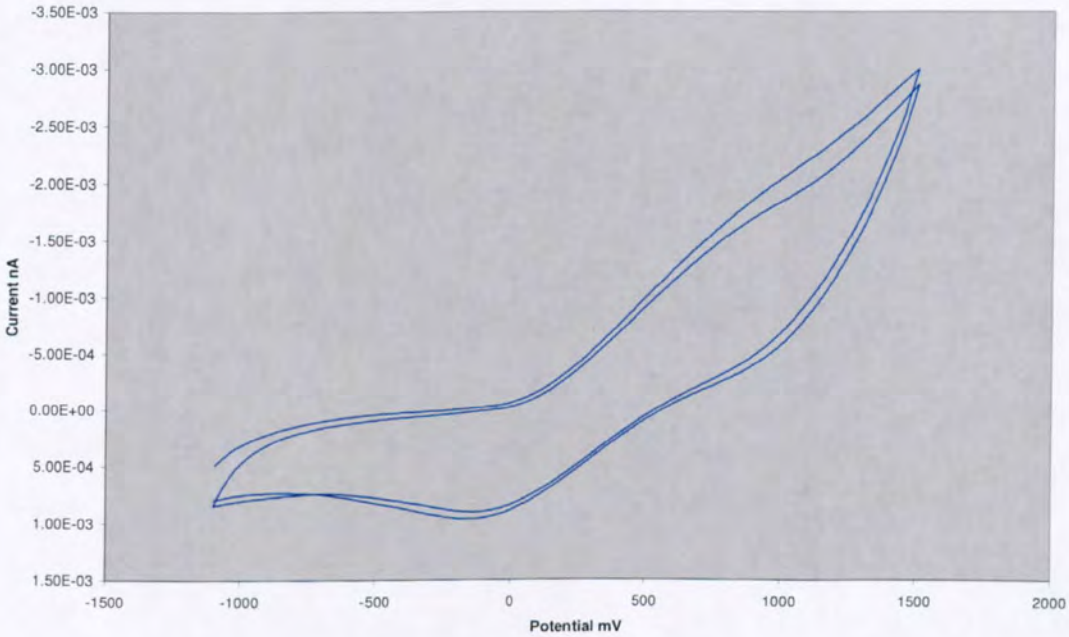


Figure 43 CV of PEDOT film on ITO glass in 0.10M Bu_4NBF_4/CH_3CN, scan rate: $50mV.s^{-1}$vs Ag^+/Ag

4.2.6 Hexyl-Substituted Poly (3,4-Ethylenedioxythiophene) PEDOT-C_6

Monomer Synthesis

The EDOT-C_6 monomer was successfully synthesised following an eight stage synthetic route and could be summarised as follows: thiodiglycolic acid was esterified with absolute ethanol (confirmed by GC-MS), and the thiophene ring was formed by reaction with diethyl

oxalate in the presence of sodium ethoxide to form the disodium salt. Acidification with HCl led to the 3,4-dihydroxy-2,5-dicarbethoxythiophene precursor (confirmed by IR and GC-MS).

A further reaction with 1,2-dibromooctane in anhydrous DMF, followed by saponification and hydrolysis, gave the EDOT-C_6 diacid. Finally, decarboxylation in quinoline in the presence of barium-promoted copper chromite catalyst, yielded the monomer EDOT-C_6. The monomer was further purified by flash chromatography and was stored under nitrogen.

GC-MS analysis revealed that product still had some impurities, mainly 2- & 3-methyl naphthalene, which were traced back to the quinoline solvent used; although extra attention was paid while vacuum-distilling the solvent, these impurities were still present at very low concentrations.

It was found that moving forward to the next step was still possible, however, as the presence of these impurities would not interfere with the polymerisation reaction; they are inert to the oxidant and can be removed in the washing process of the polymer.

Polymer Synthesis

Polymerisation of the monomer EDOT-C_6 in chloroform using anhydrous $FeCl_3$ as an oxidant proceeded well at room temperature. It was noticed that performing the reaction under nitrogen atmosphere slightly increased the yield of the product (up by 10%). The polymer was found to be soluble in common organic solvents, like chloroform, DCM and DMSO.

Elemental analysis was carried out on the pure undoped polymer resulting in the following composition:

Element	Found	Calculated for $(C_{12}H_6O_2S)_n$
C %	63.3%	61.8%
S %	13.2%	13.7%
H %	6.9%	7.3%

Table 7 Elemental Analysis of PEDOT-C_6

The polymer was studied with IR spectroscopy. Figure 44 shows the ATR-IR spectra for the neutral polymer. The following peaks were observed: 2923cm^{-1} CH_2 asymmetric stretching, 2856cm^{-1} CH_2 symmetric stretching, 1456, 1431cm^{-1} C=C symmetric stretching, 1347cm^{-1} C-C stretching and 1063cm^{-1} C-O-C deformation.

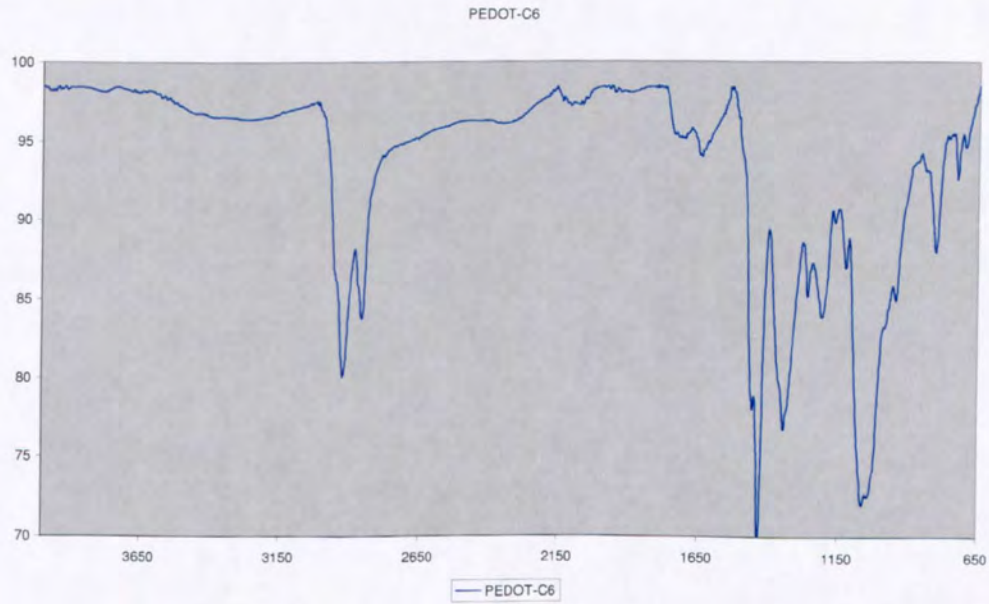


Figure 44 ATR-IR Spectrum of neutral undoped PEDOT-C_6

UV-Visible spectroscopy (Figure 45) was carried out on the polymer solution in chloroform. The spectra showed absorptions at: 472, 431 and 352nm. These correspond to $\pi \rightarrow \pi^*$ transitions for the different lengths of polymer chains in the solution.

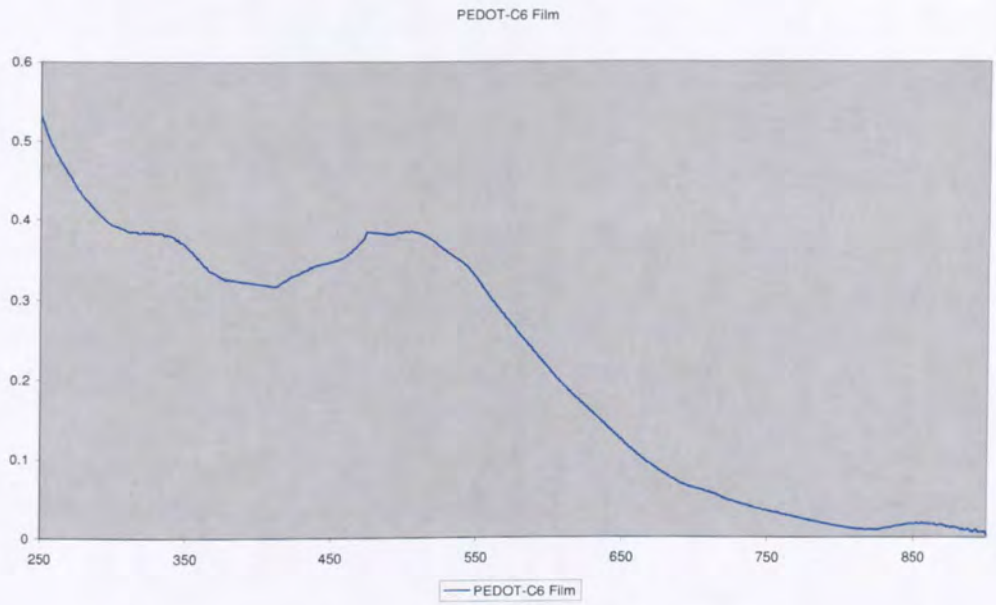


Figure 45 UV Spectrum for solid state PEDOT-C_6 film on quartz substrate.

Cyclic voltammetry analysis was done on a polymer film deposited on an ITO glass electrode. The voltammogram (Figure 46) of the polymer film in an anhydrous acetonitrile solution of tetrabutylammonium tetrafluoroborate (0.1M) showed a p-doping oxidation peak at 595mV vs. Ag^+/Ag and a corresponding reduction (dedoping) peak at 80mV vs. Ag^+/Ag.

Comparing the results between PEDOT and PEDOT-C_6, it was found that the introduction of the hexyl substituent on the oxyethylene ring has located PEDOT-C_6 on the negative side, compared to PEDOT. The present result indicates that the introduction of the hexyl group enhanced the electron-donating properties of the recurring ethylenedioxythiophene rings and the oxidation proceeds much more easily than it does for PEDOT.

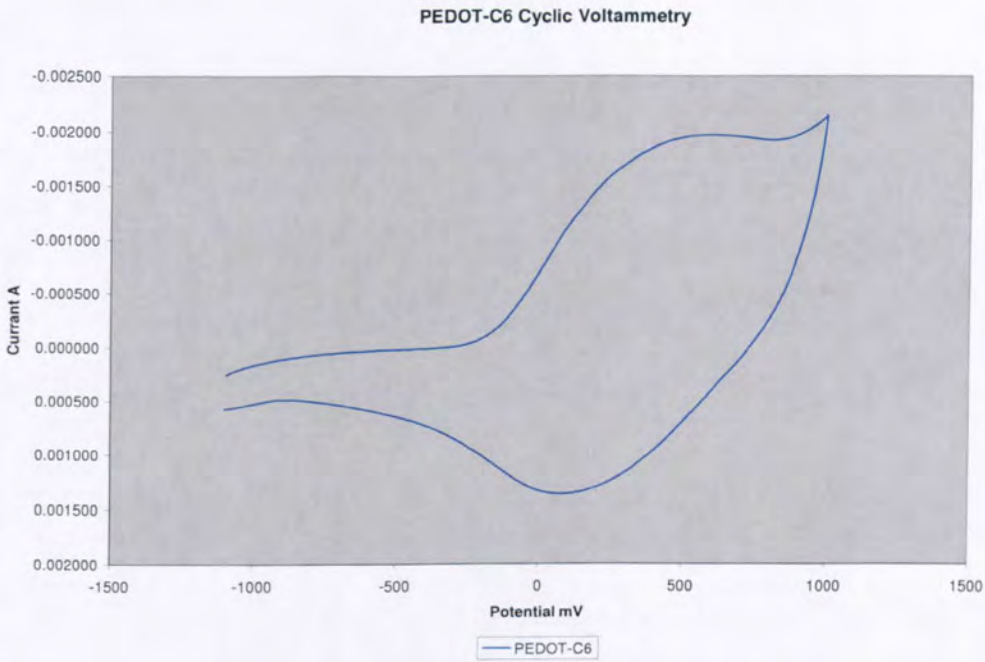


Figure 46 Cyclic Voltammogram of PEDOT-C6 a 0.1M solution of [Bu4N] [BF4] in anhydrous CH3CN (sweep rate: 50mV.s-1)

The ease of oxidation of PEDOT-C_6 over PEDOT is also evident in terms of atmospheric effects on the polymers, as it was clear that leaving PEDOT-C_6 in open atmosphere caused the polymer to oxidise and to turn black at a faster rate than PEDOT in the same conditions.

Four-probe conductivity measurement for a pressed pellet was performed, but the instrument was not able to measure due to an over-range error occurring during the measurement. Bulk resistivity was measured by a two probe contact configuration revealed that the polymer had a resistivity over $2.5G\Omega.m^{-1}$, which was outside the limits of the instrument. Thermoelectric measurements were performed and the polymer was found to generate a positive current when heated. This corresponds to the fact that the polymer is p-type and the current is generated from holes moving in the system.

4.3 Summary

Several electron rich polymers were successfully synthesised. Some were not further utilised in the blending with the electron-deficient polymer due to their insolubility in the undoped pure form.

The polymers: PEDOT and PEDOT-C_6 were characterised by infrared, UV-visible spectroscopy, and their electronic properties were studied by cyclic voltammetry and electrical conductivity measurement. The pure undoped polymers were found to be soluble in common organic solvents

As an additional, commercially available polymer, Poly[3-(2-methoxyethoxy)-ethoxymethylthiophene-2,5-diyl] [P2] was purchased from Sigma-Aldrich. The polymer was considered as a potentially good electron-rich polymer due to the multi-alkoxy side chain on the 3-position on the thiophene ring along with the region-regularity of the repeating units in the backbone. [P2] was used as received.

Chapter Five:

Electron Withdrawing Polymers;

Experimental, Results and Discussion

5 Electron Withdrawing Polymers

5.1 Experimental

5.1.1 Poly (pyridine-2,5-diyl)

Materials

2,5-dibromopyridine, 2,2'-bipyridine , Bis(1,5-cyclooctadiene)nickel(0) [$Ni^{o}(COD)_2$], anhydrous N,N-dimethylformamide (DMF), zinc powder, nickel chloride anhydrous, triphenylphosphine and ethylenediaminetetraacetic acid (EDTA) were all purchased from Sigma Aldrich and were stored and used without further purification.

Polymerisation

Organometallic Catalyst

25ml of anhydrous DMF were placed into a nitrogen flushed three neck round bottomed flask. The system was continuously flushed with a slow flow of nitrogen. 0.78g (7.22mmol) of 1,5-cyclooctadiene and 1.14g (7.35mmol) of 2,2'-bipyridine were placed into the reaction vessel to dissolve into the DMF solution. 2g (7.27mmol) of $Ni^{o}(COD)_2$ was quickly transferred from the packaging vial into the reaction vessel. 1.38g (5.83mmol) of the monomer, 2,5-dibromopyridine, was dissolved in 25ml of anhydrous DMF and was added to the reaction vessel. The reaction was left to stir under nitrogen for 2 hours at 60°C.

The reaction was cooled to room temperature and the polymer was collected by filtration and washed with hot toluene, warm aqueous solutions of EDTA (pH=3 & pH=7) and warm aqueous solution of NaOH (pH=11) and was left to dry overnight in a desiccator.

The polymer was then dissolved in formic acid and filtered to remove any insoluble impurities, then precipitated by slowly adding the solution to 1M solution of NaOH. The

polymer was then collected by filtration, washed with distilled water and left to dry under vacuum at ambient temperature overnight.

In situ Synthesis of Organometallic Catalysed Polymer

To a two neck round bottomed flask, nickel chloride 10.34g (82mmol), triphenylphosphine 22.4g (85.5mmol), zinc powder 3.75 (57.5mmol) and dibromopyridine 10.56g (43.7mmol) were added. The flask was sealed and flushed with nitrogen. 100ml of nitrogen purged anhydrous DMF was added to the reaction vessel and the reaction was stirred under nitrogen at 70°C for 16h.

The reaction was cooled to room temperature. About 250ml of acetone was added to the mixture and the precipitated polymer was collected by filtration. The polymer was processed with EDTA and then ETDA tetrasodium salt to remove any remaining transition metal, washed with hot distilled water and warm acetone and dried at room temperature under vacuum.

The polymer was further purified by dissolving in formic acid and insoluble impurities were removed by filtration. The polymer solution was then added slowly to cold aqueous ammonia, and precipitated immediately as the medium started to be neutralised. The precipitated polymer was collected by filtration, washed with distilled water and dried in the vacuum oven at 60°C overnight.

5.1.2 Poly (3-nitropyridine-2,5-diyl)

Materials

2-hydroxy-5-bromo-3-nitropyridine was purchased from Avocado Chemicals and was used without further purification. Bromine, phosphorus oxybromide, copper sulphate

pentahydrate, zinc powder and formic acid were purchased from Sigma Aldrich and were used as received without further purification.

Monomer Synthesis

10.5g (0.047mol) of 5-bromo-2-hydroxy-3-nitropyridine was placed in a 250ml round bottomed flask fitted with a thermometer, a nitrogen inlet and a drying tube. 15.5g (0.096mol) of bromine and 25g (0.087mol) of phosphorus oxybromide were added to the reaction vessel. The mixture was stirred under nitrogen at 100°C for 5 hours.

40ml of methanol was slowly added to the cooled reaction vessel followed by 118ml of distilled water. The precipitated monomer was then transferred to a beaker and carefully neutralised with aqueous ammonia, whilst always keeping the temperature under 5°C. The monomer was collected by filtration and washed with excess distilled water and methanol.

The monomer was then placed in a flask and was dissolved in chloroform for purification. Additional hexane was added as a co-solvent to aid the precipitation of the compound. Excess solvent was removed by evaporation and the yellow solution was left to recrystallise overnight. The 2,5-dibromo-3-nitropyridine crystals were collected by filtration, washed with methanol and left to dry in the vacuum oven at 40°C. [9.0g, 67% yield, *m/z* 282 (M+)]

Activated Copper

Copper sulphate pentahydrate (20g, 0.08mol) was placed in a 250ml conical flask and dissolved with water by stirring. Zinc dust (8.13g, 0.125mol) was then slowly added; a change from blue colour to red was observed. 100ml of 2N HCl was added to remove any unreacted zinc. The solution was filtered, washed with distilled water several times and then

washed with acetone and dichloromethane. The activation of copper was carefully done under nitrogen in a schlenk-tube, by washing it 5 times with a very diluted nitric acid solution (about 0.02M), 4 times with distilled water, 3 times with acetone and twice with diethyl ether. After each step of washing, the majority of the upper liquid above the copper was removed with a syringe. At the end, the process yielded pure activated copper with a gold-like colour, was placed in a vacuum oven and left to dry at room temperature overnight.

Polymerisation

Under nitrogen atmosphere, 4.60g of the monomer and 120ml of DMF were placed in a 250ml two neck round bottomed flask. 7.6g of activated copper was added to the mixture, and the polymerisation was commenced by refluxing the solution under nitrogen for 5 hours. The reaction was cooled to room temperature and the solution was filtered. The filtrate solution was poured into cold water to precipitate the polymer, which was washed with water and collected by filtration. The collected insoluble solid from the polymerisation reaction was processed with formic acid in an attempt to recover any polymer bonded to the remaining unreacted copper. The polymer was dissolved in formic acid, the acidic solutions were combined and were slowly added to cold aqueous ammonia solution to precipitate the purified polymer. The pure poly (3-nitropyridine) was collected by filtration, washed with distilled water and dried in the vacuum oven at room temperature overnight (yield 1.2g, 60%).

5.2 Results and Discussion

5.2.1 Poly (pyridine-2,5-diyl)

Polymerisation by: the catalysed organometallic dehalogenation, polycondensation and in-situ synthesis of the catalyst proceeded well in freshly distilled anhydrous DMF to yield a

yellow product soluble in formic acid. Dissolving this polymer in other polar solvents was attempted without success; the polymer was found to be insoluble in any non-acidic solvent, which in turn eliminates the usability of the polymer as an electron deficient polymer solution, as the acid present will dope the thiophene based polymers by protonation before polypyridine. Hence the use of this polymer in blending is likely to be very restricted.

5.2.2 Poly (3-nitropyridine-2,5-diyl)

The synthesis of the monomer was achieved by reacting 2-hydroxy-5-bromo-3-nitropyridine with bromine in the presence of phosphorus oxybromide. The reaction yielded a yellow solid. Mass spectrometric analysis confirmed the structure of the monomer: 2,5-dibromo-3-nitropyridine. The monomer was purified by recrystallisation from methanol and hexane to yield sharp shiny needles (yield: 9.0g, 67%). The product had a melting point of ~92°C. Purity of the monomer was tested using GC-MS, resulting in 99%.

Activated copper was prepared as described on p82. The product was used directly after production to avoid any oxidation.

Polymerisation as described in section 5.1.2 proceeded well in anhydrous DMF and was complete in 5h. The polymer was purified by re-precipitation from formic acid to yield a brown polymer. The polymer was found to be freely soluble in formic acid and also showed some solubility in hot DMSO and DMF. Elemental analysis of the polymer was done by MEDAC Ltd and returned similar results to the literature (Table 8).

Element	Found	Calculated for $(C_5H_2N_2O_2)_n$	Literature	Monomer
C %	48.6%	48.5%	48.8%	21.3%
N %	21.8%	22.6%	22.1%	9.9%
Br %	0.8%	-	0.6%	56.7%

Table 8 Elemental analysis of poly(3-nitropyridine).

ATR-IR spectroscopic data were also consistent with the structure of the polymer. As shown in Figure 47, the ATR-IR spectrum of PPy-3-NO_2 exhibits strong absorption peaks at 1575cm^{-1} (NO_2 asymmetric) and 1396cm^{-1} (NO_2 symmetric). Peaks representing C-Br in the 1100cm^{-1} region of the monomer spectra had almost disappeared after polymerisation. This agrees with the implication of the data generated from the elemental analysis, i.e. that the elimination of bromine was largely complete.

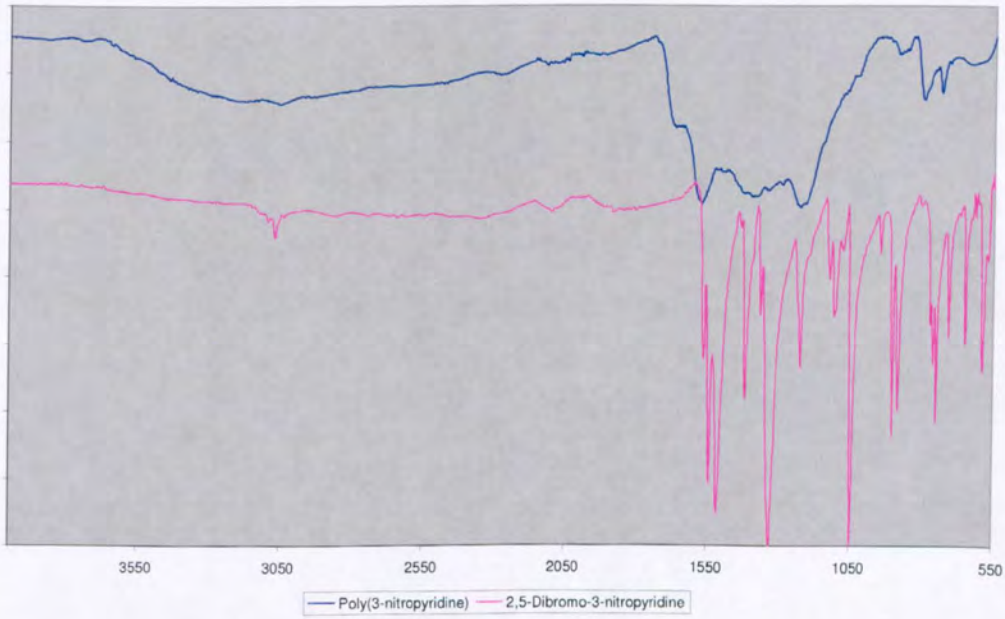


Figure 47 ATR-IR Spectrum of PPy-3-NO_2 and 2,5-dibromo-3-nitropyridine

The number average molecular weight $\overline{Mn}$=20000g.mol^{-1} was calculated from the amount of bromine found in the elemental analysis as following:

$\overline{Mn}$ = Br-$(C_5H_2N_2O_2)_n$-Br = 160+$(122)_n$.

Percentage of bromine from elemental analysis Br=0.8%

$$\%Br = \frac{160}{122n+160} = 8\times10^{-3} \Rightarrow 122n+160 = \frac{160}{8\times10^{-3}}$$

$$\Rightarrow n = \frac{(\frac{160}{8\times10^{-3}} - 160)}{122} = 162$$

$$\Rightarrow \overline{M_n} = 160 + (122)\times n \approx 20000 g.mol^{-1}$$

The UV-Visible spectrum shows an absorption peak at 325nm. The peak position is at a somewhat longer wavelength than that of polypyridine. This could be explained because on the introduction of the nitro group leads to a bathochromic effect of the absorption; this is possibly a consequence of the π-conjugation from the pyridine ring to the nitro group.[128] To eliminate any solvent effect in the analysis, solid state UV-Visible spectrometry was performed on a thin film of PPy-3-NO_2. The spectrum showed a maximum absorbance at 325nm.

Cyclic voltammetry was carried out on a polymer film deposited on an ITO glass electrode coated with a thin evaporated film of gold, to prevent any reduction of the ITO at negative potentials during the analysis. The voltammogram (Figure 49) of the polymer film in an anhydrous acetonitrile solution of tetrabutylammonium tetrafluoroborate (0.1M) showed an n-doping reduction peak at -1665mV vs. Ag^+/Ag and a corresponding re-oxidation (or n-dedoping) peak at -1100mV.

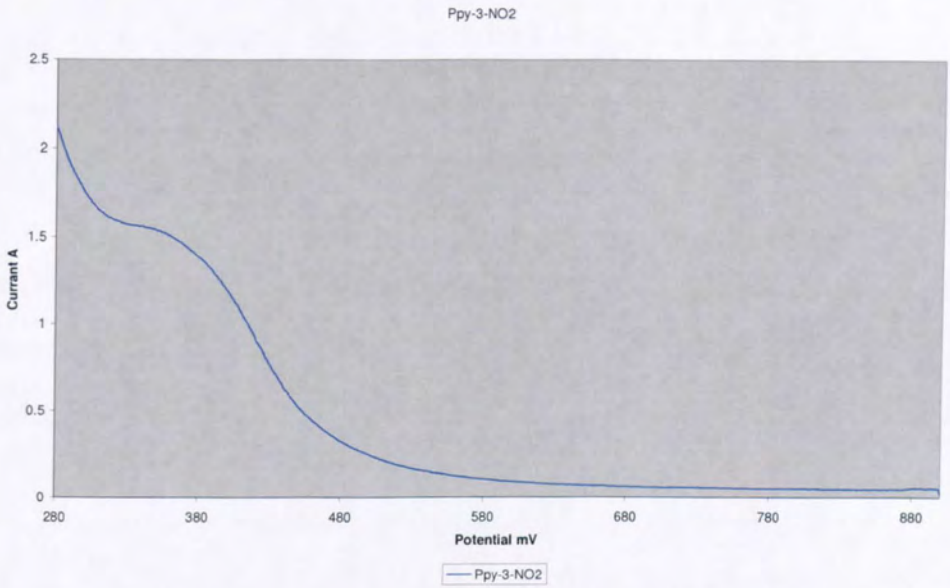


Figure 48 UV-Vis Spectrum of Poly(3-nitropyridine)

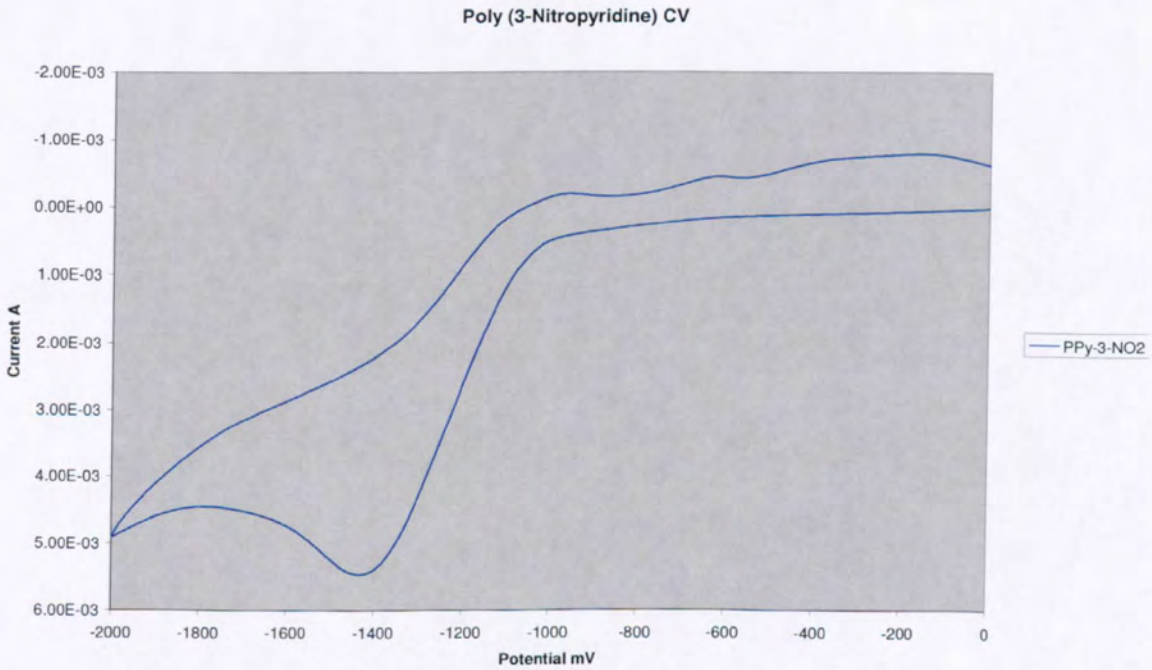


Figure 49 Cyclic Voltammogram of PPy-3-NO_2 in a 0.1M solution of $[Bu_4N]$ $[BF_4]$ in anhydrous CH_3CN (sweep rate: $50mV.s^{-1}$)

Comparing these results to those for polypyridine in the literature, it was found the introduction of the nitro group to the pyridine ring has put poly(3-nitropyridine) on the positive side of polypyridine, and the reduction potential has increased by 800mV.

The present result indicates that the introduction of the nitro group enhanced the electron-withdrawing properties of the pyridine rings and the reduction proceeds much more easily than it does for polypyridine.

DSC analysis was performed on the pure polymer. The scan shows three endothermic responses. The first one, at around 100°C corresponded to water loss from the polymer sample; the second, at around 187°C, had the typical characteristics of a glass transition. The last one, at around 260°C, corresponded to a possible loss of NO_2 side chain group on the polymer due to decomposition.

Two-probe resistivity measurement of a 5mm pellet revealed that the polymer was highly resistive. The resistance values were outside the limits of the instrument ($+2.5G\Omega.m^{-1}$). Thermoelectric testing was performed on the 5mm polymer pellet; the test resulted in no generation of current, indicating that the polymer had no charge carriers whilst in the undoped state.

Chapter Six:

Polymeric Blends Experimental, Results and Discussion

6 Polymeric Blends

6.1 Experimental

Polymer solutions were prepared by dissolving the polymers in 10ml of the relevant solvents (Table 9) and were ultrasonicated for 2h.

Polymer	Solvent
PEDOT	Chloroform
PEDOT-C_6	Chloroform
P2	DMSO
Ppyr-3-NO_2	DMSO

Table 9 Solvents used for polymeric solutions

Solutions were then kept under nitrogen. Molecular weights for the monomers in each of the polymers used in the blends were calculated as follows:

Polymer	Repeating Unit RMM
PEDOT	140g.mol^{-1}
PEDOT-C_6	224g.mol^{-1}
P2	214g.mol^{-1}
Ppyr-3-NO_2	122g.mol^{-1}

Table 10 Calculated Molecular Weights for Monomer Repeating Units

Blends of electron-rich polymers and the electron-deficient polymer solutions were prepared by adding equivalent molar amounts of each pair of polymers in solution together in a 50ml flask. The following blend solutions were prepared (Table 11)

Blend Name	Components	Weight of Components (g)
B1	PEDOT ¦ PPy-3-NO_2	0.0015 ¦ 0.010
B2	PEDOT-C_6 ¦ PPy-3-NO_2	0.0183 ¦ 0.010
B3	P2 ¦ PPy-3-NO_2	0.0175 ¦ 0.010

Table 11 Blend Compositions and Component Weights

Polymer blend solutions were constantly stirred and were stored under nitrogen.

Several films of polymers and polymer blends were prepared by solvent evaporation casting of polymer solution on different substrates, as require. Table 12 illustrates the different substrates for each of the analytical techniques used:

Substrate	Analytical Technique
Silica	UV Spectroscopy
Gold plated ITO Slides	Cyclic Voltammetry (for negative voltage sweeping)
ITO glass	Cyclic Voltammetry

Table 12 Substrates used for Various Analytical Techniques

Evacuated silica tubes were used for sample preparation for ESR spectrometry. Preparation for ESR analysis was done by evaporating the solvent from the polymeric blends and the polymer solutions; the residue was then accurately weighed and put into the silica tubes, which were evacuated using a high vacuum pump and sealed. The instrument available did not provide full ESR spectra, but calibrated spin concentrations were obtained for each polymer and blend sample.

For conductivity measurements, 5mm pellets of polymer blends and corresponding polymers were prepared by pressing the dry powder material in evacuated dies with a load of 2.0 tons. The pellets were then covered with carbon based aquadag to form a conductive layer on each side of the pellet. Additional preparation of a gold-plated slide was carried out for two-probe film conductivity measurements by evaporating gold onto a 25x25mm glass substrate masked 5mm across to form a gap. Polymer solutions were then cast over this substrate by evaporation of the solvent under vacuum.

6.2 Results and Discussion

The blending procedure was carried out in order to produce blends of electrically equivalent polymer components. That was achieved by mixing the polymers on the basis of a 1:1 ratio of their repeating units, which was likely to be close to the optimum value.

6.2.1 Electron Spin Resonance

Electron spin resonance analysis was kindly provided by the University of Surrey. The results in the following table represent the uncorrected spins for the individual polymers and their blends and the calculated spins per molecule, using TTF-TCNQ as reference.

Polymers & Blends (Assuming 50:50 in blend)	Spin Signal	Sample Weight mg	Mw of Repeating unit g.mol-1	Moles	Spin/Molec.
PEDOT	3404	7.4	140	5.3x10-5	0.00022
P2	114	6.0	214	2.8x10-5	0.000014
PEDOT-C6	23620	6.2	223	2.8x10-5	0.00290
PPy-3-NO2	8900	5.5	122	4.5x10-5	0.00068
B1 (PEDOT:PPy-3-NO_2)	9259	2.5	131	3.6x10-5	0.00167
B2 (P2:PPy-3-NO_2)	53067	6.0	168	1.9x10-5	0.00507
B3 (PEDOT-C8:PPy-3-NO_2)	62377	3.8	172.5	2.2x10-5	0.00975
TTF-TCNQ	204810	0.9	408.6	2.2x10-6	0.320

Table 13 ESR Analysis; Uncorrected spin signals and calculated spin densities per molecule

The analysis indicates a significant increase in the spin/molecule values in the blends compared to those of the individual polymers. This increase is not simply the result of addition; the result shows significantly higher spin concentrations for the blends than for the sum of the spins of the individual polymers making the blend. This tends to support the expectation of charge transfer between the two polymers (up to 0.98 free electrons per 100 molecules for the blend).

6.2.2 Electrical Properties

Electrical Conductivity

Electrical conductivity measurements were carried out on 5mm pressed pellets of the blends. A two probe resistance measurement was obtained for polymer blend pellets of known

thickness in a sample holder with two spring-loaded copper electrodes. Below are the resistance values at room temperature, and calculated conductivities:

Polymers & Blends	Resistance Ω	Conductivity $S.m^{-1}$
PEDOT	O/L	-
P2	0.11×10^{10}	4.6×10^{-8}
PEDOT-C_6	O/L	-
PPy-3-NO_2	O/L	-
B1 (PEDOT:PPy-3-NO_2)	3.5×10^{9}	1.5×10^{-8}
B2 (P2:PPy-3-NO_2)	4.5×10^{7}	1.1×10^{-6}
B3 (PEDOT-C_6:PPy-3-NO_2)	1.77×10^{9}	2.9×10^{-8}

Table 14 Bulk Conductivity of the Pure Polymers and their Blends

This analysis clearly shows that blending the electron-rich polymer with the electron deficient polymer certainly caused changes in the ability of the polymers to conduct a current. The pure polymers, in the case of PEDOT, PEDOT-C_6 and PPy-3-NO_2, all show resistances higher than detection limits (over 150GΩ). On the other hand, pure P2 shows measurable conductivity, which becomes, after blending with PPy-3-NO_2, higher by almost two orders of magnitude. This indicates that the charge transfer between the polymers is introducing new free carriers into the system.

Temperature Dependence of Conductivity

A study of the effect of temperature on charge production and mobility was done by measuring the sample conductivities as a function of temperature. This analysis was

performed under vacuum in a temperature controlled system. The temperature range was set between room temperature (~23°C) and 120°C.

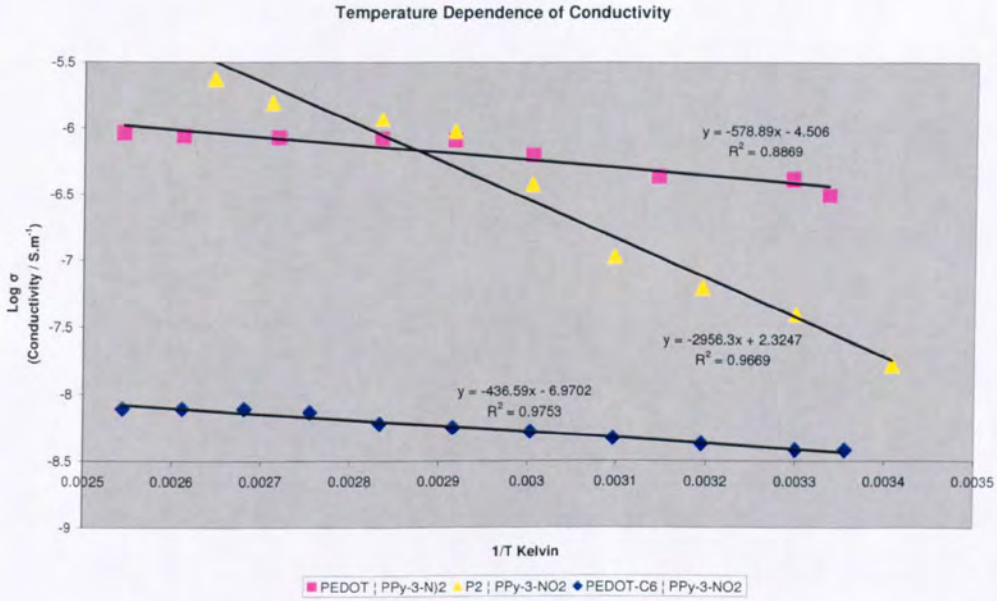


Figure 50 Temperature Dependence of Conductivity **σ** for Polymer Blends

	Resistance Ω	Conductivity $S.m^{-1}$	**σ∞**	**ΔE eV**	ESR (Spin/Molc 10^5)	Ox. Pot. mV
PEDOT	O/L	-				750
P2	$1.1x10^9$	$4.6x10^{-8}$				1500
PEDOT-C_6	O/L	-				250
PPy-3-NO_2	O/L	-				
B1 **(PEDOT¦PPy-3-NO_2)**	$3.5x10^9$	$1.5x10^{-8}$	$1.1x10^{-5}$	0.115	167	
B2 **(P2¦PPy-3-NO_2)**	$4.5x10^7$	$1.1x10^{-6}$	72.28	0.587	507	
B3 **(PEDOT-C_6¦PPy-3-NO_2)**	$1.8x10^9$	$2.9x10^{-8}$	$3.7x10^{-8}$	0.087	975	

Table 15 Summary of Temperature Dependence of Conductivity Data

Table 15 summarises the parameters obtained from the Arrhenius plots in Figure 50. The activation energy (ΔE) for the blends are observed to be in the sequence (with respect to the e-rich component) P2 > PEDOT > PEDOT-C_6.

Although the ΔE value could in principle contain a small contribution from the hopping activation energy of the charge carriers, the sequence correlated well with the trend of the donor ionisation potentials indicated by cyclic voltammetry. Hence they are likely to relate mainly to the charge-transfer process.

The extrapolated high-temperature conductivities (σ_∞) show a very different trend. They correspond to a state of maximum charge-transfer, and hence to the relative values of carrier mobility in the polymers. In this case, we see that poly(3-[2-methoxy] ethoxymethylthiophene] has an enormously higher value that the ethylenedioxythiophene polymers. Since this polymer has a high molecular weight and a 98% regioregularity, it is likely to be better organised and more highly conjugated than the EDOT polymers; consequently a much higher mobility seems to be quite reasonable.

Cyclic Voltammetry

Polymer blend solutions were cast by reduced pressure solvent evaporation of 1ml aliquots at a time, onto gold plated ITO substrates to prevent the ITO from becoming reduced due to scanning at negative potentials. The analysis was carried out in purged solution under nitrogen atmosphere. The parameters for all CV analyses were set as follows: the electrolyte was acetonitrile solution containing 0.1M [N-(n-C_4H_9)$_4$][BF_4], room temperature, Scan rate: 50mV.sec^{-1}. Figures 51, 52 & 53 show the data for each blend, along with those of the

polymers forming it. The following table summarises the observed peak positions (with respect to Ag/Ag^+):

Component	Peak Potential (mV)	
	Doping	Dedoping
PEDOT	750	-25
PEDOT-C_6	250	-10
P2	1500	500
PPy-3-NO_2	-1435	-1100
B1	-1507	-
B2	-1665	-
B3	-1730	-

Table 16 Summary of Cyclic Voltammetry Responses

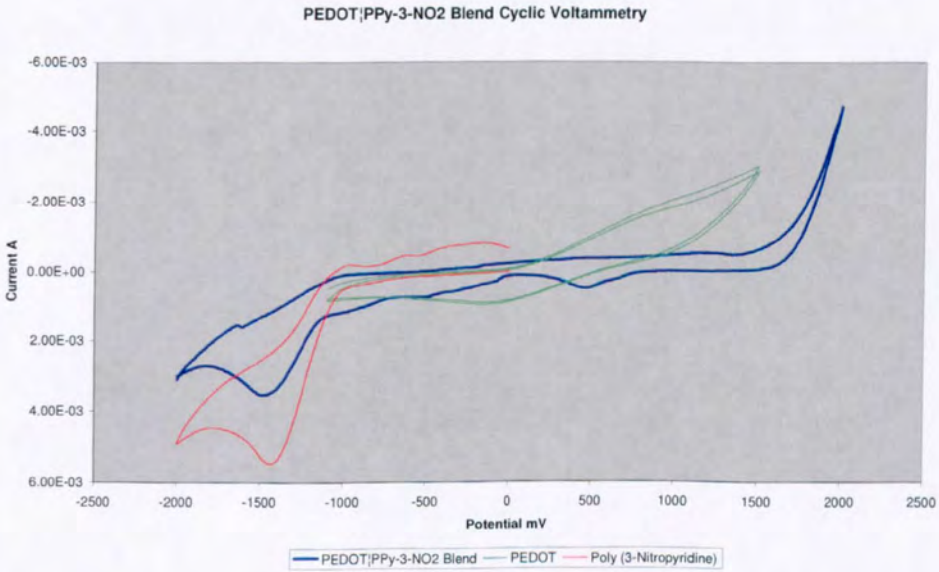


Figure 51 Cyclic Voltammogram of Blend B1

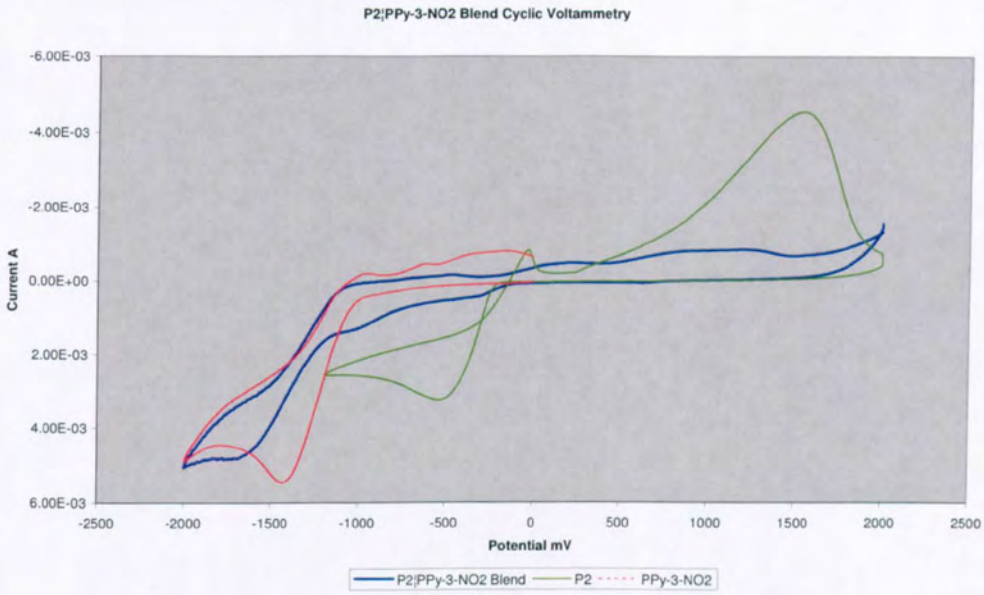


Figure 52 Cyclic Voltammogram of Blend B2

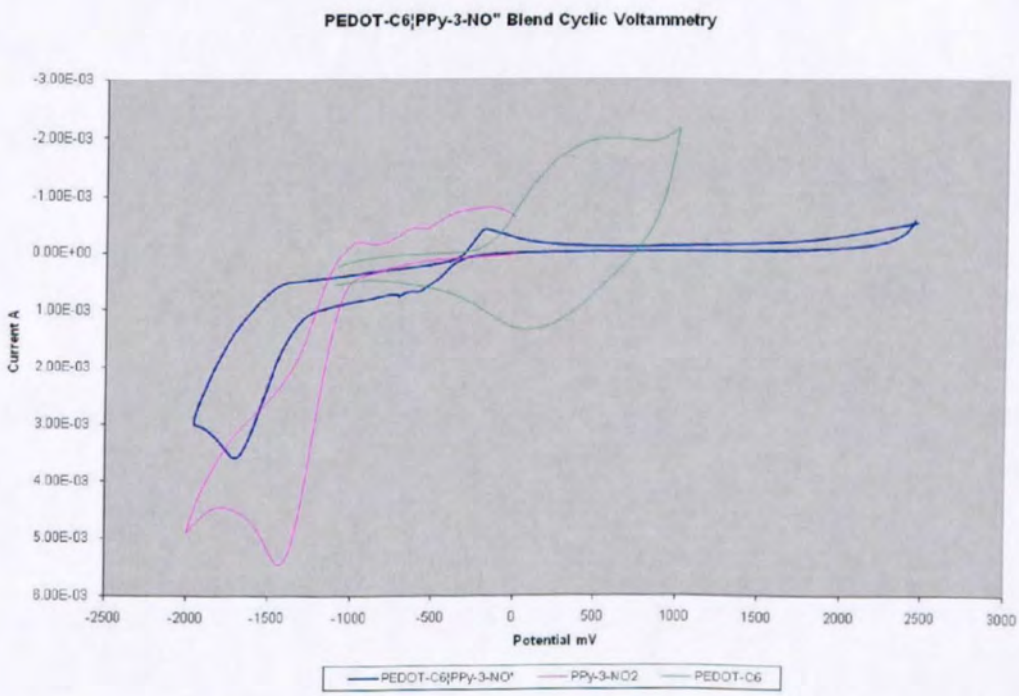


Figure 53 Cyclic Voltammogram of Blend B3 with its components

Poly (3-nitropyridine) shows an n-doping peak at -1435mV. On the other hand, P2 (figure 49) exhibits p-doping peaks at ca 1500mV and a corresponding p-dedoping peak at 500mV, and PEDOT (Figure 50) shows a doping peak at ca. 750mV and p-dedoping at ca -25mV; finally, PEDOT-C_6 (Figure 51) displays doping at 250mV and corresponding p-dedoping at -10mV.

In contrast to this, all blends show either no or very weak peaks in the positive region (corresponding to the presence of the electron donating groups in the blend and therefore the p-doping oxidation process) and they feature only one reduction peak at -1665mV.

Choi *et al* found that the presence of an electron-withdrawing group on polypyridine (PPy) caused the polymer to n-dope at a less negative potential compared with unsubstituted PPy. Here, the presence of the electron donating polymers in the matrix is causing PPy-3-NO_2 in the blend to reduce at a more negative potential compared with the unmixed polymer. This suggests that charge transfer to the electron deficient PPy-3-NO_2 is reducing the electronic effect of the electron-withdrawing group present on the PPy-3-NO_2 backbone, moving the doping potential to more negative values and making PPy-3-NO_2 harder to be electrochemically reduced.

6.2.3 UV-Visible Spectroscopy

Films of the polymer blends (0.01mm thick) were prepared on silica substrates for UV-Visible spectrometric analysis. This was achieved by solvent evaporation after coating the polymer solution on the silica substrate under vacuum. Table 17 illustrates a summary of observed absorption peaks of the individual undoped polymers of their blends:

Component	Wave length (nm)		
PEDOT	470		
P2	466		
PEDOT-C_6	431	472	
PPy-3-NO_2	326		
Blend 1	670		
Blend 2	365	485	
Blend 3	395	463	511

Table 17 Summary of UV-Visible Absorbances of the Polymers and their Blends.

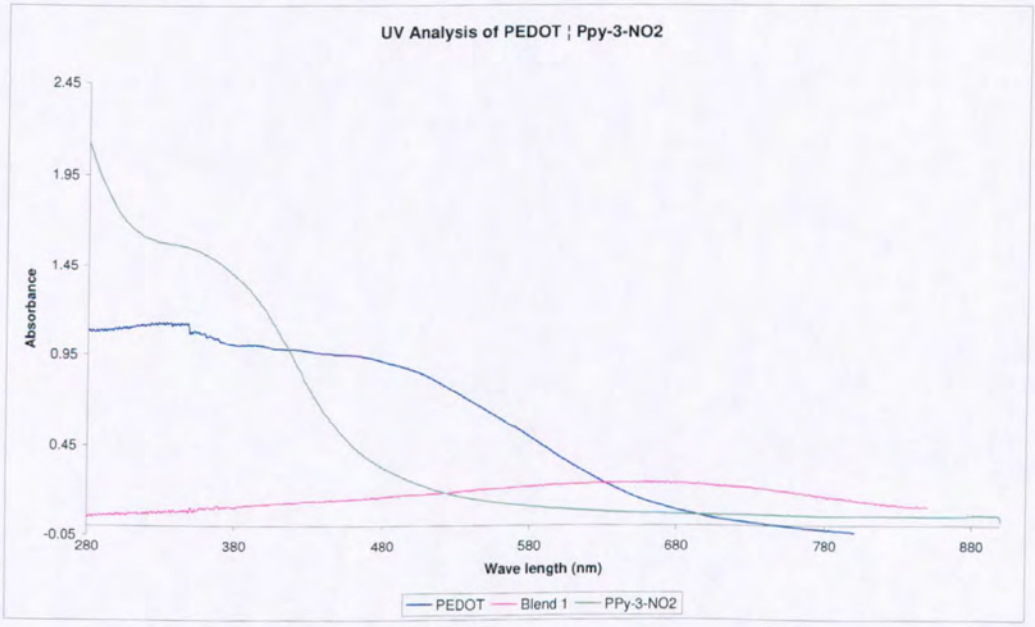


Figure 54 UV Analysis of Blend 1

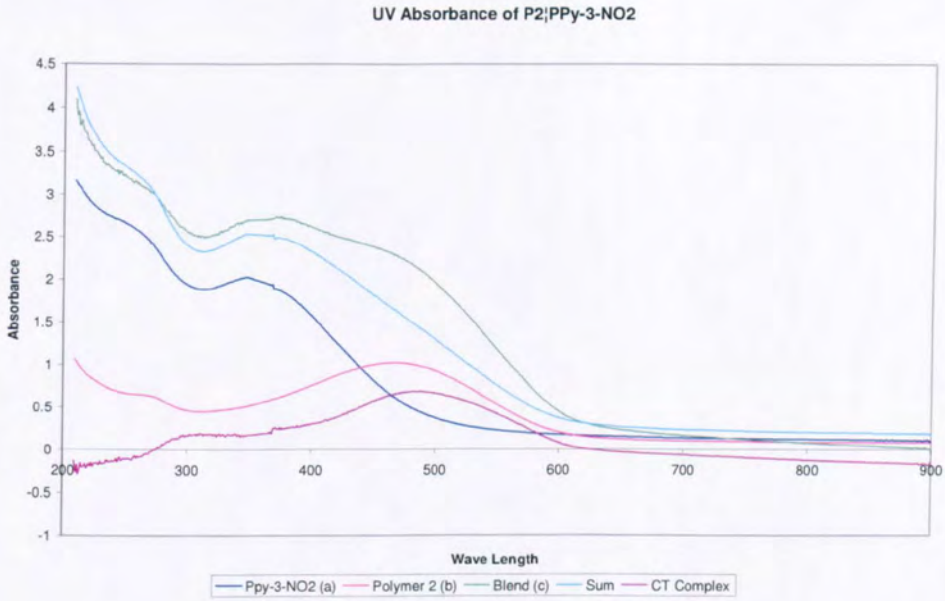


Figure 55 UV Analysis of B2

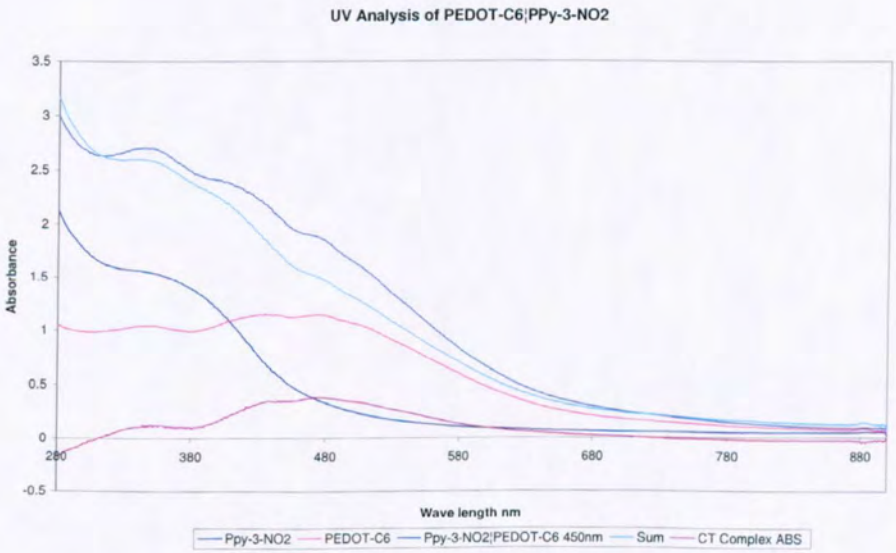
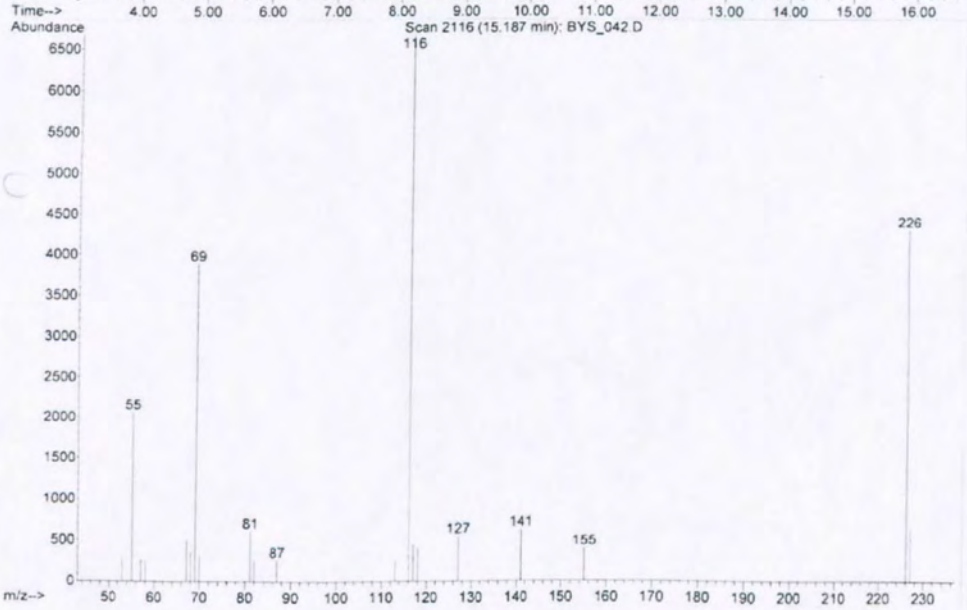


Figure 56 UV Analysis of B3

We can observe that the peaks corresponding to the presence of PPy-3-NO_2 and the electron rich polymers together in the blend have been shifted bathochromically (lower transition

9.2.5 EDOT-C_6 Stage VII

```
File        :C:\MSDCHEM\1\DATA\Snapshot\BYS_042.D
Operator    : Bassem Sabagh
Acquired    : 30 Nov 2005  17:29     using AcqMethod DEFAULT.M
Instrument :    Instrument #1
Sample Name: EDOT-C6 Dicarboxylic Acid
Misc Info  : Dried-Concentrated
Vial Number: 1
```



energy) in the spectrum of the charge transfer complex (i.e. that of the blend minus the sum of the individual polymers).

In conjugated systems[129], it is known that increasing the extent of conjugation decreases the energy gap. Here, mixing the polymers together increases the effective conjugation due to delocalisation of the charges; partial charge transfer from the electron-rich to the electron-deficient polymer has caused this effect.

6.3 Summary

Polymer blends were successfully synthesised. Evidence of charge transfer was found and confirmed by means of UV-Visible spectrometry, ESR measurements, cyclic voltammetry and DC electrical conductivity measurements.

Chapter Seven:

General Conclusion

&

Future Recommendations

7 General Conclusion

Several p-type, thiophene based, conducting polymers have been synthesised through suitably tailored synthetic routes, some of which were later decommissioned due to the insolubility of the undoped polymers. Poly (3,4-ethylenedioxythiophene) was successfully synthesised via the controlled oxidation method by Rueter *et al*[130] Spectral and electrical measurements were performed to characterise the polymer. It had a low, but sufficient molecular weight of about 1170g.mol^{-1} and was reasonably soluble in organic solvents such as chloroform, tetrahydrofuran, N,N-dimethylformamide and dimethysulfoxide.

On the other hand, polypyridine was no longer used due to its limited solubility in organic solvents. It was found to be soluble in formic acid, but this could not be considered, as the electron-rich thiophene polymers are liable to react with the solvent in preference to an interaction with the electron-deficient polymer.

Hexyl-substituted PEDOT was successfully synthesised via an eight stage synthesis by following and modifying the combined work of Raynolds *et al* and Kumar *et al*. Each step of the synthesis was characterised by IR spectroscopy and GC-MS analysis where possible. Oxidative polymerisation successfully yielded PEDOT-C_6; the polymer was found to be soluble in almost all organic solvents, particularly tetrahydrofuran, chloroform and dichloromethane. UV-visible spectroscopy and cyclic voltammetry were employed for the characterisation of the polymer's electronic structure.

Poly (3-nitropyridine) was found to be a good substitute for PPy, since the electron-withdrawing nitro-group enhanced both the solubility and the electron affinity. PPy-3-NO_2 was successfully synthesised by following a revised method of Chio *et al,* and the polymer

was found to be soluble in polar organic solvents like dimethylsulfoxide, N,N-dimethylformamide, and N-methylpyrrolidone.

Polymer blends were successfully prepared by solvent evaporation of the blend solutions in compatible solvents. Evidence of the existence of inter-polymer charge transfer was proved by spectroscopic and electrical measurements. UV-Visible spectrometric analysis showed that there was an increase in the extent of conjugation due to partial electron transfer from the electron rich to the electron deficient polymers. This was evident from the shifting in the absorbance maxima of the blend in comparison to those of the individual polymers.

In the cyclic voltammetry of the blends and their polymers, the charge transfer was evident from the shifts in the reduction peaks of PPy-3-NO_2 in the blend towards doping potentials at more negative values. The complexed PPy-3-NO_2 was harder to be electrochemically reduced, since the charge transfer from the donor polymers reduces the electronic effect of the electron-withdrawing group present on the PPy-3-NO_2 backbone.

Electron spin resonance data further demonstrate evidence of charge transfer, since the spin concentrations for the blends were significantly higher than those of the constituent polymers. These results are complementary to those of cyclic voltammetric analysis, since the higher spin blends come from polymers with less negative doping potentials for PPy-3-NO_2.

Electrical conductivity measurement was carried out on the polymers and their blends, and this analysis revealed that blending the individual polymers together increased the conductivity in comparison to those of the unmixed polymers. This increase was at least two orders of magnitude in each case.

Conductivities were measured as a function of temperature, to determine the activation energies for charge transfer. For complexes of PPy-3-NO_2 with the three electron-rich polymers, the activation energies were in the sequence P2 > PEDOT > PEDOT-C_6, as expected from the oxidation potentials for these polymers. This confirms the inter-polymer nature of the doping process.

However, the extrapolated high-temperature conductivity (σ_∞) of the B2 blend was far the highest of the three (about 72S.m^{-1}) which implies an enormously higher carrier mobility in this case; this is likely to be due to the 98% regio-regularity of the P2 polymer, and its very high molecular mass

7.1 Future Work

The polymers and blends were found to be relatively amorphous; hence no x-ray diffraction data have been presented. Since the polymers are linear and thermally stable, future work should pursue the effects of methods such as thermal annealing, in order to increase the crystallinity. This would not only aid the structural characterisation of the solid polymers, but would probably increase both the charge-transfer and the mobility of the charge carriers.

Extending studies of electrical conductivity to ultra low temperatures (liquid Helium) could be seriously considered as a suggestion for future improvement to this research. This is to investigate any possible transitions to superconductivity in the doped / insulating state at temperatures close to absolute zero.

The optoelectronic properties could also be studied. These are likely to be of interest for the 'Blend 2' because the carrier mobility is expected to be high, trap concentrations low and ohmic contacts relatively easy to achieve at the electrodes (e.g. for blends in which the

charge-transfer is only slight, the photoconductivity and its dependence on light intensity will be measured). Photo-induced interchain charge-transfer may play an important role in the photoconductivity.

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9 Appendixes

9.1 Appendix I – Publications

Synthesis of Novel Donor-Acceptor Polymer Blends and their Properties

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Key Words

Intrinsically Conducting polymers (ICP), Polythiophenes, Poly (3-Nitropyridine) (PPyr-3-NO_2), Dopant Free Conducting Polymers.

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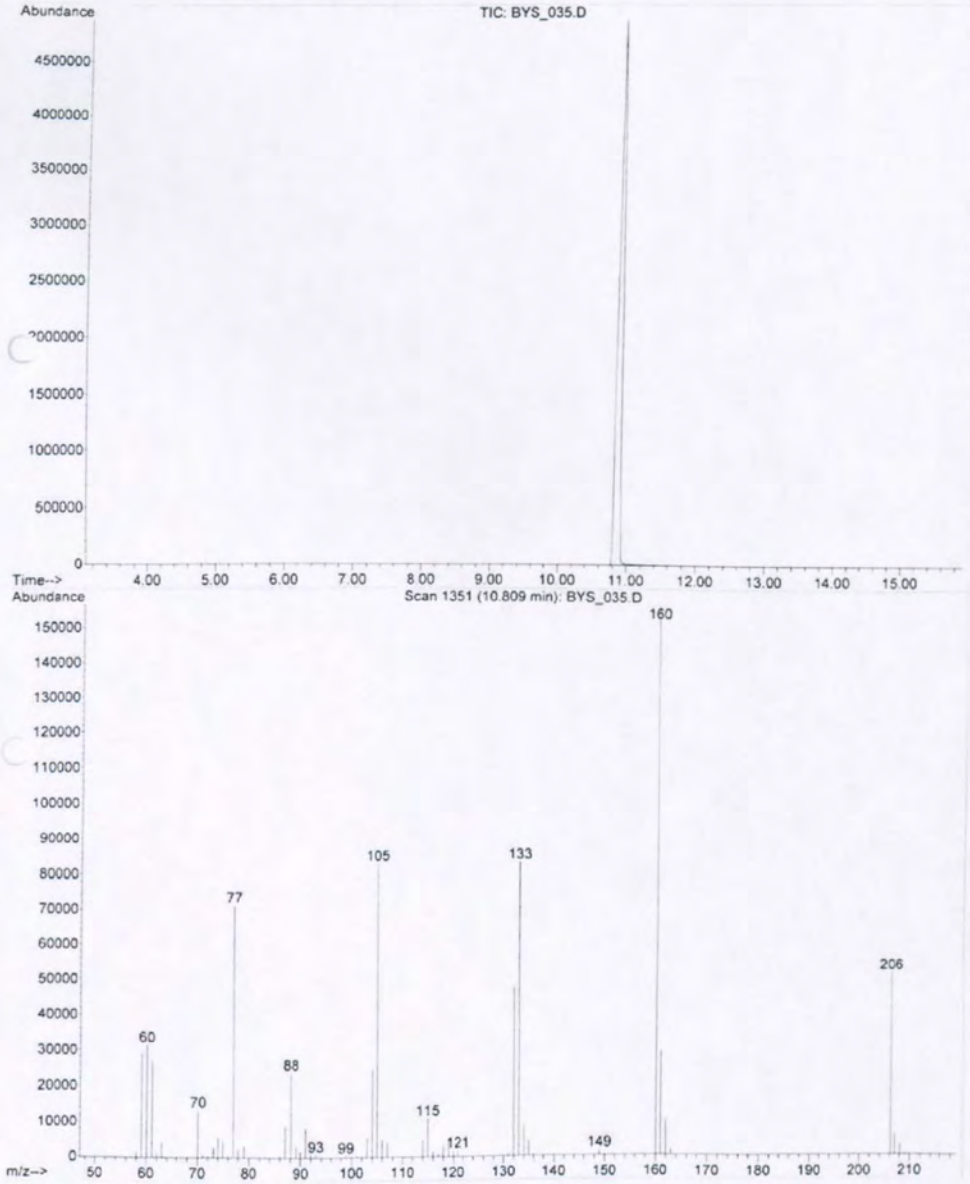
9.2 Appendix II – GC-MS Analysis

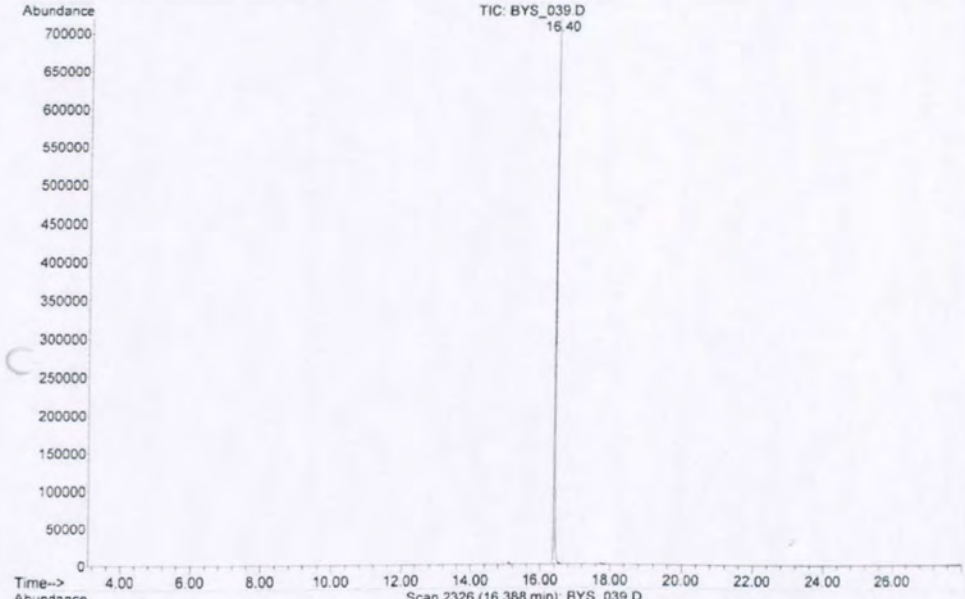
9.2.1 EDOT-C_6 Stage I

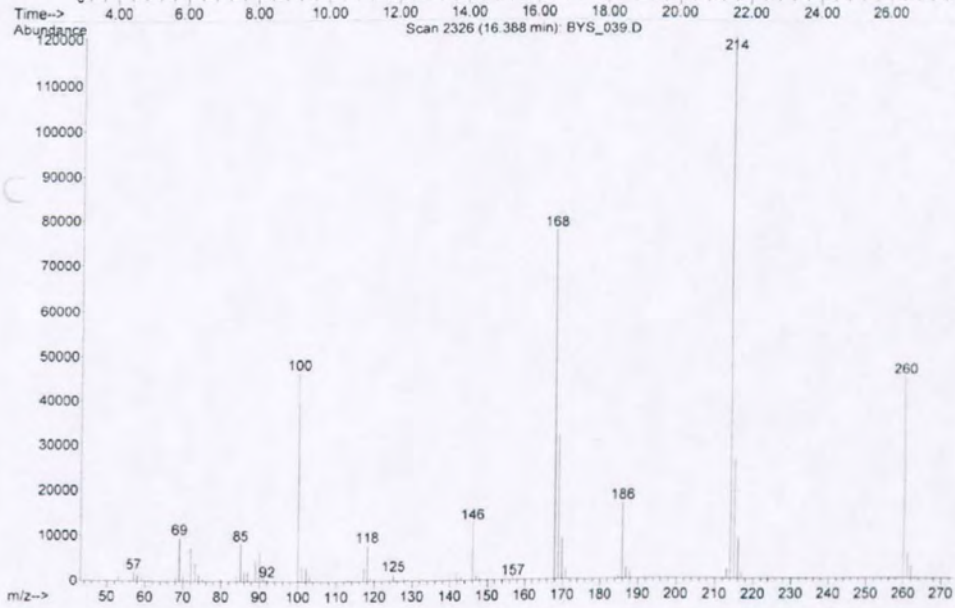
```
File        :C:\MSDCHEM\1\DATA\Snapshot\BYS_035.D
Operator    : Bassem Sabagh
Acquired    : 22 Nov 2005  18:51     using AcqMethod DEFAULT.M
Instrument :    Instrument #1
Sample Name: Diethylthiodiglycolate
Misc Info   : Distilled
Vial Number: 1
```



9.2.2 EDOT-C_6 Stage III

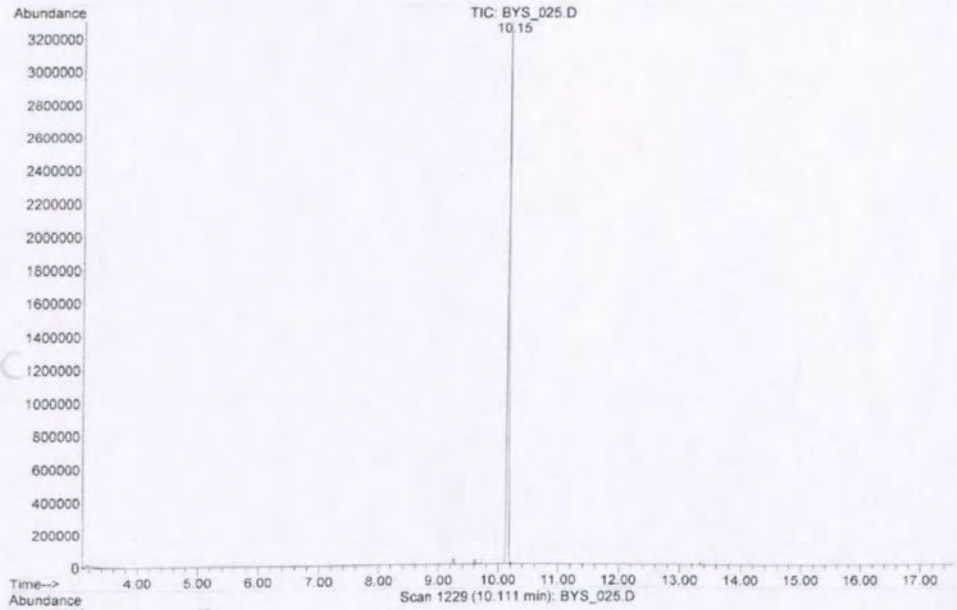
```
File        :C:\MSDChem\1\DATA\BYS_039.D
Operator    : Bassem Sabagh
Acquired    : 30 Nov 2005  16:22      using AcqMethod DEFAULT.M
Instrument :    Instrument #1
Sample Name: 3,4-dihydroxythiophene diethyl ester
Misc Info   : Dried
Vial Number: 1
```

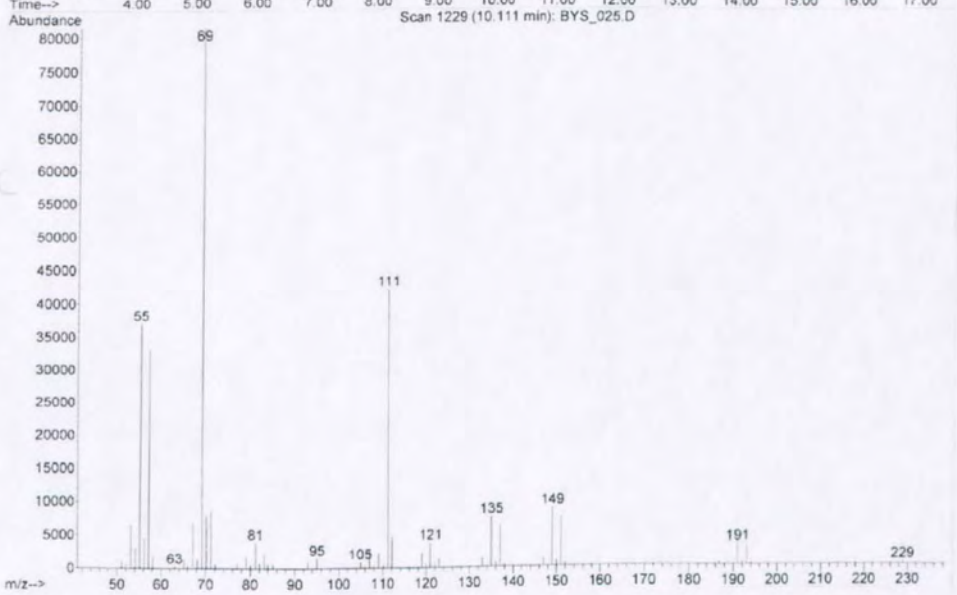




9.2.3 EDOT-C_6 1,2-DibromoOctane

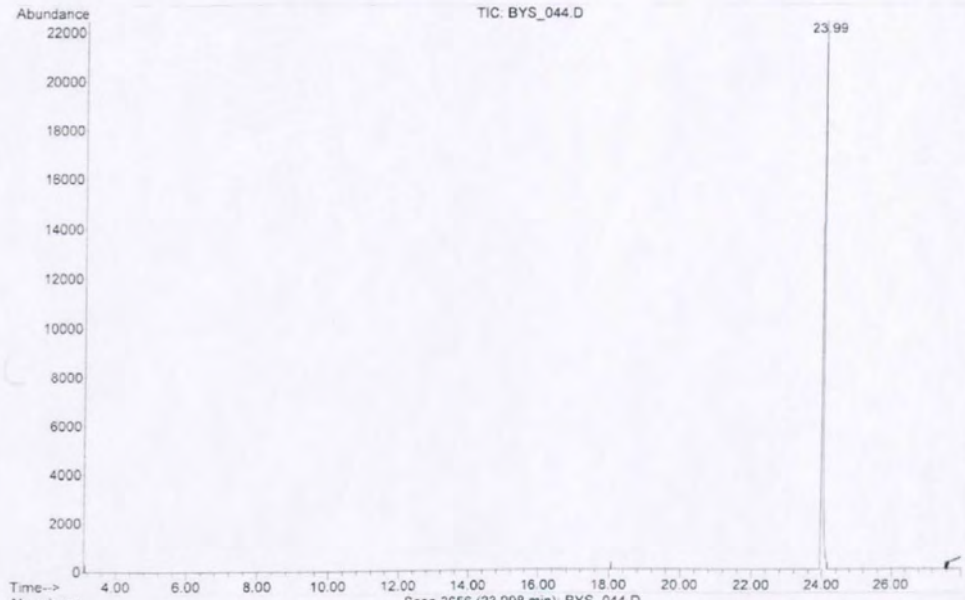
```
File        :C:\MSDCHEM\1\DATA\Snapshot\BYS_025.D
Operator    : Bassem Sabagh
Acquired    : 15 Jul 2005  15:40      using AcqMethod DEFAULT.M
Instrument :    Instrument #1
Sample Name: 1,2-dibromo Octane
Misc Info  : Pure, Redistilled
Vial Number: 1
```

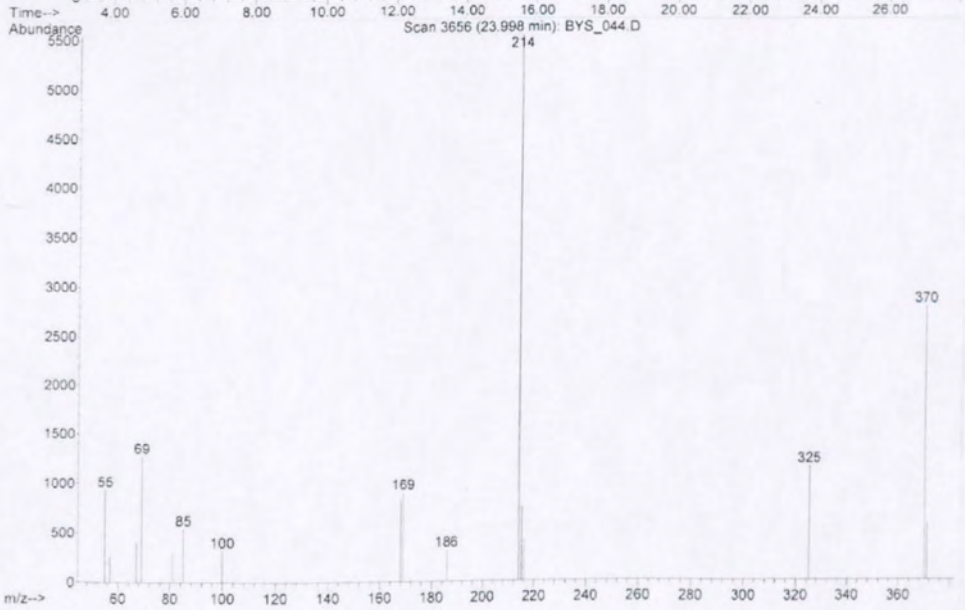




9.2.4 EDOT-C_6 Stage V

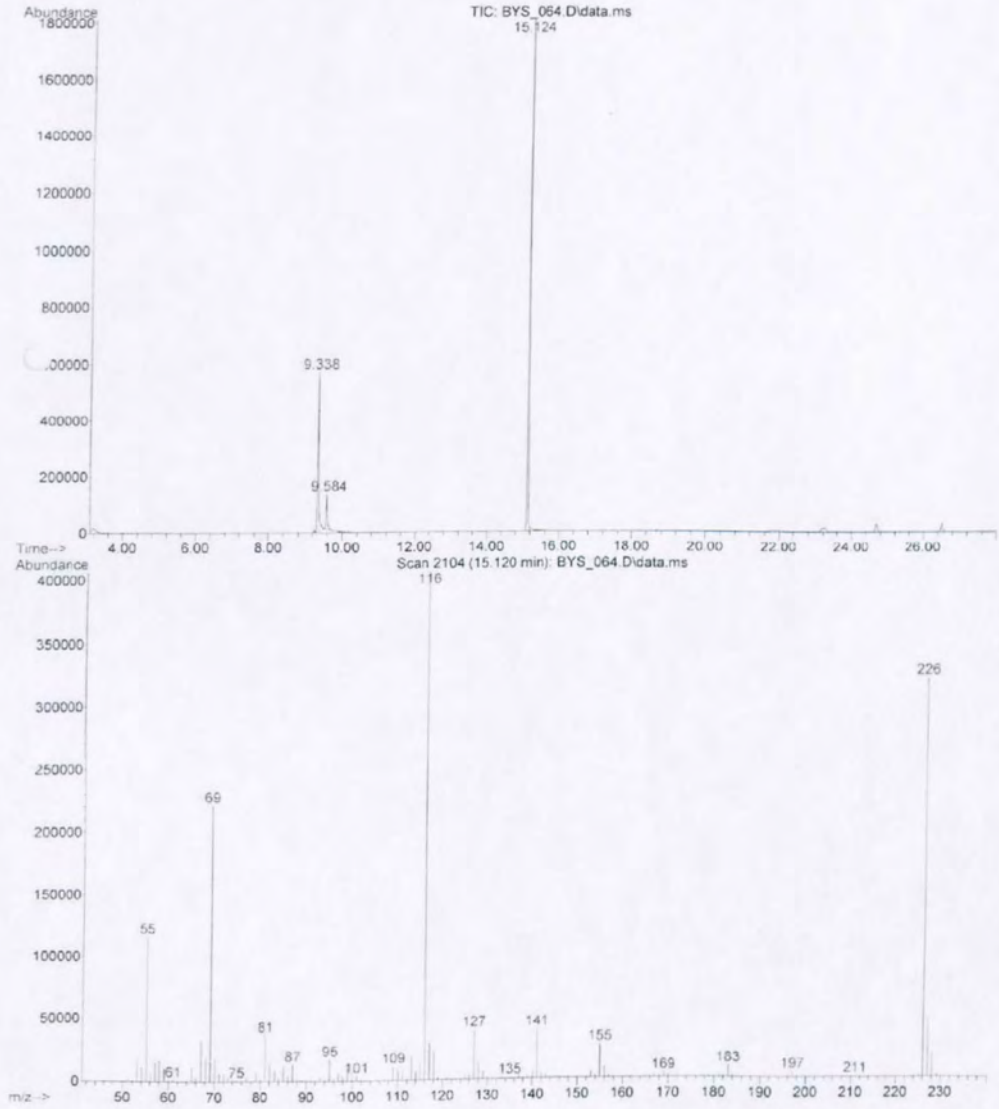
```
File       :C:\MSDChem\1\DATA\BSB\BYS_044.D
Operator   : Bassem Sabagh
Acquired   : 15 Dec 2005  14:41     using AcqMethod DEFAULT.M
Instrument :    Instrument #1
Sample Name: EDOT-C6 Diethyl Ester
Misc Info  :
Vial Number: 1
```





9.2.6 EDOT-C_6 Stage VIII

```
File        :C:\MSDChem\1\DATA\BYS_064.D
Operator    : Bassem Sabagh
Acquired    : 18 Apr 2006  12:07     using AcqMethod DEFAULT.M
Instrument :     Instrument 1
Sample Name: EDOT-C6
Misc Info  : Repurified
Vial Number: 1
```



9.2.7 2,5-dibromo-3-nitropyridine

```
File       :C:\Documents and Settings\Administrator\Desktop\DECONVOLUTION
            \BYS_029.D
Operator   : Bassem Sabagh
Instrument :    Instrument #1
Acquired   : 17 Oct 2005  17:09     using AcqMethod DEFAULT.M
Sample Name: 2,5-dibromo-3-nitropyridine
Misc Info  :
```