Probing physical and spectroscopic properties of electrochromic conjugated polymers, copolymers and layered structures

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Probing Physical and Spectroscopic Properties of Electrochromic Conjugated Polymers, Copolymers and Layered Structures

by

Emma L. Smith

A doctoral thesis submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy of Loughborough University

May 2007

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For awarding the neutron beam time, I thank the ILL, France and the CCLRC, Oxford and the instrument scientists involved in the experiments: Dr. Robert Cubbitt (D17, ILL), Dr. John Webster (SURF, CCLRC), and Dr. Robert Dalgliesh (CRISP, CCLRC). I also thank NCESS, Daresbury for the awarded XPS time, and Dr Graham Beamson who is in charge of the ESCA 300 at Daresbury.

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Finally, my thanks to my parents, John and Val, for their unwavering support and encouragement throughout all my studies, whether my mood was of elation or despair.
Abstract

This work details the properties of a copolymer system comprising the ethylenedioxythiophene (EDOT) and bithiophene (BT) monomers. By applying a number of characterisation techniques to various aspects of the copolymer system an insight into its behaviour during redox cycling has been gained.

If a copolymer is grown from a feed solution containing two different monomers, the mole fraction of monomers in the resulting copolymer will be determined by the composition of the feed solution and the relative reactivities of the two monomers. Only a small range of feed solutions yield copolymers containing substantial amounts of both components, except for pairs of monomers having very similar reactivities. X-ray Photoelectron Spectroscopy (XPS) was introduced as a technique to determine the mole fraction of monomers within a copolymer film and compared with the mole fraction of the feed solution. BT and EDOT were found to have very similar reactivities, allowing the fabrication of copolymers with a desired composition from a prescribed binary mixture of BT and EDOT monomers. Spectroelectrochemical characterisation revealed a quasi-linear trend relating the ratio of BT and EDOT in the copolymer and the $\lambda_{\text{max}}$ value of the undoped copolymers, allowing the $\lambda_{\text{max}}$ value to be predicted from the copolymer ratio and vice versa.

Neutron Reflectivity (NR) and the Electrochemical Quartz Crystal Microbalance (EQCM) were used to probe the physical changes in thickness, solvent population and ion movements of the EDOT homopolymer as a consequence of redox cycling. Potential dependent NR measurements revealed that the solvent volume of the PEDOT film was ~40% in all redox states. This high solvation for both the reduced and fully oxidised states of the film, may have allowed the easy movement of the ions required to maintain electroneutrality during redox cycling, without the need for structural reorganisation, or expansion of the film. The ion transfer reactions in an acoustically thin film of PEDOT were examined using EQCM, by monitoring the mass changes accompanying doping/dedoping. A reversible exchange of anions and solvent was observed during redox cycling. Variation of the scan rate facilitated the exploration of the kinetic effect. The number of solvent molecules that were
associated with this anion movement did not vary with the size of the anion, but was scan rate dependent.

A method was developed to obtain simultaneous spatial and temporal resolution of individual components within polymer films. The challenge was to establish counterion and solvent population changes as functions of time and distance within a redox switching film, on a time-scale of seconds. To collect real time data on a redox switching film required a time resolution improvement of 2-3 orders of magnitude on established techniques. This was accomplished by using boxcar integration during continuous potential cycling to produce the first dynamic in situ electrochemical NR measurements, with an effective time-scale of ca. 2s. The improved time resolution produced individual species profiles at buried interfaces subject to time-variant electrochemical control, providing new insights into transient population distributions.

A copolymer of EDOT and BT with a mole fraction of 0.5 was compared with the combinatorial properties of layered structures of EDOT and BT in order to gain insight into how structure affected the properties of the film. NR was employed to create a depth profile of the systems revealing that the two bilayers were found to have different structures. However, the observed optical properties and the behaviour of the mobile species within the layered structures did not differ during redox cycling. The copolymer film did exhibit different electrochemical properties from those of the layered structures, suggesting that the same combinatorial properties desired in a copolymer cannot be reproduced in layered structures

Thin films of electrochemically deposited polymers bearing functional groups are commonly being used to create complex devices with sensing applications. It has been established that activated ester groups, bound to the backbone of a polymer matrix, act as versatile substrates for a wide variety of nucleophilic functional groups. The distribution of chelated ions in polymer bound crown ether systems was probed by studying a system based on a copolymer of bithiophene with an amino 15-crown-5 functionalised pyrrole. A dramatic change in solvation occurred on functionalisation with the 15-crown-5 species. It was unusual that the immobilised 15-crown-5 moieties caused an expulsion of solvent from the polymer matrix, instead of a physical swelling of the matrix, to accommodate the crown groups in a highly
solvated environment. This relationship between the expulsion of solvent and the mechanical robustness of the polymer film has important implications for how conducting polymers are used in practical devices.

It was demonstrated that NR can give useful insights into the depth profile of a polymer and the changes in solvent volume fractions that can occur in a copolymer matrix during redox cycling, or after functionalisation of the polymer backbone with a nucleophilic group.
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<tr>
<td>ACN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BT</td>
<td>2,2’-Bithiophene</td>
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<tr>
<td>CA</td>
<td>Chronoamperometry</td>
</tr>
<tr>
<td>CE</td>
<td>Counter Electrode</td>
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<tr>
<td>CSA</td>
<td>Camphor Sulfonic Acid</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
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<tr>
<td>d-ACN</td>
<td>Deuterated Acetonitrile</td>
</tr>
<tr>
<td>E(CE)$_n$</td>
<td>Electrochemical(Chemical Electrochemical)$_n$</td>
</tr>
<tr>
<td>EC</td>
<td>Electrochromic</td>
</tr>
<tr>
<td>ECD’s</td>
<td>Electrochromic Devices</td>
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<tr>
<td>EDOT</td>
<td>Ethylenedioxythiophene (2,3-Dihydrothieno[3,4-b]-1,4-dioxin)</td>
</tr>
<tr>
<td>EQCM</td>
<td>Electrochemical Quartz Crystal Microbalance</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron Spin Resonance</td>
</tr>
<tr>
<td>h-ACN</td>
<td>Hydrogenous Acetonitrile</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>ILL</td>
<td>Institut Laue Langevin</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium-Tin Oxide</td>
</tr>
<tr>
<td>LCD’s</td>
<td>Liquid-Crystal Displays</td>
</tr>
<tr>
<td>LED’s</td>
<td>Light Emitting Diodes</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MPTS</td>
<td>(3-mercaptopropyl)-trimethoxysilane</td>
</tr>
<tr>
<td>NCESS</td>
<td>National Centre for Electron Spectroscopy and Surface Analysis</td>
</tr>
<tr>
<td>NR</td>
<td>Neutron Reflectivity</td>
</tr>
<tr>
<td>OT</td>
<td>3-Octylthiophene</td>
</tr>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
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<tr>
<td>PATs</td>
<td>Poly(3-alkyl-thiophenes)</td>
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<tr>
<td>PEDOT</td>
<td>Poly(ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PFP</td>
<td>Pentfluorophenol Activated Ester of Pyrrole-N-propionic Acid</td>
</tr>
<tr>
<td>PProDOT</td>
<td>Poly(3,4-propylene dioxythiophene)</td>
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<tr>
<td>PProDOT-Me$_2$</td>
<td>Poly(dimethyl 3,4-propylene dioxythiophene)</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(styrene sulfonate)</td>
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<tr>
<td>PVF</td>
<td>Polyvinylferrocene</td>
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<tr>
<td>RAL</td>
<td>Rutherford Appleton Laboratory</td>
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<tr>
<td>RE</td>
<td>Reference Electrode</td>
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<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
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<tr>
<td>TBAP</td>
<td>Tetrabutylammonium perchlorate</td>
</tr>
<tr>
<td>TBAPF$_6$</td>
<td>Tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>TEAP</td>
<td>Tetraethylammonium perchlorate</td>
</tr>
<tr>
<td>TOF</td>
<td>Time-of-Flight</td>
</tr>
<tr>
<td>TT</td>
<td>2,2':5'2-Terthiophene</td>
</tr>
<tr>
<td>WE</td>
<td>Working Electrode</td>
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<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
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Introduction

1.1 Electrochromism

An electrochromic material can be defined as one that exhibits a reversible and visible change in transmittance and/or reflectance, as the result of either electrochemical oxidation or reduction\(^1\). Redox processes in electrochromic conjugated polymers are accompanied by ion insertion/expulsion. These changes modify the electronic properties of the polymer, altering the band gap and therefore, the colour of the material.

There are three classes of electrochromic materials\(^3\). In all three types, the redox transition is carried out at a solid electrode in contact with a liquid electrolyte: type I materials are soluble in the reduced and oxidised (redox) states, type II materials are soluble in one redox state, but form a solid film on the surface of an electrode after electron transfer, type III materials are solids in both redox states, such as electrochromic polymers. Types II and III require no further charge injection once the redox state has been switched in order to retain the new electrochromic state. These systems are said to have ‘optical memory’. Therefore, types II and III could potentially be used to make stable electrochromic devices, ECDs. Yet, for a type I electrochromic material, the soluble electrochemically-generated product diffuses away from the electrode and in a device it is necessary to keep the current flowing until the whole solution has been oxidised.

A large number of chemical species exhibit electrochromic properties\(^3\), including metal coordination complexes (both in solution and as polymer films)\(^4,5\), metal oxides\(^3,6\), viologens\(^3,5\) and conjugated polymers\(^3,5,7,8\), such as polypyrrole, polythiophene and polyaniline. The electrochromic properties of conjugated polymers are the focus of this thesis.
There are three possible modes of controlling the colour of electrochromic conjugated polymers:

i) by substituting the repeat unit of the polymer and using the induced steric and electronic effects

ii) by copolymerisation of distinct monomers leading to a combination of the properties observed in the corresponding homopolymers

iii) by combining the electrochromic properties of several systems using blends, laminates and composites.

Even though many types of materials exhibit electrochromism, only those with certain characteristics are useful in commercial applications. Most applications for electrochromic materials require a high contrast ratio, colouration efficiency, cycle life, and good write-erase efficiency. Electrochemical techniques such as cyclic voltammetry (CV), chronocoulometry and chronoamperometry (CA), combined with in situ spectroscopic measurements, are used for characterisation.

Recent commercial applications of electrochromic materials include anti-glare car rear-view mirrors, battery state-of-charge indicators and sunglasses. Possible applications are ‘smart windows’, re-usable labels, protective eyewear, controllable aircraft canopies, devices for frozen food monitoring, camouflage materials, spacecraft thermal control and controllable light-reflective or light-transmissive devices for optical information storage.

1.2 Conjugated Electrochromic Polymers

Chemical or electrochemical oxidation of many resonance-stabilised aromatic molecules such as pyrrole, thiophene, aniline, furan, carbazole and indole, leads to the formation of electronically conjugated polymers. Conjugated polymers are finding uses in electronic applications, particularly π-conjugated oligomers, which play an important role in organic-based transistors and integrated circuits, photo-voltaic devices and organic-based light emitting devices.
Resonance (ESR) measurements have been used to show that both neutral and fully
doped conjugated polymers possess no net electronic spin, while partially doped
materials were paramagnetic. In the 1980s the concept of polarons, bipolarons and
solitons was developed to explain these observations together with the charge
transport\textsuperscript{29,30} and optical properties\textsuperscript{30,31,32,33} of conjugated polymers. The nature of the
unusual charge bearing species, and the excited states of conjugated systems, has been
the subject of a sustained research effort since then\textsuperscript{29,31,32}. The explanation of the
systems is complicated by the presence of electron-electron interactions, and the
strong connection between, and mutual influence of, the electronic and geometric
structures.

1.2.1 Electronic Structure. In conjugated polymers there is a continuous
network of adjacent unsaturated carbon atoms, \textit{i.e.} carbon atoms in the sp\textsuperscript{2} hybridised
state (see Figure 1.1) Each of these sp\textsuperscript{2} C-atoms has three \(\sigma\)-bonds, and a remaining
\(p_z\) atomic orbital which is involved in \(\pi\)-overlap with the \(p_z\)-orbitals of the nearest sp\textsuperscript{2}
hybridised C-atom. This chain of atoms with \(\pi\)-overlap of the \(p_z\)-orbitals causes the
formation of a delocalised \(\pi\)-electron system along the polymer chain. Conjugation
leads to a high density of states in both the HOMO and LUMO energy levels. This is
similar to the band gap, \(E_g\), of conventional inorganic semi-conductors and can have a
range of values (~1-4 eV)\textsuperscript{34}.

![Figure 1.1](image_url) The structure of polythiophene and the conversion of benzenoid geometry to the quinoid geometry.

The main properties of the delocalised \(\pi\)-electron system are that the polymer chains
can be easily oxidised or reduced. This is usually through charge transfer with
molecular dopant species where the carrier mobilities are large enough, that in the
doped state, there are high electrical conductivities. In addition to the covalent
framework of the linear polymer chain, the separate polymer strands interact via Van
der Waals forces.

1.2.2 Charge Carriers. Charge carrying species in conjugated polymer
systems can be described not as free electrons or holes, but quasi-particles, which can
move relatively freely through the material. In contrast with inorganic semi­
conductor materials, the structure of the charge carrier is dependent on several
extrinsic factors such as the ionic state and population. The charge bearing species
are “self localised”, as the presence of electronic charges leads to local changes in the
atomic lattice, which in turn leads to localised changes in the electronic structure.
Associated with these species are localised electronic states with energy levels within
the otherwise forbidden electron energy gap, $E_g$.

In the special case of polyacetylene, an interchange of the carbon-carbon single and
double bonds reproduces an identical structure, forming only one resonance structure.
Therefore, it is said to have a “degenerate ground-state” system. This geometric
symmetry influences the nature of the self-localised charge bearing species, known as
solitons. In the remainder of the conjugated polymers, such as polythiophene, a
simple alternation of carbon-carbon single and double bonds does not reproduce the
same ground-state geometric configuration, but produces a higher-energy geometric
configuration. As a result, these polymer systems are said to have a “non­
degenerate ground-state” system (i.e. they do not possess two equivalent resonance
structures, see Figure 1.1). This also changes the type of charge bearing species that
will occur in these polymer chains.

If excess electrons are added to any conjugated polymer chain, they lead to new
electronic states within the otherwise forbidden electron energy gap, as portrayed in
Figure 1.2 for a “non-degenerate ground-state” system. The very first electrons
added to any conjugated polymer chain form singly charged polarons, which can be
detected using ESR. A polaron is a radical-ion in association with a local
geometry relaxation. Polarons are self-localised states as shown in Figure 1.2. As
more electrons are added to the polymer chain, the mobile polarons can pair up and
form either solitons or bipolarons. In the case of polyacetylene, which has a “degenerate ground-state” system, the pairing up of polarons leads to spinless, single charged solitons. However, in non-degenerate ground-state conjugated polymers, the polarons pair up to form spinless, doubly charged bipolarons. A bipolaron is a di-ion, around which a strong localised lattice relaxation occurs.

![Energy Level Scheme](image)

**Figure 1.2** An energy level scheme of the self-localised states in conjugated polymers (A) band edges of neutral polymer, (B) polaron state formed upon the addition of an extra electron, and (C) spinless bipolaron state formed upon the addition of a second electron, which also corresponds to the combination of two polarons (adapted from ref. 34)

Electrons can be added to polymer chains in several ways. In the case of non-degenerate ground-state conjugated polymers, total energy estimates indicate that two extra electrons may go either into two independent singly charged polarons or one spinless, doubly charged bipolaron.

When a non-degenerate ground-state conjugated polymer has electrons donated to it during doping, the very first electron added must go into a polaron state (as there are no other electrons in the vicinity available for pairing). At higher doping levels, the addition of one or more electrons, results in the combination of polarons into bipolarons, if in that system, the bipolaron state is energetically favourable over two independent polarons (see Figure 1.3).
Figure 1.3 An idealised diagram of the interaction of two polarons to form a bipolaron.\textsuperscript{34}

The electronic structure of bipolarons was modelled in the early 1980's\textsuperscript{32,35} and has been studied more recently\textsuperscript{37,38}. The pattern of alternating single- and double-bonds in a non-degenerate ground-state polymer chain will change with the addition of two charges (see Figure 1.4). These changes in bond alternation pattern will occur slowly as a function of distance along the bipolaron. In moving from the left to the right side of a bipolaron, a variation would be seen from completely aromatic-like on the left to a more-or-less quinoid-like structure in the centre of the bipolaron and back to an aromatic like structure on the right. In the simple diagram in Figure 1.4 the electrons are shown as point charges, at the two idealised extremes of the geometrically altered portion of the chain. Coulomb repulsion tends to separate the two like-charges. However, by moving the isolated charges further away from one another, the bonding pattern must change from aromatic-like to quinoid-like, in order to satisfy valence requirements at each carbon atom all along the chain. The quinoid structure is a higher energy configuration, losing elastic energy to form from the aromatic structure. Therefore, separation of the two electrons is at the expense of mechanical (strain) energy, but saves in Coulomb repulsion energy, until a balance is achieved, determining the size of the bipolaron\textsuperscript{29,32}.

Figure 1.4 The pattern of alternating single and double bonds in polythiophene, after two charges have been added.\textsuperscript{34}
In practice, doping of a conjugated polymer is carried out by exposing it to oxidising or reducing agents. The insulating neutral polymer is converted into an ionic complex of a polymeric cation (or anion), and a counterion that is the reduced form of the oxidising agent (or the oxidised form of the reducing agent). The electrochemical oxidation or doping of the polymer corresponds to the transfer of one charge from the electrode to the polymer, followed by the migration of this charge using a hopping mechanism to the film-electrolyte interface. Anions present in the solution must then migrate inside the polymer to maintain electroneutrality. This process is repeated until all the electroactive sites are oxidised. The use of an oxidising agent is known as p-type doping, and a reducing agent n-type doping. However, the stability of the negatively charged polymer state is to some extent limited and n-doping is generally more difficult to achieve.

It is possible to tune the electronic properties of the polymer through control of its doping level. Changes in the doping level result in different charge carrying moieties i.e. polarons and bipolarons. Polarons carry a magnetic moment and can therefore be distinguished from diamagnetic bipolarons by ESR spectroscopy. However, at intermediate doping levels, bipolarons and polarons both exist and interact with each other, therefore the spectroscopic response of polarons are influenced by bipolarons as well as other paramagnetic species that may be present in the polymer material.

1.2.3 Conductivity. Polymer chain length is correlated with conductivity up to a number of repeat units where chain hopping then becomes more significant. Conductivity is influenced by both movement of charge carriers along the chains and hopping between chains (for a comparison of the conductivity of a conducting polymer with metals, semi-conductors and insulators see Figure 1.5). The behaviour of counterions plays an important role in the energetics and localisation of polarons or bipolarons on the polymer chain, though the mechanistic details are not clear. This is of particular importance in the stabilisation of doubly charged excited states (bipolarons), as it can screen out the repulsive Coulomb interaction between the two electronic charges on the polymer chain.
All conjugated polymers are potentially electrochromic in thin-film form since redox switching allows new optical absorption bands, along with the simultaneous transport of electrons and counter ions in the polymer matrix. The colour change between doped and undoped states of the polymer depends on the size of the bandgap in the undoped polymer. Thin films of conjugated polymers with an $E_g$ greater than 3 eV (~400 nm) are transparent or slightly coloured in the undoped form, in the doped form they are normally highly absorbent in the visible region.

1.2.4 Electrochromic Devices (ECDs) with Conjugated Polymers as the Electrochromic Layer. An Electrochromic Device (ECD) can be described as an electrochemical cell, where optical changes occur upon electrochemical reactions of two or more redox-active materials, separated by an ionic conducting layer. Electrochromic switching of these devices is limited by diffusion of ions from one
layer to another\(^4\). ECDs based on inorganic electrochromes are generally limited by charge or mass transfer rates and tend to exhibit slow switching times (multiple seconds), compared to alternative technologies such as liquid-crystal displays (LCDs), where optical changes occur through rapid alignment of molecules under an applied electric field\(^4\). However, LCDs depend on the viewing angle, are costly to process, and multiple colours cannot be obtained without the addition of dyes\(^4\).

The attempt to make faster, more stable and higher contrast ECDs has resulted in the increased number of patents and research papers, especially after the introduction of conjugated polymers as electrochromic materials. By careful selection of the electrochromic materials and novel ECD designs, electrochromic switching rates of 1-10 Hz can be obtained\(^4\). The long-term stability issues that were often a major drawback for polymer ECDs have now been overcome by the introduction of air-stable polymers, novel polymer systems\(^43^,44^,45^,46^,47\) (such as blends, copolymers, composites, laminates etc), polymer electrolytes\(^48^,49^,50\), and ionic liquids\(^51\). The availability of many solution-processible polymers has helped in the fabrication of large-area ECDs\(^23^,25\). Adapting the currently available patterning methods, microstructured ECDs have been developed\(^18\).

The colour of an ECD should be uniform and even. Patchiness is often caused by inhomogeneity of the electrochromic material, which may be improved by deposition methods\(^8\). Intensity gradation is also very common, caused by unevenness of the applied electric field or current density across the surface of the substrate, producing more intense colouration at the edges of the electrode. A highly conductive supporting material ensures a more even potential distribution and hence a more uniform appearance\(^3\).

Electrochromic devices can be evaluated using the following criteria:

i) **The Colouration Efficiency** is obtained by determining the injected/ejected charge as a function of the electrode area, and the change in optical density during a redox step of the device. Conformational changes occurring along the polymer backbone during doping are also important. As a result, measuring the colouration efficiency is difficult\(^52\).
ii) The Write-erase Efficiency: is defined as the percentage of the original colouration that can be electro-bleached, and is expressed as a ratio of absorbance changes. For display purposes, the efficiency should be close to 100%.

iii) The Response Time is the time it takes an ECD to completely colour from its bleached state. If ECDs are to be used as optical switches or in television screens, very fast response times are needed. The use of semi conducting ITO in transparent conducting electrodes limits the response times because of its only moderate conductivity. The switching speed of electrochromic materials is dependent on several factors such as the ionic conductivity of the electrolyte, accessibility of the ions to the electroactive site (ion diffusion in thin films), magnitude of the applied potential, film thickness and morphology of the thin film. Today, subsecond switching rates are easily obtained using polymers and composites containing small organic electrochromes. However, response times cannot be confidently compared, as there has been no consistency in the criteria used to determine them. It can either be the time necessary for a fraction of the colour to form; or the time for all, or part of the charge to be injected.

iv) The Cycle Life: is a measure of stability, and is the number of cycles possible before failure. An ECD can be destroyed when it is continually cycled between its coloured and bleached states, due to physical changes in solid phases or from chemical side reactions. A major aim in device fabrication is to optimise cycle life.

An absorption/transmission-type ECD (Figure 1.6a) operates by reversible switching of an EC material between a coloured (absorptive) and a transmissive (bleached) state on a transparent, conducting substrate. To achieve high contrast values, two complementary polymers are used, one electrochromic layer is in its reduced form, while the other is oxidised, i.e. one is anodically colouring and the other is cathodically colouring.
A simple dual polymer ECD comprises of a cathodically colouring polymer and an anodically colouring polymer deposited onto transparent electrodes (e.g. ITO/glass, ITO/PET or PEDOT-PSS/PET), and separated by an electrolyte (viscous gel or solid) to allow ion transport as shown in Figure 1.6b\textsuperscript{40}.

![Diagram of an ECD sandwich cell with cathodically and anodically colouring polymers](image)

**Figure 1.6** (a) Schematic representation of an absorption/transmission-type device\textsuperscript{40}. (b) Schematic diagram of a dual polymer ECD sandwich cell with complementary cathodically and anodically colouring polymers\textsuperscript{14}.

The anodically colouring polymer should ideally have a high band gap ($E_g \geq 3$eV) with $\pi$ to $\pi^*$ electronic transitions extending from the high-energy end of the visible spectrum into the ultraviolet region. In its reduced form, the polymer should be transmissive to a large portion of the visible spectrum. On oxidation, charge carrier absorptions are induced in the visible region, resulting in an opaque and/or coloured state (see the solid line in Figure 1.7).
For the cathodically colouring polymer, a complementary low band gap polymer is selected, which should be coloured and/or opaque in the neutral state. If upon oxidation, depletion of the absorption in the visible region causes the material to become transmissive and lightly coloured, the material is cathodically colouring (see the dotted line in Figure 1.7)\textsuperscript{14}. In device fabrication, both polymers are sandwiched together with one polymer doped while the other is neutral, so that when an external voltage is applied the device switches between the transmissive and absorptive state. This type of design has been used in applications such as optical shutters.

![Bleached State](image1.png)  
**Figure 1.7** Schematic representation of the visible spectra for both an anodically and cathodically colouring polymer demonstrating the concept of dual polymer ECDs for absorptive/transmissive windows\textsuperscript{15}.

Dual polymers ECDs often have different electrochemical potential windows and environmental requirements. If two electrochromic materials have quite different electrochemical windows for operation, the applied voltage to produce 100% of the optical contrast increases. Electrochromic materials that operate at low applied potentials allow longer device lifetimes, as high applied potentials are degenerative to the electrochromic film, the ITO layer, the electrolyte, and the interfacial chemistry

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between each of these materials. To maintain charge balance within the ECD, the oxidation process of the anodic electrochromic material should coincide with the reduction process of the cathodic electrochromic material\textsuperscript{13,14}.

Conjugated polymers have been used in several types of absorptive/transmissive ECD systems as anodically and/or cathodically colouring materials. Polyaniline (PANI) was commonly used as a complementary electrode with metal oxide electrochromic layers such as WO\textsubscript{3}\textsuperscript{53,54}. More recently, Tung and Ho used a PEDOT/Prussian Blue couple to fabricate ECDs\textsuperscript{55}.

ECDs with all polymer electrochromes have been widely studied in the literature. Using ITO-coated plastic substrates, many complementarily coloured polymers have been combined to obtain flexible polymer-based ECDs\textsuperscript{56,43}. DeLongchamp and Hammond have used the layer-by-layer assembly method to deposit soluble EC polymers electrostatically onto ITO electrodes and have fabricated complementary ECDs by pairing PEDOT and PANI\textsuperscript{43}. The layer-by-layer electrostatic adsorption of a sulfonated derivative of PEDOT has been investigated by the Reynolds group. The multilayer thin films exhibit a fast and reversible redox switching behaviour in aqueous media\textsuperscript{44}.

Two examples of all-polymer ECDs (where the ITO coating on the substrate has been replaced with a conducting polymer) have also been reported by the Reynolds group\textsuperscript{57}. The ITO layer has been replaced by highly conducting PEDOT-PSS to achieve all-polymer ECDs. They constructed the ECDs using different complementary pairs of EC polymers on PEDOT-PSS-coated transparent plastic electrodes, demonstrating that PEDOT-PSS is a possible replacement for ITO\textsuperscript{57}.

Electrochromism is not limited to visible colour changes, but can encompass materials that exhibit radiation modulation in the near-infrared, mid-infrared and microwave regions\textsuperscript{58,59}. This has spurred the development of ECDs that can operate at longer wavelengths, beyond the visible region, with long lifetimes and fast redox switching times. Polymer-based devices comprising polyaniline-camphor sulfonic acid (PANI-CSA) as the active EC material have been used for thermal emissivity control in the near-IR and mid-IR regions\textsuperscript{60,61}. PEDOT's IR electrochromism has been studied by
Pages et al. in broad-band ECD’s using porous gold electrodes, where they optimised the pore size and gold thickness for reflectance analysis\textsuperscript{62}.

The Reynolds group has constructed a reflective device by electrochemically synthesising poly(dimethylpropylene dioxythiophene), (PProDOT-Me\textsubscript{2}) as the surface active EC polymer onto a slitted gold-coated Mylar substrate to allow for ion transport between the polymer film and a counter electrode hidden beneath\textsuperscript{63}. The structure of the device is shown in Figure 1.8. As the film is switched from its coloured state to its bleached state, a colour change of the ECD from absorptive blue to reflective gold takes place, but it has a slow switching speed (t = 3s).

![Diagram of ECD device](image)

**Figure 1.8** Side-view schematic diagram of a dual polymer ECD for surface reflectivity control in both the visible and IR regions of the electromagnetic spectrum\textsuperscript{63}.

Later, the Reynolds group used a device design, initially developed by Bennet and Chandrasekhar\textsuperscript{64,65} (illustrated in Figure 1.9), that incorporated a highly porous metallised membrane which switched rapidly. Using this design with PEDOT, poly(propylene dioxythiophene), (PProDOT), or PProDOT-Me\textsubscript{2} as the active conducting polymer, switching times of 0.1-0.2s were obtained. During the redox switching process, the charge-carrying ions easily migrate from the polymer through the thin porous membrane, giving a small distance between electrodes\textsuperscript{66}.  

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1.3 Polythiophenes

Among all the conjugated polymers, polythiophenes are of interest to both academia and industry as electrochromic materials because the chemical synthesis of functionalised monomers is generally straightforward and the electrochemical polymerisation facile. Also the resultant polymers tend to be stable in a range of operational environments and can be solution processable. A large number of substituted polythiophenes has been synthesised, leading to an assortment of properties. Numerous novel polythiophenes have been studied, with particular interest in poly(3-substituted thiophene) and poly(3,4-disubstituted thiophenes).

1.3.1 Synthesis and Properties of Conjugated Polythiophenes. Preparation of conjugated polymers by anodic electropolymerisation is convenient for a variety of reasons: the doped conjugated polymer is directly grafted onto the electrode surface,
the film thickness is easily controlled by the deposition charge, and it is possible to perform an *in situ* characterisation of the growing process, or of the polymer, using electrochemical or spectroscopic techniques\(^9,21,70,71\).

During electropolymerisation, the charged species precursors must initially be produced by oxidation of the neutral monomer at the anode surface. Because of this, further electrochemical and chemical reactions are possible. In the first electrochemical step the monomer is oxidised to its radical cation (see Figure 1.10). As the electron transfer mechanism is much faster than the diffusion of the monomer from the bulk solution, a high concentration of radicals is maintained near the electrode surface.

![Figure 1.10 Electrochemical polymerisation mechanism](image)

In the second step, two radicals are coupled to produce a dihydro dimer dication. This produces a dimer after loss of two protons and rearomatisation (the driving force of the reaction). The oxidation potential of the dimer is less anodic than that of its parent monomer (because of resonance stabilisation), consequently the radical cation of the dimer is immediately formed, this undergoes further coupling reactions.

Electropolymerisation proceeds through successive electrochemical and chemical steps in accordance to a general E(CE)_n scheme, until the oligomer becomes insoluble
in the electrolyte and precipitates on the electrode surface. However, there are still several unanswered questions regarding the nature of the rate-limiting step, the exact role of the oligomers in the initial deposition step, and the growth of the polymer chains.

The electropolymerisation of thiophene and its derivatives involves many experimental variables. The conditions of electrosynthesis determine, to a large extent, the structure and properties of the resulting polymer. Some of the most important are listed below:

i) the solvent of the electrolyte medium,
ii) the temperature,
iii) the anode material,
iv) the electrochemical methodology,
v) the monomer concentration.

The solvent of the electrolytic medium must have a high dielectric constant to ensure the ionic conductivity, and be electrochemically resistant against decomposition at the high potentials required to oxidise the thiophene ring. The most conductive polythiophenes have been prepared in anhydrous aprotic solvents, with high dielectric constant and low nucleophilicity such as acetonitrile, benzonitrile, nitrobenzene, and propylene carbonate. Anhydrous solvents are used to prevent defects in the film caused by water. Polythiophenes are normally electrogenerated in the presence of small anions, derived from strong acids such as ClO₄⁻, PF₆⁻, BF₄⁻, and AsF₆⁻. The nature of the anion strongly affects the morphology and electrochemical properties of polythiophenes. The temperature of electropolymerisation has been reported to affect the extent of the conjugated system and hence the optical and electrical properties of the polymer. The films produced at 40°C have a shorter mean conjugation length than those prepared at 5°C.

The anode material is critical since the physicochemical properties of its surface determine the nature, and the strength of the interaction between the polymer and the electrode, which can affect both the polymerisation process and the properties of the resulting polymer. Polythiophenes are normally grown on noble metals such as
platinum\textsuperscript{79} and gold\textsuperscript{86}, or on optically transparent electrodes such as tin oxide or ITO coated glass\textsuperscript{87}.

The electrochemical methodology has a considerable effect on the structure and properties of electrogenerated polythiophenes. Polythiophenes have been deposited in potentiostatic\textsuperscript{41} or galvanostatic\textsuperscript{88} conditions, and by repetitive potential sweeps\textsuperscript{89}, or current pulses\textsuperscript{90}. The most homogeneous and conducting films are generally obtained in galvanostatic conditions\textsuperscript{88}, at potentials approximately 0.5V more positive than the onset potential of the monomer oxidation. An initial overpotential allows the instantaneous creation of a larger number of nucleation sites. This improves the compactness and thus the conductivity of the polymer. In addition to the effects on the electrical, optical and electrochemical properties of the films, electrical conditions have been shown to affect the orientation of the polymer chains, and the mechanical properties of polythiophenes.

High monomer concentrations (0.5-1M) give loose, poorly conducting films containing significant amounts of soluble oligomers\textsuperscript{91}. The decrease of monomer concentration improves both the adhesion of the films and their conductivity. The degradation of the polymer may compete with its electrodeposition, especially at highly anodic potentials, or when the monomer concentration in the medium becomes too low to sustain the rate of polymer deposition, which is imposed by the applied electrical conditions\textsuperscript{92}.

Thin polymeric films of thiophene are blue ($\lambda_{\text{max}} = 730$ nm) in the doped (oxidised) state and red ($\lambda_{\text{max}} = 470$ nm) in the undoped form. However, the electropolymerisation of 3-methyl thiophene has been studied more than the parent thiophene, due to its lower oxidation potential\textsuperscript{81,82,83,84,85,93,94}. In order to preserve the electronic, optical and electrochemical properties during functional substitution, the electronic properties of the parent monomer must be substantially preserved, as electronic effects alter the electron density of the thiophene ring, and therefore its reactivity.
Tailoring the structure of polythiophenes allows the synthesis of conducting and electroactive polymers with a broad range of electronic properties. The electronic character of the polymer can be varied by the nature of the repeat unit, and by attachment of electron withdrawing and donating groups. Steric interactions can be used to control the extent of conjugation. The distortion of the conjugated backbone caused by steric interactions between substituents grafted on adjacent monomers, decreases the overlap between the \( \pi \) orbitals on consecutive rings, and shortens the effective mean conjugation length. As the molecule is no longer planar, the ionisation potential increases and the maximum conductivity after doping drops (see Figure 1.11a & b).

Adding substituents yields changes in the polymers absorption characteristics and ultimately its colour in its neutral form. Subtle modifications to the monomer can greatly alter the spectroscopic properties. For example, depending on the relative positions of the methyl groups along the backbone of poly(3-methylthiophene), the colour varies from pale blue, blue and violet in the oxidised form, to purple, yellow,
red and orange in the reduced form. It is believed that the reason for the colour change is differences in the effective conjugation length of the polymer chain.  

Colour change modulation is difficult in conjugated polymers because the chromophore is large, delocalised and unstructured. Ferraris et al. have attempted to define the conjugation length of the electrochrome in the polymer backbone by introducing a silicon atom into the polythiophene backbone, to limit the conjugation length and the effects of potential dπ-pπ conjugation. The electron donating nature of the silicon also results in a lower oxidation potential that helps electropolymerisation and could enhance the stability of the oxidised state. Furthermore, the silicon atom allows the attachment of various substituents without modifying the polymer’s electronic structure.

Poly(3-alkyl-thiophenes) (PATs) were first synthesised in 1986, and have been the subject of intense research activity because of the improvement in solubility and fusibility, resulting from the inclusion of flexible hydrocarbon chains on the conjugated polythiophene backbone. As a consequence of steric interactions, the conductivity of these systems decreases with the length of the alkyl chain, nevertheless, it remains higher than many other polymers. Because conducting polymers have a rigid conjugated backbone and strong interchain interactions, they are generally insoluble. Nevertheless, polymers that are soluble in common organic solvents can be produced by grafting long alkyl chains onto polythiophene. PATs with alkyl groups of butyl or larger are readily soluble at room temperature, and can then be processed into films from their solutions. However, further research on electrogenerated PATs has shown that solubility, conjugation and conductivity depend strongly on the applied electrical conditions, and dependence increases with the length of the alkyl chain.

The grafting of alkyl chains onto polythiophene also modifies the morphology, and the electrochemical and optical properties of the conjugated backbone. Increasing the alkyl chain length to 7-9 carbons extends the mean conjugation length, and increases the electrochemical reversibility. This higher reversibility is attributed to the faster thermal undoping observed on PATs. Different models for the structure of PATs have been proposed; either planar chains with alternating “up and down” thiophene
rings\textsuperscript{101}, or alternation occurring after every two monomers i.e. "up-up-down-down"\textsuperscript{102}. Experimental and theoretical work suggests a helical chain structure with a \textit{syn} conformation for electrogenerated polymers\textsuperscript{103}. Study of the effects of steric factors is provided by the electronic properties of polythiophenes with 3,4-dialky1 substituents. In principle, disubstitution at the 3,4 positions should produce stereoregular polymers. However, steric interactions between substituents cause decreases in polymer conjugation length. Poly(3,4-dialky1thiophenes) often suffer from severe steric interactions that cause adjacent rings to twist out of plane resulting in polymers that have higher oxidation potentials, higher optical bandgaps, and lower conductivities compared to poly(3-alkylthiophenes)\textsuperscript{21}. Recently, one of the most important advances in polythiophene chemistry has come from the development of disubstituted cyclic dioxan-type ring systems.

1.3.2 Dioxythiophenes. Cyclisation of disubstituted thiophenes between the 3 and 4 positions tends to relieve steric interactions between neighbouring groups (see Figure 1.12)\textsuperscript{104,105,106,107,108}. Materials based on poly(3,4-(ethylenedioxy)thiophene) (PEDOT) have a bandgap lower than polythiophene and alkyl-substituted polythiophenes. The lone pairs of the oxygen atoms are pinned back, allowing them to interact with the \pi-system of the polymer backbone, relieving steric strain and donating electron density to the heterocycle. EDOT polymerises rapidly and efficiently, producing highly electroactive PEDOT films that adhere to normal electrode materials. PEDOT has a low oxidation potential which makes it useful in long-term electrochemical switching applications\textsuperscript{109,110}.

![Figure 1.12](image)

\textbf{Figure 1.12} The 3D model of two thiophene polymers show the relief of steric hindrance (see a), produced by cyclisation at the 3 and 4 positions (see b).
The band gap of PEDOT ($E_g = 1.6-1.7$ eV) is 0.5 eV lower than polythiophene, and it has a $\lambda_{\text{max}}$ of ca. 610 nm. Compared to other substituted polythiophenes, it has excellent stability in the doped state because of its more ordered polymeric backbone, associated with high conductivity. Doped PEDOT is almost transparent in the visible region (with a sky-blue tint) and the neutral polymer is deep blue. The transparent state of PEDOT could make it extremely useful in commercial application such as smart windows. The spectroelectrochemical series for PEDOT shows a very strong near-IR and mid-IR absorption, that tails strongly into the visible region as the polymer becomes conducting. As PEDOT and its alkyl derivatives are ‘cathodically-colouring’ electrochromic materials, they can be used with ‘anodically-colouring’ conjugated polymers in dual polymer electrochromic devices, ECDs\textsuperscript{111,112}

The anodic part of the PEDOT voltammogram (shown in Figure 1.13, curve a) is similar to most polythiophenes. A broad oxidation peak is observed at 0V followed by a current plateau and two cathodic peaks at -0.05 and -0.65 V on the reverse scan. Although the properties of the p-doped and neutral PEDOT polymer are well known, the properties of the n-doped material have not been well documented. Ahonen et al have tried to determine the properties of PEDOT in the reduced state\textsuperscript{113} The cathodic branch of the voltammogram (Figure 1.13, curve b), exhibits increasing cathodic currents during the downward sweep after a small shoulder at -2.2 V and a single anodic peak at -2.05 V on the return sweep. Whenever the potential sweep was extended to the opposite side of the voltammogram, sharp prepeaks on the anodic and cathodic branch were observed at -0.5 V and -1.8 V.

Ahonen attributes this to charge trapping, where charge domains are embedded within the matrix of the insulating film\textsuperscript{113}. The reduced polymer is fairly unstable even in dry conditions in an inert atmosphere. This hinders the use of n-doped PEDOT in practical applications. The maximum n-conductivity the group attained was ca 1% of the maximum p-conductivity.
Figure 1.13 Steady-state voltammograms of a PEDOT film on Pt electrode in 0.2 M TBAPF$_6$ + acetonitrile (H$_2$O < 4 ppm) Scan rate 100 mV/s (a) the anodic region (dash), (b) fifth cycle to the cathodic region (dash-dot), and (c) the wide potential range (solid)$^{113}$

The Bayer AG research labs in Germany were the first to develop PEDOT as an easily oxidised and stable conducting polymer$^{114,115}$. Water soluble polyelectrolyte (poly(styrene sulfonate), PSS) can be incorporated into PEDOT during polymerisation, using Na$_2$S$_2$O$_8$ as the oxidising agent, producing the commercially available PEDOT PSS (BAYTRON P) which forms a dispersion in water (see Figure 1.14).

Figure 1.14 PEDOT/PSS blend (BAYTRON P)$^{109}$. 

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The PSS' anion in the complex has two functions. Firstly, it acts as the charge balancing counter ion. Secondly, it keeps the PEDOT dispersed in the aqueous medium. Although the resulting PEDOT-PSS complex is not truly water soluble, it forms a stable, easy-to-process, deep blue microdispersion. As the PEDOT units formed during polymerisation are quite short, and the complex seems to be of high stability, it is believed that the structural model for PEDOT-PSS can be drawn as in Figure 1.15. In this model the oligomeric PEDOT chains are tightly attached to the PSS' having a much higher molecular weight. For PEDOT-PSS to have a high conductivity, the polythiophene chains must have a stacked arrangement, similar to the stacks with monomeric counterions depicted in Figure 1.15. As a consequence, a loosely crosslinked and highly swollen polymer gel network is developed, forming gel particles. These particles consist of approximately 90 to 95% water.

![PEDOT stacks](image-url)

**Figure 1.15** PEDOT stacks, $a =$ counter ion-dependent layer distance between stacks$^{116}$. The particles of PEDOT-PSS have excellent film-forming properties and are easy to process, which led to the use of PEDOT-PSS as a commercial material$^{117}$. PEDOT-PSS can be spin-coated onto a working electrode and electrochemically oxidised or reduced. During the reduction process, counterions (such as lithium) intercalate into the PEDOT-PSS in order to compensate for the negative charges of the $SO_3^-$ groups on the PSS polyanions. These counter ions migrate from the polymer at a certain speed, thus limiting the switching speed of the film. The EDOT monomer (3,4-(ethylenedioxy)thiophene) is also available commercially from Bayer.
Inganas and co-workers have studied the electronic structure of PEDOT by X-ray and ultraviolet photoelectron spectroscopy. Three forms of PEDOT were investigated: neutral PEDOT, PEDOT doped with the large PSS anion, and PEDOT doped with the small tosylate (p-methyl benzyl sulfonate), TsO⁻ anion. They have concluded that the polymer is stable at elevated temperatures and have observed the creation of new states upon doping. They believe the PSS⁻ anions protect the polymer, retaining a more conjugated PEDOT at the metal/polymer interface, improving the characteristics of polymer LED's shown by the material.

Lapkowski et al have undertaken a study of the ESR spectroelectrochemistry of EDOT. The aim of their research was to attempt to understand the interactions of different charge carriers to determine the bulk properties of PEDOT. This group found that during electrochemical oxidation, the concentration of paramagnetic species increases sharply, indicating the formation of polarons during oxidative doping. The type of mutual interactions of paramagnetic species also changes, indicating a transition from highly mobile groups of spin to less mobile and weaker interacting ones. Their results suggest that reduction is a stepwise process, which could be related to the movement of counterbalancing anions out of the polymer film.

Many substituted EDOT monomers have been synthesised leading to a range of variable bandgap PEDOT-based materials. By increasing the size of the alkenedioxy ring, and by increasing the number and size of the substituents on the ring, the electrochromic properties, including switching times and contrast ratios are enhanced. Using a series of oxidatively polymerisable bis-arylene EDOT monomers, polymers with high energy bandgaps ranging from 1.4-2.5 eV have been prepared. In the neutral form, a full range of colours is available from blue through to purple, red, orange, green and yellow.

Electroactive conjugated polymers have been synthesised by electropolymerisation of EDOT derivatives containing hydroxymethyl and polyether substituents. In addition to a slight decrease of the redox potential of the polymer, the grafting of the hydroxymethyl group significantly improves the ability of the monomer to electropolymerise in water, and the electroactivity of the resulting polymer in aqueous
media. The introduction of a polyether chain produces a significant increase in the effective conjugation length\textsuperscript{127}.

1.4 *Thin Film Polymer Sensors of Metal Ions*

Specialised, modified polymer electrodes have been developed for sensor applications in a wide variety of fields, such as biological and chemical analysis, detecting chiral molecules, and environmental contaminants in the form of vapours, gases, temperature, light etc. There is a large interest in fabricating polymers with crown ether substituents attached, where the sensing mode is electrochemical, gravimetric, electrochromic or luminescent.

The production of redox-active molecular receptors capable of sensing charged substrates and reporting their presence by an electrochemical response is an area of current interest\textsuperscript{128,129}. The electrochemical recognition of a guest by a guest binding site in close proximity to a redox active moiety requires that the guest binding site and the redox active group can communicate\textsuperscript{130,131}. Selective binding of a particular guest species coupled with an electrochemical response is of extreme importance for future potential prototypes of new amperometric molecular sensory devices\textsuperscript{132}.

Studies in the area of electrochemical molecular recognition involve bifunctional receptor molecules that contain both binding sites and redox-active centres whose electron transfer reaction is coupled to the receptor's complexation. Receptors designed to electrochemically recognise guest molecules must couple the complexation process to the redox reaction, i.e. the two reactions must mutually influence each other. Electron insertion (reduction) or withdrawal (oxidation) from a host molecule will change the stability constant of the complex formed, causing a change in the host's redox potential. The magnitude and the direction of the potential change will depend primarily on the reaction coupling mechanism and the properties of the complexed guest molecule\textsuperscript{133}.

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The electrochemical molecular recognition process should cause a large shift in the redox potential of the host species. Coupling has been obtained through one or a combination of the following five pathways:

i) Space electrostatic interaction between the redox centre(s) and the complexed guest molecule\(^{134}\)

ii) Bond communication normally provided by conjugated chemical bond linkage between the redox centre(s) and the binding cavity\(^{135}\)

iii) Direct coordination bond formation between the redox centre and the complexed guest molecule\(^{136}\)

iv) Conformational induced perturbation of the redox centre(s) caused by the complexation of a guest molecule\(^{137}\)

v) Interference by the guest species in communication between two redox-active centres\(^{138}\)

1.4.1 Electrochemical Recognition of Cations and Anions. Redox-active receptors for cations are either oxidisable and hence form less stable complexes with cations (e.g. ferrocene containing receptors); or reducible forming more stable complexes with cations (e.g. quinone, anthraquinone and nitroaromatic containing species)\(^{133}\). Cyclic voltammetry (CV), square wave voltammetry (SWV)\(^{139}\) and rotating disk techniques have been used to monitor perturbations in the electrochemical behaviour of redox-active receptor species. In all cases an anodic shift of the redox-process should be observed, as the positively charge cation-receptor complex will be harder to oxidise, than the neutral receptor alone.

The electrochemical recognition of anionic species is more difficult\(^{140}\). This is because of the lower charge to radius ratios, pH sensitivities and range of geometries of anions. In the chemical industry anions are used in many chemical reactions acting as nucleophiles (CN\(^{-}\)), bases (OR) and redox active centres (S\(_2\)O\(_8^{2-}\)). The environmental impact of anionic pollutants such as excess nitrates from agricultural fertilisers leads to eutrophication of rivers. However, specific ligands that have the capability to optically and/or electrochemically detect anions are rare. Electrochemical receptors for anions are expected to have cathodic shifts in their
redox-process when complexed to an anion as they are either easier to oxidise, or harder to reduce than the free redox-active receptor\textsuperscript{133}.

1.4.2 Functionalised Conducting Polymers as Redox-Active Molecular Receptors. Functionalised conducting polymers with recognition properties towards ions, molecules and biological species have recently caused growing interest, due to their large potential as molecular sensors\textsuperscript{141}. The conductivity and electrochemical and optical responses of functionalised conducting polymers can be influenced by the complexation of metal ions because of electrostatic and/or conformational perturbations of the conjugated backbone\textsuperscript{142}. Making functionalised polymers is not simple, and requires the costly synthesis of the corresponding functionalised monomers, whose polymerisation is controlled by steric and electronic effects originating from the functional group\textsuperscript{21}.

Selective host-guest interactions in combination with conducting polymers may be exploited in electronic devices where the complexation/decomplexation process allows an externally induced switching between ON/OFF states. Due to the stronger ion-dipole interactions with metal cations, crown-ether functionalised materials are particularly interesting for these applications, as it has been shown that it is possible to display a change in chemical information as a change of an electrical signal\textsuperscript{142}.

Garnier et al have proposed an alternative method for the functionalisation of a conjugated polymer. This involves the direct substitution of a precursor polymer film, containing a leaving group, such as an activated ester. When sufficiently labile, this ester group can be further substituted by a desired amine bearing group, through a homogenous-heterogenous reaction\textsuperscript{143}. They were able to substitute their polymer material with an amine bearing derivative (such as aminomethyl 18-crown-6) by soaking the supported film in a solution of acetonitrile or water, which contained a determined concentration of the amine groups. The electrochemical properties of the film, in acetonitrile with NBu\textsubscript{4}ClO\textsubscript{4} show a reversible voltammogram with a symmetrical redox peak at an anodic potential of 0.22V.

The electrochemical selectivity of a poly[pyrrole 18-crown-6] film towards the alkaline cations Li\textsuperscript{+}, Na\textsuperscript{+} and K\textsuperscript{+} was analysed by Korri-Youssoufi et al. In the
presence of Na\(^+\) or K\(^+\) instead of NB\(_4\) or Li\(^+\), a clear change in the films voltammetric behaviour appears. The anodic wave shifts from 0.22V (SCE) towards 0.4V (SCE) (see Figure 1.16). The same behaviour was observed for directly electropolymerised substituted crown ether polypyrroles\(^{144}\) and polythiophenes\(^{145}\), highlighting the selective response toward alkaline cations.

Figure 1.16 Voltammograms of poly[py18C6] analysed in ACN containing either 0.1 mol\(^-1\) NB\(_4\)ClO\(_4\) or LiClO\(_4\) (solid line), and 0.1 mol\(^-1\) NaClO\(_4\) (dashed line)\(^{143}\)

Scheib and Bäuerle electrochemically characterised a group of crown ether-oligoether- substituted bithiophenes and found an irreversible oxidation wave of the bithiophene unit in the cyclic voltammogram (CV). It was shown that even though each monomer in the series had the same electroactive bithiophene unit, the various functionalised bithiophenes had different tendencies to polymerise. Complexation of cations to the crown ether-substituted conducting polymers led to strong changes in their electrochemical behaviour. They were able to unequivocally prove that a host-guest-interaction occurring at a remote molecular recognising group affects changes in the electronic properties of the conjugated backbone\(^{142}\).

1.5 Project Aims

Conjugated polymers have generated a great deal of interest because they are relatively easy to prepare, either by electrochemical (anodic) deposition, or by spin coating of soluble systems. They also undergo a variety of colour changes that are a function of the doping level of the conjugated material. The nature of a heterocyclic
polymer precursor makes it possible to alter the electrochromic properties of the polymer by fine-tuning of the chemical functionality. These materials can also be copolymerised with other conjugated polymer systems to make hybrid materials.

This project focussed on the properties of polymers derived from the EDOT monomer, both as a homopolymer and as copolymers, where these are formed by anodic copolymerisation from mixtures of EDOT and a chosen thiophene monomer. EDOT was of interest because of the unusual blue to transparent colour change it undergoes during redox cycling. Here the properties of the EDOT containing copolymers have been investigated as a function of composition. It was important that the polymerisation reaction rates of EDOT and the other thiophene monomer that comprises the copolymer system were very similar. This was essential because control of the composition of the film was desired, in order to produce a variety of copolymer ratios that undergo a range of colour changes.

The copolymer film compositions of a variety of thiophene monomers combined in different ratios with EDOT had to be analysed to ascertain a system that would allow a range of copolymer films to be polymerised. It was decided that X-Ray Photoelectron Spectroscopy (XPS) would be employed to establish the mole ratio of EDOT within the copolymer films. After carrying out trial experiments using different thiophene monomers it was found that EDOT and BT had very similar reactivity ratios. Once a system in which a range of copolymer ratios could be achieved had been identified, the aim was to correlate the absorbance characteristics of the electrochromic polymers and copolymers with dopant level and electrochemical potential. Spectroelectrochemistry was employed to quantify the colour change of the copolymer.

The emphasis of this project then became the influence of polymer structure and composition upon the electrochromic response of the EDOT/BT copolymer system. In order to address this, homopolymer, copolymer and layered systems containing EDOT and BT, were studied. In addition, the interfacial/internal structure, together with charge/mass transfer and solvent dynamics of the doped and undoped materials, have been investigated using a variety of characterisation techniques, including X-ray Photoelectron Spectroscopy, Neutron Reflectivity, IR, UV-Vis spectroscopy and a
range of electrochemical methods (including Electrochemical Quartz Crystal Microbalance)

The homopolymers were characterised thoroughly in order to identify the properties and responses of the individual monomer components in the copolymer films. PEDOT was studied in depth using both Neutron Reflectivity (NR) and Electrochemical Quartz Crystal Microbalance (EQCM). Potential dependent NR had to be refined in order to look at changes in the spatial distribution of mobile species within a PEDOT film, whilst it was undergoing redox transformations, allowing the distribution of ion and solvent species at different stages in the redox transformation of films to be compared. EQCM was employed to monitor the permeation of mobile species from the electrolyte solution into PEDOT polymer films. It was important to determine whether the entering group was an ion required to maintain overall electroneutrality within the film, solvent, or both.

Furthermore, the properties of bilayer systems were studied to try to establish the structure of the EDOT/BT copolymers and to investigate the possibility that combining the electrochromic behaviour of discrete polymer layers could be an alternative route to combine the properties of two monomers that had very different reactivity ratios. EQCM was identified as a suitable technique to allow a comparison of the ion and solvent movement within the copolymer films and layered structures of the two monomers. NR was employed to give a greater insight into how the structure could affect the properties of the copolymer film. It was used to create a depth profile of the bilayers, allowing the investigation of the ‘buried interface’ of the two layers.

Additionally, copolymer systems containing crown ether substituents were examined, because of the associated application of these groups in sensor applications. The distribution of chelated ions in polymer bound crown ether systems was investigated by studying a system based on a copolymer of BT and an amino 15-crown-5 functionalised pyrrole. XPS was again used to determine the mole fraction of the monomers in the copolymer film. NR was employed as a tool to investigate the polymer and solvent volume fraction profiles of the films (and related to the mole ratio of BT and PFP in the copolymer film), and to probe the distribution of chelated ions in the polymer bound crown ether system.
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Experimental Methods

This chapter describes the experimental methods employed for the growth of conjugated polymer films, along with the electrochemical and optical characterisation of these polymers. It also contains information on the characterisation techniques of X-ray Photoelectron Spectroscopy (XPS), the Electrochemical Quartz Crystal Microbalance (EQCM) and Neutron Reflectivity (NR). These methods will be frequently referred to throughout the subsequent chapters. All experiments were carried out using the conditions and methods described in this chapter, unless otherwise stated.

2.1 Chemicals and Materials

HPLC grade acetonitrile (ACN) was purchased from Aldrich and dried over alumina before use. Lithium perchlorate (LiClO₄), tetrabutylammonium perchlorate (TBAP), potassium hexafluorophosphate (KPF₆) and (3-mercaptopropyl)-trimethoxysilane (MPTS) were purchased from Aldrich and used without any further purification. Tetraethylammonium perchlorate (TEAP) was not bought commercially. The monomers 2,3-Dihydrothieno[3,4-b]-1,4-dioxin (EDOT), 2,2'-Bithiophene (BT), 2,2':5'2-Terthiophene (TT) and 3-Octyli thiophene were also purchased from Aldrich and used without any further purification. PEDOT-PSS (BAYTRON P) was obtained from Agfa Gaervert. The pentafluorophenol activated ester of pyrrole-N-propionic acid (PFP) and d₄-ethylenedioxythiophene (d₄-EDOT) (see Figure 2.1 and Appendix II) were not commercially available.

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*a* Supplied by Dr A Gidle, Glasgow University

*b* Supplied by Dr J Young and Dr G Weaver, Loughborough University
Figure 2.1 The reaction scheme for the synthesis of d₄-ethylenedioxythiophene (d₄-EDOT)

ITO coated glass slides were purchased from Delta Technologies (50 x 75 mm) and cut to the required size (30 x 10 mm) for optical characterisation of the polymers. Prior to use the slides were sonicated in acetone (15 min) followed by air drying. The 10 MHz quartz crystals were purchased from the International Crystal Manufacturing Company, Inc. Oklahoma City, OK and were AT-cut plates with gold electrodes evaporated onto both sides.

2.2 Preparation of Metal Coated Electrodes

Gold deposition was carried out on microscope slides, using a custom built gold coater based on a Balzer's Turbo vacuum system. Approximately 1000 Å (100nm) and 500 Å (50nm) of Au was deposited on microscope slides for substrates used in XPS and spectroelectrochemistry respectively. Before metallisation, the substrates were silanised to ensure the good adhesion of the gold layer (the silanisation process is described below). The electrode surface for the NR experiments was prepared by sputtering gold or platinum –220 Å (22nm) onto a polished, single crystal quartz or silicon block (10cm x 4cm x 1cm).

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* Gold deposition and silanisation of the microscope slides was carried out using equipment at the Electronics Department, Glasgow University.
* Silanisation process and subsequent Au and Pt deposition of the large area quartz and silicon blocks was carried out by Dr. A. Gidde at Glasgow University.
2.2.1 Silanisation Process. The substrates were sonicated in Decon, rinsed and then sonicated in distilled water, followed by drying with compressed air. The substrates were held at reflux in isopropanol (400 ml) containing fresh MPTS (12 ml) and distilled water (12 ml) for 15 min. They were then rinsed and sonicated in clean isopropanol and blown dry with compressed air. The reflux and rinsing processes were repeated a further two times. The slides were kept under vacuum in a clean dessicator and metalised within a day of preparing.

2.3 Film Deposition Method - Cyclic Voltammetry

Electrochemistry is the study of electron transfer reactions between electrodes and reactant molecules. Applying a potential to an electrode induces current to flow, causing exchange of electrons between the electrode and molecules in solution, altering the oxidation state of the molecule and ‘electrolysis’ occurs. The transfer of electrons can be in either direction; a molecule in solution may accept an electron from the electrode and become reduced or an electron can be removed from the molecule by the electrode oxidising the molecule.

Cyclic voltammetry (CV) was used as a technique for the growth of the electrochromic polymers and combined with other characterisation techniques to study these polymers. In CV, the current flowing at the working electrode/solution interface is monitored as a function of the applied potential, allowing both quantitative and qualitative data to be obtained. A cyclic voltammogram (see Figure 2.2) depicts the potentials at which oxidation and reduction processes occur, the potential range over which the solvent is stable, and the degree of reversibility of the electrode reaction. Repeated cycling reveals the electrochemical stability of electroactive species.

The potential range is scanned from the initial potential to the vertex potential ($E_{\text{switch}}$); initially no current is passed as the applied potential is not great enough to induce electron transfer (see Figure 2.2). As the potential is swept to more oxidising potentials, it reaches values that are capable of inducing oxidation of A to B and current starts to pass. As more positive potentials are reached, the current rises less...
quickly and eventually a maximum is reached (\(E_p^{\text{ox}}\)), after which the current drops to the diffusion controlled limit. On reaching \(E_{\text{switch}}\), the direction of the scan is reversed, reducing species B to A. A current opposite to the forward scan is seen due to the reduction. This current increases initially as a high concentration of B is in the diffuse layer and the kinetics for the conversion of B to A becomes more favourable as the potential becomes more negative. Gradually all of B in the diffusion layer is converted back to A, with the current reaching a maximum value at \(E_p^{\text{red}}\) eventually dropping to zero. Multiple cycles can take place, producing a plot of current versus potential. The oxidation and reduction peak potentials (\(E_p^{\text{ox}}\) and \(E_p^{\text{red}}\) respectively) are characteristic to the material being analysed.

![Cyclic Voltammogram (CV) for a reversible one-electron transfer reaction](image)

**Figure 2.2** Cyclic Voltammogram (CV) for a reversible one-electron transfer reaction

The peak potential and peak size in **Figure 2.2** reflect the reversibility of the A/B redox couple. In the case of the reversible one electron transfer reaction in **Figure 2.2**, the heights of the forward and reverse current peaks are of the same magnitude and are separated by a potential of approximately 59mV which is independent of scan rate. The absolute magnitude of the peak currents for both forward and reverse scan varies as the square root of the scan rate. If the potential is swept more rapidly, relatively less time is available for electrolysis and the depletion of A near the electrode decreases, resulting in a thinner diffusion layer and hence a steeper concentration gradient, resulting in a larger peak current value.
Adsorption is the interaction of species from the solution phase with the electrode surface. The species adsorbed may be the reactant, an intermediate, or the product of the electrode reaction. An electrode reaction which involves the oxidation of an adsorbed layer will produce a cyclic voltammogram with quite different characteristics to that of the oxidation of a species in solution. The difference in the voltammetry is mainly because the amount of reaction is determined by the number of sites on the electrode surface where adsorption can occur. In the example in Figure 2.3, for an ideal monolayer, the peak is symmetrical with the current density dropping to zero beyond the peak when the reactant is fully consumed, the peak current is linearly proportional to the scan rate (compared to the peak current being proportional to the square root of the scan rate when solution species are oxidised), and the separation between the forward and reverse peaks is 0 mV for a rapid electron transfer couple because diffusion plays no role in the process.

![Cyclic voltammogram for the reversible oxidation of an adsorbed layer of reactant (J = current and E = potential)](image)

In an ideal monolayer the electrode reaction is controlled only by electron transfer kinetics and not by a coupled problem of diffusion and electron transfer, therefore no peak separation is witnessed. However, in a comparatively thick conjugated polymer adsorbed onto the electrode surface, an intermediate response between an ideal monolayer and an electroactive species in solution is witnessed. Close to the electrode surface there are confined redox active species similar to a monolayer with similar characteristics, but as the film is thick there are diffusional components (counter ions) so characteristics are also observed for solution bulk species.
2.3.1 Experimental Setup. All electrochemistry was performed using an EG&G PAR model 263A potentiostat/galvanostat under computer control. A three-electrode electrochemical cell containing a gold-coated glass or ITO/glass substrate as the working electrode (WE), a platinum gauze as the counter electrode (CE), and a fixed potential silver/silver nitrate reference electrode (RE) (supplied by CH Instruments Inc. and filled with a 10mM silver nitrate/electrolyte solution, with the electrolyte being the same as used in the experiment), was used for the electrodeposition of polymer films via potentiodynamic methods (see Figure 2.4). The CE was held in another compartment separated from the main chamber by a glass frit. As electrolysis occurred at the CE, a frit was used to prevent any contaminants which may have formed, from entering the WE compartment.

![Figure 2.4 Three-electrode electrochemical cell with fixed Ag/Ag⁺ reference electrode and platinum gauze counter electrode.](image)

The polymerisation potential was set 200-250 mV positive of the foot of the wave for the monomer with the most anodic process, in order for the polymerisation reaction to proceed under diffusion control.

2.4 Characterisation Techniques

2.4.1 Spectroelectrochemistry. Spectroelectrochemistry was used to examine the optical responses of the electrochromic polymers during electrochemical doping and dedoping. Changes in absorbance were a consequence of alteration in dopant level which could be quantified by charge injection. One of the aims of this
research was to correlate absorbance changes in electrochromic polymers and copolymers with dopant level and electrochemical potential.

Measurements were carried out with a Hewlett Packard 8452A Diode Array Spectrophotometer. An *in situ* UV-Vis spectroelectrochemical solution cell was designed for the measurement of the homopolymer and copolymer films. A diagram of the one-compartment cell can be seen in Figure 2.5.

![Diagram of UV-Vis Spectroelectrochemical Cell](image)

**Figure 2.5** UV-Vis Spectroelectrochemical Cell.

The working electrode was a copolymer film which had been grown *ex-situ* (described in Section 2.4) onto a thin gold-coated glass or ITO/glass slide and then mounted in the cell. A silver wire and a platinum loop were used as reference and counter electrodes respectively. A blank gold-coated or ITO glass slide was used to obtain the reference spectrum. For the p-doping experiments, a polymer film was cycled between -0.5V and +1.0V in monomer free electrolyte solution. During cycling, *in situ* UV-Vis spectra were recorded every 15s, at a scan rate of 5 mV/s. In the n-doping experiments, the spectra were recorded every 20s, with the film cycled between +1.0 V and -2.0V.
2.4.2 X-Ray Photoelectron Spectroscopy (XPS). XPS measurements provided elemental analysis close to the exposed surface of the sample. In this thesis, the composition of copolymer films was determined using XPS. A number of copolymer films with varying compositions were grown from a solution containing a binary mixture of monomers. Monomer species with different functional groups, or longer chains, react at different rates during polymerisation. As a result, the relative proportions of monomer units in the copolymer film are often very different from that of the feed solution the polymer was grown from.

X-ray photoelectron spectrometers became commercially available in 1969 and were first used to study polymers shortly after. XPS is now the most widely used analytical technique for studying polymer surfaces. X-Ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a surface analysis technique used for obtaining chemical information regarding the surfaces of solid materials. The composition of both insulators and conductors can be easily analysed from areas of a few microns and larger. The main component parts of the spectrometer are the rotating anode X-ray source, quartz crystal monochromator, high transmission/imaging lens, hemispherical analyser and multichannel detector. The analysis is carried out by irradiating a sample with soft x-rays to ionise atoms, releasing core-level photoelectrons. The kinetic energy of the escaping photoelectrons limits the depth from which it can emerge. This gives XPS its high surface sensitivity and a sampling depth of a few nanometres. Photoelectrons are collected and analysed by the instrument to produce a spectrum of emission intensity versus electron binding energy. The binding energy of the peaks is characteristic of each element. The peak areas can be used (with appropriate sensitivity factors) to determine the composition of a material surface. The shape of each peak and the binding energy is dependent on the chemical state of the component atom. Hence, XPS can also provide chemical bonding information.

2.4.2.1 Experimental Setup. XPS measurements were performed using a Scienta ESCA 300 instrument (see Figure 2.6) at the National Centre for Electron Spectroscopy and Surface Analysis (NCESS), CCLRC Daresbury Laboratory, UK. The ESCA 300 utilises a high-power rotating anode X-ray source. This source
provides X-ray flux which, after monochromation, can be as large as an order of magnitude higher than conventional unmonochromated sources.

Monocromated Al Kα radiation was used with a take-off angle of 90°, a typical slit width of 1.1mm and a flood gun energy of 2eV (to compensate for the poorly conducting glass substrates).

Figure 2.6 The ESCA300 X-Ray Photoelectron Spectrometer at NCESS, Daresbury.

2.4.2.2 XPS Data Analysis for the EDOT/BT Copolymers. The quantitative elemental analysis of the copolymer films was carried out using data from the C (1s) and S (2p3/2) spectral regions. Before fitting was carried out, two corrections were applied to all C (1s) data:

1. Using the Analysis XPS software, a baseline correction was made with either a linear or Shirley\textsuperscript{11} background.\textsuperscript{e}

2. The binding energy of the C (1s) regions of the spectra was synchronised using the S (2p3/2) peak as a reference. The sulphur peak was used as a reference because surface aerobic contamination generally contains both C and N, but does not usually contain S.

\textsuperscript{e} In a Shirley background the intensity $I_0$ is taken as a background and subtracted from the intensity through the valence-band energy range:

$$I'_s(N) = I_s(N) - I_0$$

where the intensity in channel N after this correction is denoted by $I'_s(N)$.
Quantification of the copolymer ratio from the XPS data was carried out either from the ratio of C:S atoms, determined by integration of the S (2p) and C (1s) regions of the XPS spectrum, or by iterative curve fitting of the sample (copolymer) data using the component homopolymers as reference ("library") spectra. The data for the two homopolymers and the copolymer of interest were inserted into an Excel spreadsheet. A transform was then applied to linearly combine the two homopolymers using different mole ratio combinations that did not have the unity constraint. Consequently, the sample data represents a linear sum of the proportionate fractions of each "pure" homopolymer where that proportionate fraction is an expression of the mole fraction. Iterative curve fitting was carried out using the solver functionality of Microsoft Excel until the difference between the calculated, proportionate sum of the library spectra and the sample data reached a minimum (close to zero).

### 2.4.2.3 XPS Data Analysis for the BT/PFP Copolymer Films

The Analysis XPS software was used to subtract a linear background from the S (2p3/2) and N (1s) regions of the copolymer spectrum. The software then calculated the percentage concentration of each atom in the film. There were two sulphur atoms for each BT monomer and one nitrogen atom for each PFP monomer in the unreacted copolymer. The amount of sulphur in the copolymer was divided by two and the S/N ratio was then calculated for each of the copolymers. The S/N was then the ratio of BT and PFP within the copolymer film. In the reacted copolymer an extra nitrogen atom was added to the PFP monomer, as a result, no division of the concentration of the atoms was needed and the S/N ratio calculated was the ratio of the BT/PFP within the reacted film.

#### 2.4.3 Neutron Reflectivity (NR)

Neutron reflectivity (NR) is one of the few techniques that can probe below the surface of materials, and is sensitive to the chemical speciation. For studies at interfaces NR offers many advantages over conventional techniques as well as to X-ray reflection. It has a resolution of a fraction of a nanometre in the direction perpendicular to the electrode surface, due to the short wavelengths available (depending on momentum). As neutrons are electrically neutral, NR is a non-destructive technique that can penetrate deep into matter. Scattering interactions occur via nuclear collisions rather than through the electron density.
In a reflection experiment, a well collimated beam is brought in at a glancing angle ($\theta$) to the surface of a polymer. The intensity of the reflected beam is then measured as a function of the momentum transfer ($Q$) defined by:

$$Q = \frac{4\pi \sin \theta}{\lambda} \quad \text{(Equation 2.1)}$$

where $\lambda$ is the neutron wavelength. The variation of the reflectivity with $Q$ depends on the scattering length density profile along the normal of the interface.

The scattering length density, $N_b$, depends on the number of nuclei per unit volume, $n_j$, and their neutron scattering length, $b_j$:

$$N_b = \sum b_j n_j \quad \text{(Equation 2.2)}$$

The scattering length describes the strength and character of interaction of low-energy neutrons with individual nuclei and atomic structures. The values of scattering lengths vary irregularly from one nucleus to another, due to their strong dependence on the details of the individual nuclear interaction. A typical plot of reflectivity vs. $Q$ contains a critical edge, if there is sufficient difference in the scattering length densities of the substrate and the bulk surface of the sample (see Figure 2.7).

![Figure 2.7 A typical reflectivity plot](image-url)
The Q value corresponding to the critical edge, $Q_c$, is determined by the difference in the neutron scattering length densities on either side of the interface, $\Delta N_b$:

$$Q_c = (16\pi \Delta N_b)^{1/2} \quad \text{(Equation 2.3)}$$

Knowledge of the critical edge allows the interfacial scattering length density change to be determined. The layer thickness, $d$, can be calculated from the Q spacing of the interference fringes, which arise from reflection at the interfaces of a layer:

$$d = \frac{2\pi}{\Delta Q} \quad \text{(Equation 2.4)}$$

The amplitude of the fringes in a reflectivity profile depends on the change in scattering length density across an interface, damping of the fringes indicates diffuseness of the interface.\(^{14}\)

Neutrons can distinguish between different elements and their various isotopes through nuclear interactions, so it is possible to selectively deuterate components within the film, such as a functional group in the polymer or the solvent component, and thus modulate features in the reflectivity profile. Model fitting of the NR profiles, yield scattering length ($N_b$) profiles, which are indicative of the spatial distribution of species within the film. Comparison of these profiles for hydrogenous and deuterated systems highlights the spatial location of certain features e.g. solvent or counterions. Consequently, one of the principal contrast mechanisms involves substitution of deuterium (neutron scattering length, $+6.64 \times 10^{-15}$ m) for hydrogen (neutron scattering length, $-3.74 \times 10^{-15}$ m). In the interpretation of reflectivity data, the loss of phase information and reliance on modelling could lead to ambiguity of interpretation. However, in most cases sufficiently different measurements, with differently labelled combinations, allow analysis that is much less model dependent.

Typically, a reflectivity profile comprises interfacial reflectivity values over the momentum transfer (Q) range 0.008-0.12 Å\(^{-1}\). Fringes in the reflectivity profile can be used to determine the interfacial structure. Generally, film thickness can be calculated from the periodicity of the fringes. The rate at which the polymer and
solution fringes decay is a consequence of the roughness of the interfaces. When more than one distinct layer is present (as in a polymer on a metal electrode, for example) the measured fringe pattern corresponds to a complex mixing of the patterns arising from the individual layers. The range of film thickness that can be measured are between 250-900 Å.15

2.4.3.1 Experimental Setup The NR measurements were performed on either the D17 time-of-flight reflectometer at the Institut Laue Langevin (ILL), France, or the CRISP time-of-flight reflectometer at the ISIS facility (RAL), UK. Kinetic experiments are usually carried out in the Time-of-Flight (TOF) mode, where the scattering angle, $\theta$, is kept constant during any given measurement and all the available wavelengths in the beam are used. Typically three reflection angles are used to encompass the desired range of $Q$. The basic features of a reflection experiment are: a radiation source, a wavelength selector or chopper(s), a system of collimation, the sample and a detection system. The objective is to measure the reflectivity as a function of the wave vector perpendicular to the reflecting surface, $Q$ (see Figure 2.8)

![Figure 2.8 A side view of the instrument in TOF mode](#)

In TOF mode the time resolution of the neutron beam is determined by the phase angle between a double rotary chopper system. Since the path length of the spectrometer and the mass of the neutron are both constant, the TOF of the neutron beam is a measure of momentum and hence energy (wavelength). Between the collimation slits is a vertically focusing guide that increases the flux at the sample position, at the cost of increased vertical divergence of the beam. The slits define the beam in the horizontal direction (see Figure 2.8)
The collimation slit sizes of the instrument are chosen so that the sample is under illuminated. If a sample is over illuminated the beam covers the whole of the sample, making alignment much easier, however flux is lost. Alignment must be accurate if a sample is 'under illuminated', as the beam only covers part of the sample. The wavelength and hence the momentum transfer, Q, were measured by pulsing the incoming beam and recording the arrival time to the detector. The range of Q covered for a given θ depends on the useful wavelength range. The highest Q (and lowest reflectivity) is measured by the shortest wavelength.

For dry film NR measurements, the substrates were simply placed on the reflectometer sample mount, but for measurements of the films immersed in solvents, a solution cell was used. The sample was then roughly aligned using a laser. The detector was set at the correct specular scattering angle, and the height and angle of the sample to the beam were scanned for maximum intensity to the detector and set at the optimum value.

The solution neutron-electrochemical cell (see Figure 2.9) was of box-like construction, with the working electrode forming the top, a Teflon spacer formed the walls (with ports for solvent inlet/outlet and for counter and reference electrodes) and a glass block as the base. The effective area of the working electrode was approximately 30 cm² which was defined by the walls of the Teflon cell. The counter electrode, located next to the glass block used as a cell base, was Pt gauze. The reference electrode was a saturated calomel electrode (SCE), relative to which all potentials are quoted. All film samples were prepared outside of the electrochemical cell and then mounted face down on the Teflon spacer and secured.16

Figure 2.9 A schematic diagram of the Neutron Reflectivity cell.
2.4.3.2 Neutron data fitting procedure  Model fitting of NR profiles was performed using the Parratt32 software\textsuperscript{17}, used with the permission of the Hahn-Meitner Institut. The Parratt software was used to calculate the NR pattern on the basis of a physical model that describes the essential features of the polymer electrode assembly. This model consisted of a number of adjacent (in the plane of the electrode), non-identical layers. Each layer had parameters such as layer thickness (d/Å), scattering length density (rho/Å\(^2\)) and the roughness of the layer (sigma/Å), which described it. The minimum number of layers was chosen for the model so that it was:

(i) consistent with the data  
(ii) physically reasonable.

The model for the polymer electrode systems studied here consisted of the substrate (quartz or silicon), a thin layer for the MPTS, the metal layer (Au or Pt), the polymer and then the solution (or air for dry films). There was more than one layer for the polymer if it had marked gradations in internal structure, solvation or composition. Initial values for the thickness of the metal layer were found from Dektak\textsuperscript{TM} measurements of the film after its deposition\textsuperscript{5}. The starting point for the polymer thickness was a Dektak estimate of the dry film (taken after the neutron experiments had been performed). Neutron data is reported in Ångstrom in this thesis, following convention. Bulk Nb values for the quartz, silicon, Au, Pt, MPTS and solvent were derived from standard tables or previous experiments (see Table 2.1).

<table>
<thead>
<tr>
<th>Layer</th>
<th>Scattering Length, N(b) x 10(^{-6}) (Å(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>4.182</td>
</tr>
<tr>
<td>Silicon</td>
<td>2.07</td>
</tr>
<tr>
<td>Au</td>
<td>4.49</td>
</tr>
<tr>
<td>Pt</td>
<td>6.25</td>
</tr>
<tr>
<td>MPTS</td>
<td>3.475</td>
</tr>
<tr>
<td>h-ACN</td>
<td>1.32</td>
</tr>
<tr>
<td>d-ACN</td>
<td>4.923</td>
</tr>
</tbody>
</table>

Table 2.1 Bulk scattering length values (Institut Laue-Langevin, Neutron Data Booklet, A - J Dianoux & G Lander eds)

\textsuperscript{5} Dektak measurements were carried out by Dr. A Glidle at Glasgow University
The roughness parameter employed in the fitting routines described the shift in the $N_b$ profile at the interface between adjacent layers, which had different bulk $N_b$ values. Although this region is often only a small fraction of a particular layer, this parameter can have a significant effect on the shape of the reflectivity profile (see Figure 2.10 for the Parratt 32 interface).

![Diagram of the Parratt 32 interface](image)

**Figure 2.10** The Parratt 32 interface, depicting a NR plot and resultant profile calculated from the fitting parameters inputted.

The first region was between the substrate and the metal layer of the film electrode (including the MPTS layer). The next interfacial region was that between the polymer and the metal electrode. The final region was the polymer/solution interface (or the polymer/air interface when the film was measured dry).

In the Parratt32 program, the $\chi^2$ minimisation is implemented as a simplified one-dimensional Newton-Raphson method. This method converges quadratically into the nearest minimum. However, by selecting different combinations of parameters to be optimised, a lower minimum can be found compared to those found when all the parameters are optimised at the same time. Thus, optimisation using various combinations of parameters was performed in attempts to find the overall minimum.
If after fitting the starting model the optimised $\chi^2$ values were greater than ca. 2-3, additional polymer layers were added to see if further optimisation gave a significantly lower $\chi^2$. If additional layers were added it was important that the 'new' model film structure was consistent with other information available (e.g. spectroscopic and electrochemical assays) and model fits for the same film measured in other neutron contrasts of the same solvent system. In general, iterative model fitting was performed until $\chi^2$ values for best fit models to NR data are less than 2.15

### 2.4.4 Electrochemical Quartz Crystal Microbalance (EQCM).

Mass changes can occur at an electrode surface as oxidation and reduction take place during an electrochemical reaction. The quartz crystal microbalance utilises the piezoelectric qualities of quartz crystals to measure changes in the attached surface mass\(^{18}\). The quartz crystals used here were coated with a gold disk on both sides, one side was exposed to the solution in the electrochemical cell, while the other was exposed to air. The working electrode was the gold disk exposed to the solution in the cell. It was possible to simultaneously measure the mass and the current.

The quartz crystal measures mass using the inverse piezoelectric effect. The application of an electric field to the quartz crystal causes a shear deformation (strain) (see Figure 2.11). This arises from the realigning of dipoles in the crystal structure with the applied electric field. The application of an alternating electric field at a characteristic frequency to a quartz crystal of a known mass causes it to resonate. The quartz is cut to a thickness of \(-0.17\text{mm}\) so it will resonate at a frequency of \(10 \pm 0.05\text{ MHz}\). Depositing gold onto the quartz crystal shifts the resonant frequency and when the crystal is placed in solution in a cell, the resonance is dampened by viscous loss. Deposition of a mass to this gold surface will further shift this frequency.

![Figure 2.11](image-url)
Experimentally, the change in the mass of the ‘electrode’ (substrate along with attached film(s) and electrolyte) causes a change in resonant frequency ($\Delta f$) of the quartz crystal oscillator from its fundamental value ($f_0$). A change $\Delta M$, in the attached mass gives rise to a shift of resonant frequency to a lower value described by the Sauerbrey equation\(^\text{19}\) (provided that the attached mass layer is rigid), see \textbf{Equation 2.5}:

$$\Delta f = -\frac{2f_0^2}{\rho
u} \Delta M \quad \text{(Equation 2.5)}$$

where $\rho$ is the density of the quartz crystal and $\nu$ the wave velocity. When using this equation to convert measured frequency changes to mass changes, film rigidity is implicitly assumed. If the attached mass is not rigid, the frequency change will be less than predicted by the Sauerbrey Equation. It is therefore crucial to establish rigidity. If the film is non-rigid, the frequency difference is smaller when the quartz crystal is in solution.\(^\text{20}\)

\subsection*{2.4.4.1 Experimental Setup.} Experiments were performed at room temperature in a three electrode electrochemical cell (see Figure 2.12). One of the gold electrodes on the quartz crystal was the working electrode, platinum gauze was used as the counter electrode, and the potential of the working electrode was measured against a silver wire reference electrode.

The potential was measured with a EG&G PAR model 263A potentiostat/galvanostat, under computer control (Model 270/250 Research Electrochemistry Software 4.30). Routine measurements involved frequency differences relative to a reference crystal. These frequency differences were converted to voltages (using a frequency-to-voltage converter) for analogue recording. The frequency (mass)-time and associated potential-time were recorded digitally with a Das800 Series data acquisition card controlled by Easyest AG software.
2.4.4.2 Data Analysis. The change in mass of the quartz crystal was calculated by applying the Sauerbrey Equation (Equation 2.5) to the frequency values recorded for the polymer films. Further data analysis was carried out on the experimental data and the theory is explained together with the results in the subsequent chapters.

2.5 Experimental for Chapter 3

Copolymer materials were polymerised both onto 1000Å (100nm) Au coated glass electrodes (ca. 1cm²) for XPS experiments, and onto 500 Å (50nm) Au coated glass (ca. 2x1cm) for spectroelectrochemistry. The polymers were grown potentiodynamically by cycling twice from −0.2 to +1.2V and back to −0.2V, at a scan rate of 50 mV/s.

2.5.1. EDOT:BT Copolymers. An EDOT homopolymer film was grown from a 0.05M EDOT/0.1M LiClO₄/ACN feed solution. BT was then added to the same solution and the 0.1B:0.9E copolymer film was deposited onto a fresh substrate. Sequential addition/deposition steps, onto fresh substrates, were then carried out,
according to the desired solution composition (see Table 2.2) and copolymers containing both EDOT and BT were grown, after every addition, onto fresh substrate. Homopolymers of BT were separately prepared from a 0.05M BT/0.1M LiClO₄/ACN solution

<table>
<thead>
<tr>
<th>$X_{BT}/X_{TT}/X_{OT}$ in feed solution</th>
<th>$X_{EDOT}$ in feed solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1 0</td>
</tr>
<tr>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 2.2 Mole ratios of monomers in feed solutions $X_{BT}$, $X_{TT}$, $X_{OT}$ are the mole ratios of BT, TT, and OT respectively $X_{EDOT}$ is the mole ratio of EDOT

In the XPS technique verification section, the films were grown differently (see Table 2.3). As the films described above were grown by sequential additions of one monomer to the solution, changes in the total concentration of the solution may have been altering the results. The composition of films grown by potential step from $-0.2V$ to $+1.2V$ was examined

<table>
<thead>
<tr>
<th>Total Concentration (M)</th>
<th>Growth Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>CV</td>
</tr>
<tr>
<td>0.2</td>
<td>CA</td>
</tr>
<tr>
<td>0.1</td>
<td>CV</td>
</tr>
<tr>
<td>0.05</td>
<td>CV</td>
</tr>
</tbody>
</table>

Table 2.3 Film growth conditions for verification of techniques.

All four films had a feed solution mole ratio of 0.5 EDOT:0.5 BT. The first film was grown using the same method as above. The film grown using chronoamperometry was stepped from $-0.2$ to $+1.2V$ and held there for 20s. Removing half the solution volume and replacing it with fresh electrolyte reduced the total concentration of the
solution by half. This was then repeated to produce total concentrations of 0.1 and 0.05M.

2.5.2 EDOT:TT and EDOT:OT Copolymers. TT (or OT) homopolymers were grown from a 0.1M TT/0.1M LiClO₄/ACN (or 0.1M OT/0.1M LiClO₄/ACN) feed solution. Sequential additions of EDOT were then made according to the mole ratio (see Table 2.2), and copolymers were grown. Homopolymers of EDOT were separately prepared from a 0.1M EDOT/0.1M LiClO₄/ACN solution.

2.6 Experimental for Chapter 4

2.6.1 Potential Dependent NR Samples. PVF films were spin-coated onto a 200Å (20nm) Au coated quartz substrate. The neutron cell was filled with either 0.1M NaClO₄/H₂O or 0.1M NaClO₄/D₂O. The film was cycled at scan rates of 1, 5 and 10mV/s.

2.6.2 The Application of Potential Dependent NR to PEDOT Sample Preparation. The PEDOT film was electrochemically grown onto an Au coated quartz block from a solution of 0.05M EDOT/0.1M TEAP/ACN. The cell was rinsed with ACN and dried under a flow of nitrogen. The cell was then filled with a monomer free solution of 0.1M TEAP/d-ACN or 0.1M TEAP/h-ACN. The PEDOT film was cycled to condition the film and then held at either -0.575 V, -0.3 V and +0.5V during analysis.

2.6.3 EQCM Samples. To deposit the film, a polished Au quartz crystal was glued to the EQCM cell. The cell was filled with a 0.05M EDOT/0.1M LiClO₄/ACN solution. The potential was cycled once from -0.2 V to +1.2 V and back again at a scan rate of 50mV/s and the frequency change recorded. The cell was then rinsed several times with ACN and dried under a flow of nitrogen. The cell was filled with a monomer free solution of 0.1M LiClO₄/ACN, 0.1M NB₄ClO₄/ACN or 0.1M KPF₆/ACN for the EQCM experiments. The PEDOT film was potentiodynamically cycled three times from -0.2 to +1.15V at different scan rates of 20, 50, 100, 150 and 200mV/s.
2.7 Experimental for Chapter 5

2.7.1 Spectroelectrochemistry, AFM and NR Sample Preparation.
Homopolymer films of d₄-EDOT and BT and two bilayer films of d₄-EDOT/BT and BT/d₄-EDOT were electrochemically grown onto Au coated quartz blocks from solutions of 0.05M d₄-EDOT/0.1M TEAP/ACN and 0.05M BT/0.1M TEAP/ACN. The films were rinsed with ACN and dried under a flow of nitrogen. The NR data of the films was then recorded in d-ACN and h-ACN.

2.7.2 EQCM Sample Preparation. To deposit the 50:50 BT/EDOT copolymer, the cell was filled with 0.05M EDOT/0.05M BT/0.1M LiClO₄/ACN. The potential was cycled from -0.2V to +1.2V and back again at a scan rate of 50mV/s and the mass change recorded. The cell and film was then rinsed several times with ACN and dried under a flow of nitrogen. A new cell was filled with a 0.05M EDOT/0.1M LiClO₄/ACN and a film grown while the mass was recorded, and then the cell was rinsed and dried with nitrogen. 0.05M BT/0.1M LiClO₄/ACN was then added to the cell and another film grown on top to grow the layered structures. The process was repeated using the 0.05M BT solution first, to grow a BT film next to the Au electrode.

2.8 Experimental for Chapter 6

2.8.1 XPS Samples. Copolymer materials were electrochemically polymerised onto Au coated glass electrodes (ca. 1cm²). The solution contained 0.1M LiClO₄/ACN as supporting electrolyte. The polymers were grown potentiodynamically by cycling from -0.2 to +1.2 and back to -0.2V, at a scan rate of 50 mV/s. A 0.025M PFP solution was prepared and sequential additions of BT were then made to achieve the required mole ratio (see Table 2.4). In order to functionalise the PFP with the amino 15-crown-5 group, copolymer films of each composition were soaked in an ACN solution of 50mM amino 15-crown-5 for ca. 4hrs. The films were then rinsed well with ACN.
2.8.2 QCM. A copolymer film was deposited from a feed solution of 0.92BT 0.08PFP/0.1M TEAP/ACN. The film was grown by potentiostatically cycling from -0.2V to +1.2V at a scan rate of 20mV/s. The cell and film were then rinsed several times with ACN and dried under a flow of nitrogen. The mass was recorded dry and in fresh ACN. The film was then soaked in a 15% DMSO/85% 0.1M NaOH/H2O solution and left to hydrolyse for 4hrs. The film was rinsed well with H2O, 20mM NaOH/H2O, H2O, HCl and H2O. It was dried under a flow of nitrogen and the dry mass recorded after every solution change.

2.8.3 Samples for NR. Results from the XPS investigations were used to decide the mole fraction of the deposition solution. The deposition solution contained a binary mixture of BT and PFP in 0.1M LiClO4/ACN electrolyte (see Table 2.5 for the mole fractions of BT and PFP, the metal layer and the substrate). The electrode was mounted face down on the specially designed sample cell, described previously. After dry characterisation, and in h- and d-ACN; the films were soaked in an ACN solution of 50 mM amino 15-crown-5 for 4-8hrs to produce the reacted film. After reaction with the 15-crown-5 solution, the films were rinsed with ACN and dried. The reacted copolymer, functionalised with the 15-crown-5 group, was then characterised as a dry film and in h- and d-ACN.

<table>
<thead>
<tr>
<th>Feed Solution Ratio</th>
<th>Substrate</th>
<th>Metal Coating and Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.89 BT : 0.11 PFP</td>
<td>Quartz</td>
<td>Au 215</td>
</tr>
<tr>
<td>0.92 BT : 0.08 PFP</td>
<td>Silicon</td>
<td>Au 240</td>
</tr>
<tr>
<td>0.96 BT : 0.04 PFP</td>
<td>Quartz</td>
<td>Pt 210</td>
</tr>
</tbody>
</table>

Table 2.5 The substrate and metal electrode material of each sample
After characterisation, the reacted 0.92 BT:0.08 PFP copolymer, had Ba^{2+} and K^+ ions chelated to the amino 15-crown-5 functional group. Two films polymerised from the same feed solution, under the same conditions, were soaked in solutions of Ba(ClO_4)_2/ACN and KPF_6/ACN, for 4 hrs each. The films were thoroughly rinsed with ACN and characterised again in h- and d-ACN.

### 2.9 References

Copolymers of EDOT and BT

The ability to produce polymers containing long sequences of two or more different monomers has led to new products with unique and valuable properties. The properties of copolymers are altered by the mode of polymerisation (chemical or electrochemical), by the sequence of the repeating units (random or block), by the ratio of monomers and also by the conservation (or not) of fully π-conjugated systems in the copolymer backbone.

Copolymerisation can result in copolymers with properties intermediate between those of the homopolymers, or in some cases, a copolymer with completely different properties. In the 1930s it was found that monomers differed distinctly in the ratio they entered into copolymers. This is now described by the monomer reactivity ratio which is the ratio of the rate constant for a given radical adding its own monomer, to the rate constant for its adding to the other monomer (e.g. cross reaction). Adding a functional group, or making a chain longer, will cause a monomer species to react at different rates during polymerisation.

A copolymer system is said to be ideal when the two radicals show the same preference for adding one of the monomers over the other. In this case the two monomers are arranged at random along the chain, in relative amounts determined by the composition of the feed solution and the relative reactivities of the two monomers. However in the case of an alternating system, each radical prefers to react exclusively with the other monomer, resulting in the monomers alternating regularly along the chain, regardless of the composition of the monomer feed solution. Most actual cases lie between the ideal and the alternating systems.

In general, the mole fraction of monomers within a copolymer film does not equal the mole fraction of the monomers in the feed solution. If one monomer is much more reactive than the other, at high mole fractions of the more reactive monomer, the
polymer formed mostly contains the more reactive monomer. At low mole fractions of the more reactive monomer, only small amounts of the less reactive monomer are incorporated into the copolymer.

Here, XPS analysis has been used to determine the mole fraction of monomers within three series of copolymer films. The films all contained ethylenedioxythiophene (EDOT) as one component of a binary mixture, combined with one other species; this being either bithiophene (BT), terthiophene (TT) or octylthiophene (OT) (see Figure 3.1). Compared to other substituted polythiophenes, PEDOT has excellent stability in the doped state. Doped PEDOT was transparent with a blue tint and the neutral polymer was deep blue. Transparency in its doped state could make PEDOT very useful in commercial applications and was the reason it was chosen as one of the components of these copolymers.

Figure 3.1 Monomer 1 BT, 2 EDOT, 3 TT, 4 OT

Quantification of the copolymer ratio for the XPS data was carried out either from the ratio of C:S atoms, determined by integration of the S(2p) and C(1s) regions of the XPS spectrum (Table 3.1), or by iterative curve fitting of the sample (copolymer) data (Table 3.2) using the component homopolymers as reference (“library”) spectra (Section 2.4.2.2).

To make a comparison of the reactivities of the monomers in the three series, the mole fraction of EDOT within the copolymers was calculated using XPS and is shown in Table 3.1.
Table 3.1 Feed solution and copolymer composition expressed as the mole fraction of EDOT.

<table>
<thead>
<tr>
<th>$X_{EDOT}$ in Feed Solution</th>
<th>$X_{EDOT}$ in EDOT/BT Copolymer</th>
<th>$X_{EDOT}$ in EDOT/TT Copolymer</th>
<th>$X_{EDOT}$ in EDOT/OT Copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.9</td>
<td>0.86</td>
<td>0.34</td>
<td>0.95</td>
</tr>
<tr>
<td>0.7</td>
<td>0.75</td>
<td>0.1</td>
<td>0.97</td>
</tr>
<tr>
<td>0.5</td>
<td>0.55</td>
<td>0.08</td>
<td>0.99</td>
</tr>
<tr>
<td>0.3</td>
<td>0.46</td>
<td>0.01</td>
<td>0.98</td>
</tr>
<tr>
<td>0.1</td>
<td>0.28</td>
<td>0.07</td>
<td>0.97</td>
</tr>
<tr>
<td>0.0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 3.2 shows that the copolymers grown from the solution mixture containing OT had a much higher EDOT content, whereas in comparison, the TT/EDOT copolymers contained hardly any EDOT in the majority of the feed solution ratios. This indicates that TT was much more reactive (towards film formation) than OT under these conditions. Intermediate to the reactivities of TT and OT was that of BT, which reacted at a similar rate to EDOT.

Figure 3.2 Composition of copolymer films of EDOT/BT, EDOT/TT and EDOT/OT.
The relative reactivities of the monomers can be summarised as follows:

$$TT > EDOT > BT > OT$$

where TT is the most reactive and OT is the least reactive. It is possible that TT was more reactive than BT because TT already had an extra thiophene molecule per monomer group and would form a longer chain much faster. OT was the least reactive, as more monomer units needed to link together to form the same length chain as in BT and TT. The octyl group may have also caused steric effects within the polymer chain or produced more soluble oligomers during the polymerisation process.

Because the reaction rates of the EDOT and BT monomers were very similar, a large range of copolymer film ratios were achieved, increasing the likelihood of a range of optical responses for the different films. It was for this reason, that the EDOT/BT copolymer system was chosen to be studied in more detail. BT is also relatively easy to polymerise, and has a distinctive and different colour from that of the EDOT monomer, undergoing a red to blue colour change from the neutral to doped state, compared with deep blue to transparent for EDOT. The change in the spectroscopic properties of copolymer films with different mole fractions of EDOT and BT, are investigated in this chapter by growing copolymers from different feed solution ratios. XPS was used to quantify the ratio of EDOT and BT in the copolymer film. Spectroelectrochemistry has been used to record the spectra of the copolymer films, to determine if the electrochromic response can be correlated with the copolymer composition.

### 3.1 A Comparison of Copolymer Composition with Feed Solution Monomer Ratios

The characterisation of copolymer films of EDOT and BT are described here in detail. XPS was used to determine the proportion of monomer units in the copolymer films as described above. Figure 3.3 shows a series of XPS spectra in the C (1s) region for a range of copolymers grown from solution mixtures of the monomers EDOT and BT.
The C(1s) XPS spectrum of the homopolymer of BT in Figure 3.3 shows predominantly one broad peak, indicating the presence of aromatic C, whereas the C(1s) spectrum of the pure EDOT polymer shows a more complex mix of C environments at higher binding energies. This is consistent with the presence of the O substituents and methylene ring -CH₂- units. The copolymer spectra show a combination of these two homopolymers. The composition of these copolymers in terms of their BT components is shown in Table 3.2.

<table>
<thead>
<tr>
<th>X_{BT} in feed solution</th>
<th>X_{BT} in copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>0.0</td>
<td>0.00</td>
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<tr>
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<td>0.9</td>
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</tbody>
</table>

Table 3.2 Correlation of solution and copolymer composition expressed as the mole ratio of BT (X_{BT}).
These experiments were carried out in duplicate (labelled A and B, Table 3.2) for consistency with the films grown under identical conditions from the same feed solution compositions. The data in Table 3.2 are presented graphically in Figure 3.4. Allowing for experimental error, it can be seen that there was reasonable agreement between the two sets of results.

![Figure 3.4 Composition of a range of copolymers in terms of the bithiophene mole ratio versus the mole fraction of bithiophene in the feed solution. Data from Table 3.2.](image)

Films were grown by sequential additions of one monomer to the solution. Consequently, the total concentration of monomers in the solution was increased during the experiment. Also, all of the films were grown potentiodynamically (multisweep CV), rather than potentiostatically via chronoamperometric potential step e.g. from -0.2V to +1.2V. Further experiments were carried out to determine if either of these factors influenced the copolymer composition. These data are summarised in Table 3.3.

In a sample copolymer growth, CA was used in place of CV, all other conditions being the same (Table 3.3). This resulted in less BT being incorporated into the copolymer than when using CV as a growth technique. This was almost certainly because of differing mass and potential profiles during the film growth, but, rather than make an exhaustive comparison, CV was chosen as a growth technique for the remainder of this study. The data in Table 3.3, however, clearly show that the total
concentration of the feed solution did not have a strong influence on the composition of the copolymer film.

<table>
<thead>
<tr>
<th>Total Concentration (M)</th>
<th>Growth Technique</th>
<th>X\textsubscript{BT} in feed solution</th>
<th>X\textsubscript{BT} in copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>CV</td>
<td>0.5</td>
<td>0.38</td>
</tr>
<tr>
<td>0.2</td>
<td>CA</td>
<td>0.5</td>
<td>0.19</td>
</tr>
<tr>
<td>0.1</td>
<td>CV</td>
<td>0.5</td>
<td>0.27</td>
</tr>
<tr>
<td>0.05</td>
<td>CV</td>
<td>0.5</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 3.3 Correlation of solution and copolymer composition for the different growth techniques expressed as the mole ratio of BT (X\textsubscript{BT}). (CV = cyclic voltammetry, i.e. potentiodynamic growth, CA = chronoamperometry, i.e. potentiostatic growth).

As the films were deposited by potentiodynamically cycling, the relative amounts of monomers within the copolymers could correlate with potential. To avoid this, the potential was cycled to 100mV above the highest monomer onset oxidation potential; however, one monomer will always be in the oxidation window for a longer time period than the other. Yet, if the films are grown by CA, one monomer can be over oxidised, and no information can be gained during polymer deposition. For instance, it is impossible to ascertain whether the polymer is electroactive without removing the film and cycling it in fresh electrolyte. For these reasons, CV was used to grow the polymer films in all further experiments.

The data in Figure 3.4 show, that to within a reasonable margin of error, it is possible to deposit copolymer films of a desired composition, from a prescribed binary mixture of BT and EDOT monomers. This was then carried forward to the deposition of copolymer samples over the mole fraction range for subsequent characterisation.

### 3.2 The Optical Characteristics of the Copolymers

The in situ characterisation of the electrochromic properties of copolymer films during doping and dedoping was studied here, using a combination of time-resolved UV-Vis spectroscopy and Cyclic Voltammetry (spectroelectrochemistry). Changes in optical absorbance are a consequence of changes in dopant level that are quantified by
charge injection. One of the aims of this research was to correlate absorbance changes in electrochromic polymers and copolymers with dopant level and electrochemical potential.

The CVs presented in Figure 3.5 show the electrochemical activity of both BT and EDOT polymers. Both p-doping (anodic oxidation) and n-doping (cathodic reduction) processes are possible. These will be examined here separately. p-Doped PEDOT and polyBT have redox peaks at an anodic potential of +0.25V and +1.1V (Ag wire) respectively. As shown in Figure 3.5, the anodic wave shifts during n-doping to +0.3V and +1.15V (Ag wire) for PEDOT and polyBT respectively.

![Figure 3.5 Cyclic voltammogram of a film of: a) PEDOT, potentiodynamically cycled from -0.76 to +1.2V (p-doped) and from +1.2 to -2.0V (n-doped); and b) polyBT, cycled from 0 to +1.2V (p-doped) and from +1.2 to -2.0V (n-doped). All in 0.1M NBu4ClO4/ACN, scan rate 50mV/s, 2nd cycle, gold disk electrode.](image-url)
3.2.1 p-Doping. In the following results the BT homopolymer and the copolymers have been cycled from -0.5V to +1.0V, and PEDOT was cycled from -1.0V to +1.0V to collect the complete p-doping results. The electronic spectra of the undoped (neutral) homopolymers in the range 350nm < \lambda < 800nm are quite distinct, each showing a broad absorption. The \( \lambda_{\text{max}} \) value of 582 nm for PEDOT correlates with its blue colour (absorbing in the red), whereas the \( \lambda_{\text{max}} \) value for the undoped polyBT of 464 nm correlates with its red colour in the undoped state. The \( \lambda_{\text{max}} \) values for the undoped (neutral) copolymers can also be seen in Table 3.4.

<table>
<thead>
<tr>
<th>X&lt;sub&gt;B&lt;/sub&gt;T in Feed Solution</th>
<th>Undoped, ( \lambda_{\text{max}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>582</td>
</tr>
<tr>
<td>0.1</td>
<td>564</td>
</tr>
<tr>
<td>0.3</td>
<td>518</td>
</tr>
<tr>
<td>0.5</td>
<td>504</td>
</tr>
<tr>
<td>0.7</td>
<td>488</td>
</tr>
<tr>
<td>0.9</td>
<td>466</td>
</tr>
<tr>
<td>1.0</td>
<td>464</td>
</tr>
</tbody>
</table>

Table 3.4 \( \lambda_{\text{max}} \) values of the PEDOT/BT copolymer series

As more BT was incorporated into the film, the maximum wavelength shifts to a lower value. The data from Table 3.4 are presented graphically in Figure 3.6; there was a trend relating the ratio of BT and EDOT and the maximum wavelength of the peak in the spectrum, such that the \( \lambda_{\text{max}} \) value of the copolymer material can be predicted (or prescribed) from the copolymer ratio and vice versa. The potential dependent spectra of the copolymer series are shown in Figure 3.7. Here, the potential of the film was scanned from -0.5V to +1.0V at a scan rate of 5mV/s. The UV-Vis spectra were acquired at intervals of 15s corresponding to a 75mV separation in the potential domain. The films became p-doped as the potential neared +1.0V. In the spectra of the PEDOT homopolymer (Figure 3.7a), the absorbance decreased as the film became p-doped. The resultant featureless spectrum in the visible region corresponded to the virtually transparent appearance of the film (this is one of the reasons why PEDOT is so interesting). Yet, as the potential proceeded into the p-doping region, a strong new absorbance in the near IR region (\( \lambda > 800 \text{ nm} \)) appeared to be evolving. This was consistent with the onset of electronic conduction. The conduction band of the p-doped polymer is known to absorb in the near IR.
In the case of the BT homopolymer, the peak at 464nm (Figure 3.7g) decreased as the film became p-doped. But, in contrast to PEDOT, a new peak appeared at 750nm in the visible region of the spectrum, corresponding to the observed red/brown/blue colour transition of the film. The spectra for the copolymer films in Figure 3.7b-f show that at low mole fractions of BT, the characteristics of the copolymer films were similar to that of PEDOT. At high mole fractions of BT the films appeared to have characteristics comparable to the homopolymer. At intermediate mole fractions, the films exhibited absorbance characteristics that represented a stoichiometric combination of the two components. Unsurprisingly, an isosbestic point is not observed in the spectra. The total absorbance is not due to one individual species within the polymer films, but a range of species (the reason for the broad peaks observed in the spectra), transferring from one range of energy to a different range of energies. This range in energies is due to different species (bipolarons and polarons), populating and depopulating energy levels during redox cycling.

The data shown in Figure 3.7 are also represented in Figure 3.8; here the potential scale of the CV was shown as an additional axis on the 3D plot. The surface shown on the plot defines the complete wavelength, absorbance and potential (time) response of the film. In the 3D plot in Figure 3.8a for the PEDOT homopolymer there was a peak in the absorbance at -1.0V, but this dropped off quickly as the potential was increased anodically, until 0V was reached where a plateau was formed, spanning ca.
+2.0V. The beginnings of a broad peak above 800nm were just seen, spanning the width of the plateau. The absorbance did not begin to increase until 0V was again reached. The film slowly returned to its full absorbance state as -1.0V was reached on the reductive sweep. For the BT homopolymer (Figure 3.8g), the absorbance showed a peak in the potential regime from -0.5V to +1.0V which then dropped off quickly, and a narrow plateau formed. A new peak was observed above 600 nm which spanned the width of the plateau. The absorbance began to increase rapidly after just a few mV and the film quickly returned to its full absorbance state. The relative narrow plateau region, in the potential domain, compared to PEDOT (Figure 3.8b), reflects the proximity, in potential terms, of the p-doping redox reaction, to the vertex potential of the CV (+1.0V). This shows that the polyBT film oxidised at a more anodic potential than the corresponding homopolymer of EDOT. The 3D plots of the copolymer films, in Figure 3.8b-f, incorporate features from both the homopolymers. As more BT was incorporated into the copolymer (and the amount of PEDOT decreased), the characteristics of the film resembled the BT homopolymer. The width of the plateau between the peaks decreased. The peak that was beginning to appear above 800nm in the PEDOT homopolymer began to span less of the potential scale and appeared at lower wavelengths until a full peak was seen near 600nm.

Whilst the graphical representations shown in Figure 3.7 and Figure 3.8 provide a good picture of potential dependent wavelength/absorption properties of each polymer and copolymer film, they give no information about the correlation of absorbance changes with injected (or removed) charge. Since electrical current is the flux of charge, with time, \( i = \frac{dQ}{dt} \), the cyclic voltammogram represents the flux of charge as a function of applied potential (also as a function of time related by the potential scan rate). The data presented in Figure 3.9 show the CV (dQ/dt versus E) for each film, overlaid by the derivative curve for the absorbance (dA/dE) at \( \lambda_{\text{max}} \). Each of these curves is normalised to provide a dimensionless common scale. The overlay of these two differential flux curves (charge and absorbance) provides a visual representation of the synchronisation between the charge flux (current) and the absorbance flux (colour change) for the p-doping process of each film. For all the graphs shown in Figure 3.9 the film potential was scanned in the CV from -1.0 V (or -0.5V) to +1.0V and back at a scan rate of \( v = 5\text{mV/s} \). The cathodic limit of the scan
potential was chosen so as to encompass the complete range of electrochemical/optical activity in the same scan. This required anaerobic conditions in order to avoid the electrochemical reduction of dissolved molecular oxygen.

**Figure 3.9a** shows the two flux plots for a homopolymer of EDOT, the mid point potential for the p-doping process taken from the CV was *ca* -250mV. The optical absorbance was monitored at the $\lambda_{\text{max}}$ value of 574nm. As anodic current began to flow, corresponding to the electrochemical p-doping, optical absorbance was rapidly bleached. The two curves tracked quite closely, up to ca. +0.1V, indicating that charge injection was rapid in the time scale of the experiment. However, at potentials $+0 \text{V} < E < +1.0\text{V}$, the current remained anodic (increasing slightly as the solvent limit was reached), but absorbance did not change. This means that all the colour change was accomplished within the initial phase of oxidation (p-doping). This was an important result because the remainder of charge flux (current) at potentials $E > +0.1\text{V}$ was effectively wasted from the perspective of the colour transition. This might be important for the energy conservation or switching time for a practical device. On the return, cathodic, scan the situation was similar, with all the absorbance flux occurring in the potential region $-0.6\text{V} < E < +0.1\text{V}$.

**Figure 3.9g** shows a similar plot for the homopolymer of BT. Here the mid point potential was much more anodic at *ca* +700 mV, and the situation was quite different: the two curves tracked quite closely across the whole of the potential window. While the current remained anodic, the absorbance flux increased. For BT, the whole region of charge flux was involved in colour transition. Additionally there was evidence of some structure in the absorbance flux curve. This might suggest that colour change was associated with polaron formation. However, on the return, cathodic, scan the colour change was accomplished at much more anodic potentials, demonstrating substantial hysteresis in the absorbance response. This has important consequences for practical device applications (over drive). The remaining plots for the copolymers, **Figure 3.9b-f**, once again show intermediate responses to those of the homopolymers. The mid point potential shifted to a more anodic value as more BT was incorporated, but the absorbance flux plots (taken at $\lambda_{\text{max}}$ for each film) mostly resembled that of PEDOT in shape and symmetry.
Figure 3.7  p-doping spectra of the EDOT/BT copolymer series a) PEDOT Homopolymer, b) 0.9EDOT : 0.1BT, c) 0.8EDOT : 0.2BT, d) 0.51EDOT : 0.49BT, e) 0.47EDOT : 0.53BT, f) 0.26EDOT : 0.74BT, g) BT Homopolymer cycled in 0.1M LiClO₄/ACN at a scan rate of 5mV/s.
Figure 3.8 3D plots of the p-doping spectra of the EDOT/BT copolymer series a) PEDOT Homopolymer, b) 0.9EDOT : 0.1BT, c) 0.8EDOT : 0.2BT, d) 0.51EDOT : 0.49BT, e) 0.47EDOT : 0.53BT, f) 0.26EDOT : 0.74BT, g) BT Homopolymer cycled in 0.1M LiClO4/ACN from -0.5 to +1.0V at a scan rate of 5mV/s.
Figure 3.9 Overlaid $dA/dE$ and $dQ/dE$ plots for the p-doping of the EDOT/BT copolymer series a) PEDOT Homopolymer, b) 0.9EDOT : 0.1BT, c) 0.8EDOT : 0.2BT, d) 0.51EDOT : 0.49BT, e) 0.47EDOT : 0.53BT, f) 0.26EDOT : 0.74BT, g) BT Homopolymer cycled in 0.1M LiClO$_4$/ACN from -0.5 to +1.0V at a scan rate of 5mV/s. Black arrows depict the direction of potential.
3.2.2 n-Doping. The n-doping spectra of the same copolymer films were collected by cycling the films potentiodynamically from +1.0 to -2.0 V at 5mV/s. The UV-Vis spectra were acquired at intervals of 20s corresponding to a 100mV separation in the potential domain. Figure 3.10 illustrates that as the potential neared -2.0V the films became n-doped. A single peak was not observed in the visible region for the PEDOT homopolymer (Figure 3.10a), instead two broad peaks were seen between 400 and 700nm. The features in the region between +1.0 and -1.0V do not correspond with those seen in Figure 3.7a for the polymer film when it had only been p-doped. It is most likely that the polymer degraded as a result of being n-doped immediately before entering the p-doping region, and this was not a true feature of the PEDOT film. In the copolymer spectra (Figure 3.10b-f), the peak at ~500nm disappeared as the film became n-doped and a broad peak above ~600nm was observed forming. The sharper peak at ~500nm seen in the copolymer spectra was due to BT being incorporated into the copolymer film. The broad peak appeared at lower wavelengths as more BT was incorporated into the copolymer film.

Figure 3.11 shows 3D plots of the n-doping spectra relating the wavelength, absorbance and electrochemical potential of the film. Figure 3.11a for the PEDOT homopolymer shows that at +1.0V, the absorbance was low in the visible region, though a peak could be seen around 800nm (conduction band). After 0.0 V was passed, two peaks began to form in the visible region. The broad peak around 800nm did not begin to drop off until -1.0 V was reached. As 0.0 V was reached, the absorbance in the visible region sharply dropped, and the beginnings of a new peak above 800nm were seen.

The BT homopolymer (Figure 3.11g) had a sharp peak in the visible region of the spectrum spanning the whole potential window. The start of a peak above 800nm was only just visible. The 3D plots for the copolymer films (Figure 3.11b-f) incorporated features from both homopolymers. As for BT, a sharp peak was seen in the visible region of the spectrum. The width of this peak increased as more BT was incorporated into the film. For the films with more PEDOT, a broader peak was seen above 800nm. The less PEDOT within the copolymer film, the higher the potential at which the peak above 800nm appeared.
Figure 3.10 n-doping spectra of the EDOT/BT copolymer series a) PEDOT Homopolymer, b) 0.9EDOT : 0.1BT, c) 0.8EDOT : 0.2BT, d) 0.51EDOT : 0.49BT, e) 0.47EDOT : 0.53BT, f) 0.26EDOT : 0.74BT, g) BT Homopolymer cycled in 0.1MLiClO$_4$/ACN at a scan rate of 5mV/s.
Figure 3.11 3D plots of the n-doping spectra of the EDOT/BT copolymer series a) PEDOT Homopolymer, b) 0.9EDOT : 0.1BT, c) 0.8EDOT : 0.2BT, d) 0.51EDOT : 0.49BT, e) 0.47EDOT : 0.53BT, f) 0.26EDOT : 0.74BT, g) BT Homopolymer cycled in 0.1M LiClO₄/ACN from +1.0 to -2.0V at a scan rate of 5mV/s.
3.2.3 **Counterion effects.** Since the electrochemical doping processes are influenced or controlled (depending on the time scale) by the nature of the counterion\(^7\,8\,9\), the copolymer and homopolymer films were also cycled in 0.1M NBu\(_4\)ClO\(_4\)/ACN to compare the responses with those of LiClO\(_4\) (described above). It is generally believed that the cation is involved in charge balancing the n-doping process, if this is the case then cation substitution effects are most likely to be observed in the n-doping region.

The p-doping behaviour of the films was initially recorded in 0.1M NBu\(_4\)ClO\(_4\)/ACN, in order to confirm that changing the cation had no affect on the electrochromic (colour) p-doping response of the polymers. The films were again potentiodynamically cycled from -0.5 to +1.0V. Comparing these results with those acquired for 0.1M LiClO\(_4\)/ACN, it can be seen that the films colour response did not alter. The plots for the films cycled in 0.1M NBu\(_4\)ClO\(_4\)/ACN are depicted in **Figure 3.12** and **Figure 3.13**, as with the films in 0.1M LiClO\(_4\)/ACN (**Figure 3.8**), as more BT was incorporated into the copolymer, the characteristics of the film became more like that of the BT homopolymer. The width of the plateau between the peaks decreased and the peak above 800nm was barely visible. It was concluded that changing the cation did not affect the p-doping electrochromic response of the copolymers.

The n-doping spectra in 0.1M NBu\(_4\)ClO\(_4\)/ACN can be seen in **Figure 3.14** and the 3D plots for the n-doping of the films are in **Figure 3.15**. In comparing the n-doping data for 0.1M NBu\(_4\)ClO\(_4\)/ACN with the n-doping data for 0.1M LiClO\(_4\)/ACN (**Figure 3.10** and **Figure 3.11**) it was concluded that, under these experimental conditions, the cation did not affect the electrochromic response of the copolymer films. The dips or troughs seen at -2.0V in **Figure 3.15** were a feature of the spectrometer and not an experimental result for the film. The reason an electrochromic effect was not observed with a change in cation, may be because the experiment was carried out at a slow scan rate. At fast scan rates the electrode kinetics of a film are much faster than the rate of diffusion of the solvent. However, when a film is cycled at slow scan rates there is time for the mass transport reactions within the film to equilibrate.
Figure 3.12 p-doping spectra of the EDOT/BT copolymer series a) PEDOT Homopolymer, b) 0.9EDOT : 0.1BT, c) 0.8EDOT : 0.2BT, d) 0.51EDOT : 0.49BT, e) 0.47EDOT : 0.53BT, f) 0.26EDOT : 0.74BT, g) BT Homopolymer cycled in 0.1M NBu_4ClO_4/ACN at a scan rate of 5mV/s.
Figure 3.13 3D plots of the p-doping spectra of the EDOT/BT copolymer series a) PEDOT Homopolymer, b) 0.9EDOT : 0.1BT, c) 0.8EDOT : 0.2BT, d) 0.51EDOT : 0.49BT, e) 0.47EDOT : 0.53BT, f) 0.26EDOT : 0.74BT, g) BT Homopolymer cycled in 0.1M NBu₄ClO₄/ACN from -0.5 to +1.0V at a scan rate of 5mV/s.
Figure 3.14 n-doping spectra of the EDOT/BT copolymer series a) PEDOT Homopolymer, b) 0.9EDOT : 0.1BT, c) 0.8EDOT : 0.2BT, d) 0.51EDOT : 0.49BT, e) 0.47EDOT : 0.53BT, f) 0.26EDOT : 0.74BT, g) BT Homopolymer cycled in 0.1M NBu4ClO4/ACN at a scan rate of 5mV/s.
Figure 3.15 3D plots of the n-doping spectra of the EDOT/BT copolymer series a) PEDOT Homopolymer, b) 0.9EDOT : 0.1BT, c) 0.8EDOT : 0.2BT, d) 0.51EDOT : 0.49BT, e) 0.47EDOT : 0.53BT, f) 0.26EDOT : 0.74BT, g) BT Homopolymer cycled in 0.1M NBu₄ClO₄/ACN from +1.0 to -2.0V at a scan rate of 5mV/s.
3.3 Conclusion

A series of copolymers containing EDOT and another thiophene based monomer were grown and the amount of EDOT within the copolymer was quantified using XPS, in order to confirm the ratio that the monomers entered into copolymers. It was found that adding a functional group, or making a chain longer, caused monomer species to react at different rates during polymerisation.

It was proven that copolymers of BT and EDOT had a similar monomer ratio to the feed solution composition they were deposited from. As the reaction rates of EDOT and BT were very similar, it was possible to deposit copolymer films of a desired composition from a prescribed binary mixture of BT and EDOT monomers, producing a range of optical responses.

In combining the characterisation techniques of XPS and spectroelectrochemistry a quasi-linear trend was found relating the ratio of BT and EDOT in the copolymer and the $\lambda_{\text{max}}$ value of the undoped (neutral) copolymer, such that the $\lambda_{\text{max}}$ value of the copolymer material could be predicted from the copolymer ratio and vice versa.

At low mole fractions of BT, the p-doping characteristics of the copolymer films were similar to that of PEDOT. At high mole fractions of BT the films appeared to have characteristics comparable to the homopolymer. At intermediate mole fractions, the films exhibited absorbance characteristics that represented a stoichiometric combination of both components.

Overlaying the differential flux curves for charge and absorbance provided a visual representation of the synchronisation between charge and absorbance flux for the p-doping process of each film. In the EDOT homopolymer, charge injection (or removal) was rapid, with all the colour change accomplished within the initial phase of oxidation (or later phase of reduction). The remainder of the charge flux (current) at $E > +0.1\,\text{V}$ was effectively wasted from the perspective of the colour transition. This is an important factor when considering the colour switching time for a practical device. In contrast, in the BT homopolymer, the whole region of charge flux was involved in colour transition. The colouration efficiency of conducting polymers has
been addressed by Reynolds et al who developed a general method for measuring the efficiency of colour change with respect to structure

The trends in the p-doped optical responses are very clear with evident correlations for the charge and absorbance flux. Trends in the n-doped cycle are less clear, partly because the magnitude of change was less, and partly because the stability of the n-doped polymers and copolymers was very poor. Investigations into cation substitution were inconclusive; there were no observed effects on the electrochromic responses of the copolymer films with changing cations. This could be due to the mass transport reactions that occurred at the slow scan rate of the experiments.

In one sense these results are unsurprising, in that they show that the properties of the copolymer scale stoichiometrically with the properties of the individual components. In fact this type of structure property relation is very useful from the point of view of device fabrication, since it allows for the prescriptive formulation of property types. Certainly, in binary monomer mixtures where reactivity ratios are very different, obtaining hybrid or combinatorial properties can be very difficult.

**Strategy:** There were two possible ways to proceed with this investigation. One route would be to further examine or screen the structure/property relationships of the many probable combinations of EDOT and another thiophene monomer. For example EDOT could be combined with a long chain alkylthiophene or a thiophene with an electrochemical chromophore such as a viologen attached. However, an alternative direction was chosen here; the remainder of this thesis is concerned with the study of the internal structure of the EDOT/BT polymer films, together with charge/mass transfer dynamics of the system. Here the focus moves to issues (e.g. rate, efficiency, reversibility, and energy) that might affect the function of the colour transition, such as the identity of the mobile species (counterions and/or solvent molecules) that accompany redox cycling. Also, the rate at which the mobile species moved in and out of the copolymer film was probed, and the internal structure of the film was studied. Physical changes associated with the electrochromic response of a polymer were another avenue that was explored. Thickness, solvation and ion population of the copolymers were investigated and contrasted with the behaviour of layered structures.
3.4 References

2 Staudinger, H.; Schneiders, J. Justus Liebigs Ann Chem 1939, 541, 151-195
10 Gaupp, C.L.; Welsh, D M.; Rauh, R D.; Reynolds, J.R. Chem Mater 2002, 14, 3964
In the quest to study the charge/mass transfer dynamics of the copolymer films described in Chapter 3, the PEDOT homopolymer was first investigated. The NR and EQCM studies of polyBT have already been well documented in the literature\textsuperscript{1,2,3,4,5,6} and the EQCM behaviour of PEDOT have been investigated\textsuperscript{7,8,9,10,11,12}. The behaviour of a polymer film which is being electrochemically cycled is affected by the permeation of mobile species into the polymer. The permeating group may be a target species to be oxidised or reduced, an ion ('dopant') required to maintain overall electroneutrality within the film, or solvent. If large thickness changes take place because of the movement of mobile species in a polymer, the film can be placed under great mechanical stress. The amount of mechanical stress a film undergoes will influence the lifetime of the film and needs to be taken into account if the film is to be used in devices such as electronic actuators.

This chapter examines the physical changes in PEDOT homopolymers which are undergoing potential control. The techniques of Neutron Reflectivity (NR) and Electrochemical Quartz Crystal Microbalance (EQCM) were used to probe the thickness, solvent population and ion movements in a PEDOT film under potential control.

\textbf{4.1 Potential Dependent NR}

A vast array of surface-sensitive spectroscopic\textsuperscript{13,14}, imaging\textsuperscript{15}, electrical\textsuperscript{16}, chemical\textsuperscript{17} and acoustic\textsuperscript{18} probes have been coupled with electrochemistry to characterise the structure, composition, and dynamics of polymer modified electrodes as functions of time and space. However, the spatial distribution of species at the interface has not been characterised. NR has many similarities to ellipsometry\textsuperscript{19} but with the added advantage of isotopic sensitivity. The contrast variation gained from using different isotopes in NR allows a selected species to be highlighted, giving unique fits to
complex interfacial structures. NR has previously been used to probe the solvation and thickness of polymer films, along with their interfacial roughness. However, this provides limited information as it does not give insight into how a polymer film behaves under potential control. The effect of potential on a polymer film can be investigated by two methods: fixed potential NR and varied potential NR.

4.1.1 Fixed Potential NR Measurements. NR has been developed to study buried interfaces under potential control. It has been used to distinguish composite and bilayer polymer films, revealed permeating solvent in electroactive polymer and metal hydroxide films and revealed 1D profiling of diffusion and reaction within a film. A polymer film can be held at a fixed potential while the NR of the film is recorded as described in Chapter 2. By examining the CV of the film and strategically choosing potentials of interest, an insight into the behaviour of the polymer can be developed and buried interfaces under potential control can be studied.

4.1.2 Varied Potential NR Measurements. The NR studies mentioned previously have data acquisition time scales of 1-2hrs. As a result, equilibrated films can be observed as a function of potential, but not by the dynamics of interconversion. A technique to allow in situ NR measurements during electrochemical cycling has been developed here to give complete information on the temporal resolution of the film. The objective was the simultaneous acquisition of population changes of the individual components (polymer, solvent and ions) within polymer films, as functions of time and distance within a redox switching film. In order to collect real-time data, on a time scale of seconds of a redox switching film, a time resolution improvement of 2-3 orders of magnitude is needed in established techniques. This cannot be accomplished via an increase in incident flux or detector efficiency. Here, boxcar integration within continuous multiple linear potential cycles was used to yield the first dynamic in situ electrochemical NR measurements, with an effective time scale of ca. 2s.

* Technique developed in collaboration with Dr. A. Glidle and Dr. N. Gadegaard from Department of Electronics, University of Glasgow, Prof. A. R. Hillman, Department of Chemistry, University of Leicester; Dr. R. Cubitt, ILL, Grenoble; and Dr. R. M. Dalghiesh, ISIS Facility, RAL, Didcot
The polymer film was continually electrochemically cycled to collect profiles which corresponded to the dynamically changing polymer during a redox cycle. Each time the electrochemical potential passed through a pre-defined voltage, a program accumulated the incremental NR data in a memory bin. After the acquisition ended, the data bins were written to disk and the reflectivity angle changed. Data acquired over multiple cycles was sequentially stored in bins associated with 20mV potential windows. The film was repetitively cycled for many hours in order to obtain NR profiles for narrow voltammetric bins which had a low statistical noise.

Polyvinylferrocene (PVF) was used as a model polymer system to perfect the technique, as previous investigations\textsuperscript{28,29,30} have proven that it is extremely stable during redox cycling (see Figure 4.1 for the CV) and the NR response has been well characterised. H\textsubscript{2}O/D\textsubscript{2}O switching was used to locate the solvent distribution within the PVF films.

![Figure 4.1](image_url)

\textbf{Figure 4.1} Cyclic Voltammogram of PVF in 50 M NaClO\textsubscript{3}/H\textsubscript{2}O. Scan rate 5mV/s, electrode area 27cm\textsuperscript{2}

\textbf{Figure 4.2} shows $E_-(t)$ resolved $R(Q)$ profiles for two PVF films of different surface coverage and cycled at different scan rates to accentuate the effective time-scale differences. Fringes of different periodicity, representing the Au electrode and PVF film thickness were clearly distinguished. This proved that \textit{in situ} high quality NR profiles could be acquired for an electroactive film that was under electrochemical control.
Features due to the PVF layer were most apparent at low Q (\(<0.6\text{nm}^{-1}\)). At higher Q, film roughness effects dampened the PVF contributions to the reflectivity, and fringes due to the underlying metal electrode dominated the profile (see Figure 4.2). The film thickness of PVF varied with potential. Film oxidation (or reduction) resulted in fringe compression (or expansion); since Q represents inverse space, the film was swelling upon oxidation and shrinking upon reduction. This was chemically reversible over a complete redox cycle. However, on the time-scale of individual profiles, swelling occurred over a narrower region of potential than shrinkage.\(^{31}\)
Also of interest here was the extent to which changes in thickness (\(d\)) correlated with electrochemical charge (\(Q\)). Figure 4.3 shows a 3D plot of thickness and charge as functions of potential (\(E\)). This is a dynamic compositional map of the system, where film thickness is dominated by the solvent level and the charge represents the ion content. As the PVF film is oxidised, charge is steadily incorporated and solvent ingresses into the film, demonstrated by an increase in film thickness as the polymer matrix swells to incorporate the solvent molecules. Upon reduction, charge is steadily lost from the film accompanied by the expulsion of solvent. The 2D \(d(Q)\) and \(Q(E)\) projections of the 3D compositional vector show that solvent is equilibrated with the redox state, which is kinetically controlled.

![Figure 4.3](image)

**Figure 4.3** Film thickness and charge as functions of applied potential for Figure 6a. The projections are the black traces and the red trace is the 3D vector.

Further analyses of the profiles for the films in H\(_2\)O and D\(_2\)O show that the film had an interior region and compositionally distinct interfacial regions near the electrode and solution. The interior region had a spatially uniform composition when the film was fully reduced, but had a solvent rich centre when the film was partially oxidised.
4.2 The Application of Potential Dependent NR to PEDOT

The objective was to use potential dependent NR to probe the distribution of solvent and roughness of a PEDOT film. The changes in a PEDOT film under potential control were investigated. A ~400 Å thick (measured using both Dektak and NR) PEDOT film was electrochemically deposited onto a gold-coated quartz substrate using cyclic voltammetry as described in Section 2.6.2. In order to highlight the solvation of the film, data were collected for PEDOT in solutions of both 0.1M TEAP/d-ACN and 0.1M TEAP/h-ACN. Three potentials -0.575 V, -0.3 V and +0.5V were chosen for analysis. The positions of these on the CV of the PEDOT film can be seen in Figure 4.4.

Figure 4.4 Cyclic voltammogram for the ~400 Å thick PEDOT film.

Figure 4.5 shows the NR profiles for the PEDOT film towards the extremities of the potential region (-0.575V and +0.5V), and the potential corresponding to the beginning of the anodic ‘peak’ (-0.3V). The change in these NR profiles for the film at different potentials appeared to be small, as confirmed later by the model fits to the data. The NR profiles show reflectivity fringes due to both the Au layer and the polymer deposited on top. The thickness of the Au can be estimated from ΔQ as
described earlier (Section 2.4.3). The d-ACN profiles show a critical edge corresponding to total internal reflection of the neutron beam. A critical edge is not seen for h-ACN because the scattering length densities of the solvent and the quartz/Au interface are more closely matched.

Figure 4.5 NR measurements for the PEDOT film in 0.1M TEAP/d-ACN and 0.1M TEAP/h-ACN. Spectra for the two different solvents are offset by 1000 for clarity. The film was held at -0.575 V (---), -0.3 V (--), and +0.5 V (---).

The profiles shown in Figure 4.6 contain information on the thickness, scattering length density and roughness of the PEDOT film. If the interface between layers was depicted by a sharp peak, the two surfaces were smooth. If there was a gradual slope, the layer was rough; the smaller the gradient of the slope, the rougher the layer.

The values for the thickness and scattering length of the gold layer were already known and are 220 Å and 4.49 x 10^{-6} Å^{-2} respectively. The gold/PEDOT interface (depicted at 220 Å in Figure 4.6) was sharp, indicating that the polymer film was smooth near the electrode. As expected, the dry PEDOT film was much thinner, only 400 Å compared to 580 Å when solvated. In the solvated films, the PEDOT layer was relatively smooth until it reached the point where the solution was ingressing into the film.
The solvent volume fraction of the film was calculated using Equation 4.1:

\[ V_f = \frac{N_b (z_{\text{film}})^{d-\text{ACN}} - N_b (z_{\text{film}})^{h-\text{ACN}}}{N_b^{(d-\text{ACN})} - N_b^{(h-\text{ACN})}} \]  

(Equation 4.1)

The scattering length of the film in hydrogenous acetonitrile \((N_b(z_{\text{film}})^{h-\text{ACN}})\) was subtracted from the scattering length of the film in deuterated acetonitrile \((N_b(z_{\text{film}})^{d-\text{ACN}})\). This value was then divided by the scattering length density of deuterated acetonitrile \((N_b^{d-\text{ACN}})\) with the scattering length density of hydrogenous acetonitrile \((N_b^{h-\text{ACN}})\) subtracted.

The solvent volume fraction of the polymer in all redox states was -40% (see Figure 4.7). This high solvation for both the reduced and fully oxidised states of the film, may have allowed the easy movement of the ions required to maintain electroneutrality during redox cycling, without the need for any structural reorganisation, or expansion of the polymer film.
The simplistic movement of ions during a redox cycle, and the ability of the matrix to accommodate changes in the ion population without structural reorganisation, may be significant in explaining the stability of PEDOT films to extended periods of repetitive cycling, compared to many other conducting polymer systems\textsuperscript{33,34,35}. The film swelled by $\sim$30\% from the dry to the solvated polymer film, providing further evidence that the matrix was able to accommodate the ingress of solvent species. The varied potential measurements for a PEDOT film also exhibited little change in the solvation of the polymer when the film was electrochemically cycled, this could be an artifact of the fibrillar structure of PEDOT reported by Wudl \textit{et al}\textsuperscript{36}.

\subsection*{4.3 \textit{The Mobile Species in Potentiodynamically Cycled PEDOT}}

Positive charges are formed in the polymer backbone during oxidation of conducting polymer films. In order to maintain electroneutrality, anions are incorporated or cations are ejected. Often, this ion transfer is accompanied by the exchange of solvent molecules\textsuperscript{37,38,39,40,41,42}. Ion transfer reactions in an acoustically thin film of PEDOT were examined using EQCM, by monitoring the mass changes accompanying doping/dedoping.
The deposition of PEDOT onto the quartz crystal (see Figure 4.8), caused a frequency shift, $\Delta f \approx -1.9$ kHz. From this the mass of the polymer film was calculated, $m = 8.92 \mu g cm^{-2}$. Assuming a density of $\rho = 1.3-1.5 g cm^{-3}$, this corresponds to a layer of ca. 77-50 nm thickness, i.e. 770-500Å and therefore comparable in thickness to the neutron experiment.

![Figure 4.8](image-url)  
\( \text{a)} \) The cyclic voltammogram of the growth of the PEDOT film, \( \text{b)} \) The change in mass measured during the growth of the PEDOT film.

The thin PEDOT film was conditioned and cycled in clean 0.1M LiClO$_4$/ACN, 0.1M NBu$_4$ClO$_4$/ACN and 0.1M KPF$_6$/ACN, at different scan rates. Figure 4.9 shows the current trace of the film under potential control in the three electrolytes, collected whilst the frequency of the quartz crystal was being recorded.
Figure 4.9 Film cycling in a) 0.1M LiClO$_4$/ACN, b) 0.1M NBu$_4$ClO$_4$/ACN, and c) 0.1M KPF$_6$/ACN at scan rates of 20, 50, 100, 150, and 200mV/s.
Experimentally, the change in resonance frequency of the quartz crystal oscillator resulting from a change in the mass of the electrode was measured. A change $\Delta M$ in the rigidly attached mass gave rise to a resonant frequency change described by the Sauerbrey equation (Equation 2.5, repeated below for clarity). **Equation 2.5** describes the behaviour of a rigid resonator (i.e. little or no viscoelastic loss) therefore this assumption was a prerequisite to any calculation involving the interconversion of $\Delta f$ and $\Delta M$ values. In this context, these calculations were justified because the film was very thin, also supplementary measurements using acoustic impedance spectroscopy show that these films behaved as rigid resonators.

$$\Delta f = -\frac{2f_0^2}{\rho \nu} \Delta M \quad \text{(Equation 2.5)}$$

If the attached mass was not rigid, then the frequency change would be less than predicted by **Equation 2.5**, i.e. the mass change associated with film deposition and mobile species transfer would have been underestimated. Hillman *et al.* have illustrated that the rigidity of polyBT films is dependent on their thickness$^2$. For films where ca. 50nmol cm$^{-2}$ or less of electroactive sites were immobilised, rigid characteristics were observed. It was shown that as films became thicker, the Sauerbrey equation could not be applied, as they became increasingly less rigid. As the film grown here contained 63nmol cm$^{-2}$ of electroactive sites, rigidity was assumed and the Sauerbrey equation was employed to convert the measured frequency changes to mass changes.

It was observed in **Figure 4.10**, that the mass of the film increased steadily until +0.9V was reached. At this point, the mass change began to level off, and by +1.15V the mass of the film had ceased to increase. On reduction, mass was not lost from the film until +1.0V was reached. After this point, mass was lost from the film at the same rate it was previously incorporated into the film. At -0.2V, no more mass could be lost from the film. The same events were observed in the film for the second and third cycle.
The charge injection into the polymer film was calculated by numerical integration using Equation 4.2 below:

\[ Q = \sum_{i} \frac{i(E_{i+1} - E_{i})}{v} \]  

(Equation 4.2)

where \( i \) is the current, \( E_1 \) and \( E_2 \) are the vertex potentials of the voltammogram and \( v \) is the scan rate. Because the potential is a discontinuous function, the calculation had to be applied to the data in stages. Figure 4.11 is a plot of the charge increase within the polymer film versus the potential.

Charge steadily increased within the film, through the whole of the potential window (see Figure 4.11). Charge was still incorporated into the film at the two extremes of potential, even though the mass did not appear to change in this region in Figure 4.10. As with the mass, the charge incorporated within the film during oxidation was lost at the same rate during the reduction of the film. In the CV of the film (Figure 4.9a, green trace), current quickly increased, but then remained constant for virtually the whole of the potential window.
Figure 4.11 A plot of charge versus potential for the PEDOT film cycled in 0.1M LiClO₄/ACN at 100mV/s.

The shape of the ΔM(E) (Figure 4.10) and ΔM(Q) (Figure 4.12) are similar, i.e. in the latter stages of doping and undoping, charge was injected/removed with no apparent mass (frequency) change. In Figure 4.12 mass was incorporated into the film quickly, until 4.5x10⁻⁴ C cm⁻² was reached, where the mass in the film levelled off. Mass was lost from the film after 4.5x10⁻⁴ C cm⁻² was reached on the return sweep, and levelled off after 1x10⁻⁴ C cm⁻².

Figure 4.12 A plot of mass change versus charge for the PEDOT film cycled in 0.1M LiClO₄/ACN at 100mV/s.
4.3.1 Calculation of the Molar Mass of the Mobile Species (\(M_{\text{app}}\)). Bund and Neudeck have reported that the molar mass of the mobile species, \(M_{\text{app}}\), can be calculated from the ratio of mass to charge, \(\Delta m/\Delta Q\) (i.e. the slope of the curve shown in Figure 4.12):

\[
M_{\text{app}} = zF \frac{\Delta m}{\Delta Q} \quad \text{(Equation 4.3)}
\]

where \(z\) is the charge of the anion and \(F\) is the Faraday constant \((96,484.56 \text{ C mol}^{-1})^{12}\).

In order to obtain values of \(M_{\text{app}}\) for these experiments, \(\Delta m/\Delta Q\) was calculated using the linear regression of the \(\Delta\) Mass versus Charge plots (e.g. Figure 4.12). In this case, the \(M_{\text{app}}\) value represents an average value for the corresponding potential range. Multiplying this by the charge of the anion and the Faraday constant allowed the \(M_{\text{app}}\) value to be calculated. Figure 4.13 shows the \(\Delta m/\Delta Q\) determined from the data shown in Figure 4.12 for the PEDOT film cycled in 0.1M LiClO\(_4\)/ACN at 100mV/s.

![Figure 4.13](image)

Figure 4.13 A plot of mass change versus charge for the first cycle of the PEDOT film cycled in 0.1M LiClO\(_4\)/ACN at 100mV/s with the linear regression function overlayed (— line); a) \(\Delta m/\Delta Q\) value for oxidation (— line) and b) \(\Delta m/\Delta Q\) value for reduction (— line).
Bund and Neudeck also reasoned that the measured $M_{\text{app}}$ value represents the sum of the masses of mobile ion and the solvation shell where $\alpha$ represents the number of solvent molecules transferred per anion and $M_{\text{solv}}$ is the molar mass of solvent, see Equation 4.4.

$$M_{\text{app}} = M_{\text{amon}} + \alpha M_{\text{solv}}$$  \hspace{1cm} (Equation 4.4)

where $M_{\text{amon}}$ is the molar mass of the anion\(^\text{12}\).

$M_{\text{app}}$ could be measured directly and $M_{\text{amon}}$ and $M_{\text{solv}}$ were known, consequently $\alpha$ was calculated using Equation 4.4. This procedure of analysis was carried out on all data for the film in 0.1 M LiClO$_4$/ACN, 0.1 M NBu$_4$ClO$_4$/ACN and 0.1 M KPF$_6$/ACN at 20, 50, 100, 150 and 200 mV/s. Similar trends were seen in all data. The data in Table 4.1 show that at scan rates of $100 < \upsilon < 150$ mV/s the anion was the dominant mobile species with little or no solvent transfer. This is evident from the values of $M_{\text{app}}^b$ which are close to 99 (RMM of ClO$_4^-$) for LiClO$_4$ and NBu$_4$ClO$_4$, and 144 (RMM of PF$_6^-$) for KPF$_6$. At slower scan rates the movement of additional solvent molecules was also observed. At $\upsilon > 150$ mV/s, PEDOT behaved like a capacitor, trapping out charge movement.

<table>
<thead>
<tr>
<th>Scan Rate (mV/s)</th>
<th>LiClO$_4$</th>
<th>NBu$_4$ClO$_4$</th>
<th>KPF$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{\text{app}}^b$ (gmol$^{-1}$)</td>
<td>$\alpha$</td>
<td>$M_{\text{app}}^b$ (gmol$^{-1}$)</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>20</td>
<td>299</td>
<td>5</td>
<td>345</td>
</tr>
<tr>
<td>50</td>
<td>177</td>
<td>2</td>
<td>155</td>
</tr>
<tr>
<td>100</td>
<td>106</td>
<td>0</td>
<td>101</td>
</tr>
<tr>
<td>150</td>
<td>90</td>
<td>0</td>
<td>85</td>
</tr>
</tbody>
</table>

Table 4.1 Apparent molar mass ($M_{\text{app}}$) and number of transferred solvent molecules ($\alpha$) for the PEDOT film in 0.1 M LiClO$_4$/ACN, 0.1 M NBu$_4$ClO$_4$/ACN, and 0.1 M KPF$_6$/ACN. The RMM values for the electrolyte components are ACN = 44, ClO$_4^-$ = 99, PF$_6^-$ = 144, Li$^+$ = 7, NBu$_4^+$ = 242, K$^+$ = 40

\(^b\) $M_{\text{app}}$ was acquired by calculating $\Delta m/\Delta Q$ using least squares. There is some error in the determination of the slope ($R^2 = 0.99$). However, $M_{\text{app}}$ is a function of charge propagation, so real error is very difficult to determine. These results are one-off measurements so an average cannot be reported.
At scan rates slower than 100mV/s the values of $M_{app}$ were larger than the corresponding value for the RMM of the anion alone. This was interpreted as being the consequence of additional solvent movement associated with the anion transfer\textsuperscript{12,43} \textit{i.e} that $\alpha \geq 1$, \textbf{Equation 4.4}. The value of $\alpha$ varied from 1 up to 6 at very slow scan rates. This could be because; at slower scan rates there was more time for the diffusion of solvent molecules within the polymer film, allowing the film to equilibrate, whereas, at fast scan rates, only the electrostatic interactions are satisfied, resulting in just anion movement. The value of $M_{app}$, and hence $\alpha$, indicated that the solvent moved with the anion. The sign of $\alpha$ signified the direction of the solvent movement (i.e. if $\alpha$ was positive, solvent ingressed into the film, if $\alpha$ was negative solvent was expelled from the polymer). These data are shown graphically in \textbf{Figure 4.14a}.

Variation of experimental time scale (scan rate) facilitated the exploration of the kinetic effect, including relative rates of movement of solvent and counter ion. At faster scan rates, $u > 150mV/s$, a different picture emerged, giving negative values for $\alpha$. Two arguments presented themselves in explanation of this phenomenon:

\begin{itemize}
  \item i) solvent was ejected as a consequence of rapid anion inclusion
  \item ii) the rate of anion inclusion was limited on the time scale of the experiment.
\end{itemize}

The second of the two explanations may be more likely, effectively the rate of potential scan was trapping out anion movement. Such activated processes would probably be sensitive to changes in temperature, but this has not been addressed here.

The shape of the plot of the $M_{app}$ values for the different electrolytes (see \textbf{Figure 4.14b}) generally followed the same trend as for the $\alpha$ values shown in \textbf{Figure 4.14a}. In all but the slowest scan rate the $M_{app}$ values for 0.1M KPF$_6$/ACN were larger, reflecting the movement of the heavier PF$_6$- anion. However, the number of solvent molecules associated to an anion within the polymer film in 0.1M KPF$_6$/ACN was very similar to the electrolytes containing ClO$_4^-$. At the faster scan rates of 100, 150 and 200mV/s, no solvent molecules were associated with the anion regardless of its size.
Figure 4.14 a) number of transferred solvent molecules ($\alpha$) and b) apparent molar mass ($M_{app}$) for the PEDOT film at each of the scan rates evaluated in 0.1M LiClO$_4$/ACN, 0.1M NBu$_4$ClO$_4$/ACN, and 0.1M KPF$_6$/ACN.

The method described above calculates $M_{app}$ values that represent an average for the corresponding potential range. However, the derivative $dm/dQ$ can also be used to calculate $M_{app}$ in order to obtain a potential dependent value$^{12}$. Differential analysis tends to increase the noise in any data; however, in order to decrease the noise in the $M_{app}$ values, the data were smoothed using a sliding average.
Figure 4.15 is the $M_{\text{app}}$ plot for all three cycles of a PEDOT film in 0.1M LiClO$_4$/ACN. It can be seen that the apparent molar mass incorporated during the oxidation process was fully expelled during reduction. This occurred in all three cycles of the film, demonstrating the reversibility of the process i.e. there was no (or little) charge mass hysteresis. Figure 4.15 and Figure 4.16 show the value of $M_{\text{app}}$ as a function of potential throughout the CV scan. Consequently, if the identity of mobile species remained constant throughout the scan, these plots would resemble step functions. However, it was clear that at the beginning and end of the charging process, the value of $M_{\text{app}}$ was smaller than the maximum value. This tends to suggest that in the initial and final phases of doping/undoping, the expulsion of solvent masked the movement of the anion.

A comparison of the PEDOT film, cycled at 100mV/s in all three electrolytes, can be seen in Figure 4.16. When cycled in 0.1M KPF$_6$/ACN, the largest molar mass incorporated into the film represented a PF$_6^-$ anion (RMM = 144), accompanied by the equivalent of half a solvent molecule. The results for 0.1M LiClO$_4$/ACN and 0.1M NBu$_4$ClO$_4$/ACN were very similar. At this scan rate, only ClO$_4^-$ contributed to the apparent molar mass of the film.
Figure 4.16 $M_{\text{app}}$ plot for the first cycle of the PEDOT film cycled at 100mV/s in different electrolytes: 0.1M LiClO$_4$/ACN, 0.1M NBu$_4$ClO$_4$/ACN, and 0.1M KPF$_6$/ACN. The dashed lines represent the RMM values for the anions.

In order to compare the $M_{\text{app}}$ plots of PEDOT at different scan rates, the charge data in the subsequent figures were divided by the scan rate. Figure 4.17 contains the $M_{\text{app}}$ data for PEDOT cycled at different scan rates in 0.1M LiClO$_4$/ACN. At the fast scan rates of 150 and 200 mV/s the $M_{\text{app}}$ value was approximately 100 after the initial ion/charge injection. This would indicate that only the ClO$_4^-$ ion was moving during cycling.

In the centre of the plot for the film cycled at 100mV/s, the $M_{\text{app}}$ value was again 100. However, the increase in $M_{\text{app}}$ was much slower at the beginning of the scan, and dropped off at the end of the cycle, even though charge was still increasing. This would suggest that in the middle of the potential region only ClO$_4^-$ ions were moving. Yet, at low potential values, something other than perchlorate (solvent) was moving within the PEDOT film. At the two slower scan rates of 20 and 50mV/s extremely large $M_{\text{app}}$ values were observed, indicating that something other than ClO$_4^-$ was moving in and out of the film. In the case of PEDOT at 50mV/s the $M_{\text{app}}$ value was 180. This suggests that two molecules of solvent were also moving in the film.
The $M_{\text{app}}$ data for PEDOT cycled at different scan rates in 0.1M NBu₄ClO₄/ACN can be found in Figure 4.18. The same observations made in 0.1M LiClO₄/ACN were seen in the plots for 0.1M NBu₄ClO₄/ACN. The results for 150mV/s (---) have been discounted in this discussion, as the $M_{\text{app}}$ value was virtually 0 throughout the potential cycle. This was anomalous, and probably due to instrumental malfunction.
During cycling at 200 and 100mV/s, ClO$_4^-$ was the only mobile species during the majority of the potential cycle (see Figure 4.18). However, at extremes of potential solvent was again observed moving out of the film when cycling at 100mV/s. At slower scan rates of 20 and 50mV/s solvent also appeared to be ingressing into the film along with ClO$_4^-$ . It was concluded that cation substitution did not change the behaviour of the film, which was consistent with data presented in Chapter 3.

The effect of anion substitution can be seen in the equivalent plot for PF$_6^-$ in Figure 4.19. The $M_{\text{app}}$ values for the PEDOT film at 200, 150 and 100 mV/s were approx. 145, indicating that only PF$_6^-$ was moving within the film at these scan rates. Yet, at the slower scan rates of 50 and 20mV/s the $M_{\text{app}}$ values were much higher, demonstrating that more than the anion was being incorporated into the film with potential. Mass was lost from the film, though charge was still being incorporated into PEDOT. This would suggest that solvent was being expelled from the film.

![Figure 4.19 $M_{\text{app}}$ plot for the PEDOT film cycled in 0.1M KPF$_6$/ACN at different scan rates: 20, 50, 100, 150, and 200mV/s.](image)

Large numbers of solvent molecules were not accompanying ion transfer at fast scan rates because the electrode kinetics of the film were much faster than the rate of diffusion of the solvent. However, at slow scan rates there was time for the mass transport reactions within the film to take place and be recorded.
4.3.2 Calculation of the Mass Fluxes within the PEDOT Film. The total mass of the film, \( M_{[\text{film}] \rangle} \), must have been the sum of the mass of the polymer, \( M_{[\text{polymer}] \rangle} \), combined with the mass of the anion, \( M_{[\text{anion}] \rangle} \), and the mass of the solvent, \( M_{[\text{solvent}] \rangle} \), contained within the polymer film (see Equation 4.5).

\[
M_{[\text{film}] \rangle} = M_{[\text{polymer}] \rangle} + M_{[\text{anion}] \rangle} + M_{[\text{solvent}] \rangle} \quad (\text{Equation 4.5})
\]

Hence, the total mass flux of the film, \( \frac{dm_{[\text{film}] \rangle}}{dt} \) (see Figure 4.20) must have been the sum of the differential of the mass of the anion and the solvent. The mass of the polymer was not included in Equation 4.6 as \( \frac{dm_{[\text{polymer}] \rangle}}{dt} \) will always be zero as the mass of the polymer on the electrode does not change, i.e.

\[
\frac{dm_{[\text{film}] \rangle}}{dt} = \frac{dm_{[\text{anion}] \rangle}}{dt} + \frac{dm_{[\text{solvent}] \rangle}}{dt} \quad (\text{Equation 4.6})
\]

where \( \frac{dm_{[\text{anion}] \rangle}}{dt} \) and \( \frac{dm_{[\text{solvent}] \rangle}}{dt} \) is the mass flux of the anion and the solvent respectively.\(^{12}\)

![Figure 4.20](image)

*Figure 4.20* The mass flux of the film during redox cycling (100mV/s) of PEDOT in 0.1M LiClO\(_4\)/ACN.
By assuming that all passed charge leads to the incorporation of anion within the film, the mass flux of the anions $dm[\text{anion}]/dt$ (see Equation 4.7 and Figure 4.21) was calculated:

$$\frac{dm[\text{anion}]}{dt} = i \frac{M}{zFA} \quad \text{(Equation 4.7)}$$

where $i$ is the current, $A$ is the area of the electrode and $M$ and $z$ are the molar mass and the valence of the anion respectively.

![Figure 4.21](image)

**Figure 4.21** The mass flux of anion during redox cycling (100mV/s) of PEDOT in 0.1M LiClO\textsubscript{4}/ACN.

Once $dm[\text{anion}]/dt$ and $dm[\text{film}]/dt$ had been calculated using the $i$ vs. $t$ and $\Delta m$ vs. $t$ plots respectively, the mass flux of the solvent, $dm[\text{solvent}]/dt$ (see Figure 4.22), was calculated by subtracting the $dm[\text{anion}]/dt$ response from that of $dm[\text{film}]/dt$.

**Figure 4.23** shows the calculated mass fluxes for the PEDOT film cycled in 0.1M LiClO\textsubscript{4}/ACN. The mass flux of the anion remained virtually constant through the whole of the potential window. It was only at the extremes of potential that a gradual rise (or fall) in mass was seen. In contrast, there was a sharp decrease in the mass flux of the solvent with potential until 0.1V, followed by a gradual increase. There was a
potential region of 0.2-0.8V where solvent did not move. Solvent was then lost from the film until the direction of potential was reversed. Solvent within the film did not move between 0.8 and 0.2V in the reduction of the film. This was followed by an increase in solvent until the end of the cycle was reached.

Figure 4.22 The mass flux of solvent during redox cycling (100mV/s) of PEDOT in 0.1M LiClO₄/ACN.

A comparison of the calculated mass fluxes for the PEDOT film cycled in 0.1M NBU₄ClO₄/ACN can be seen in Figure 4.24. At the beginning of the redox cycle, solvent was rapidly ejected from the film. A change in the mass flux of the solvent was not observed again, until the end of the potential range, when more solvent was lost from the system. As the direction of potential was reversed, there was a sharp ingress of solvent into the film. This quickly stabilised, until after 0V when more solvent entered into the film.
The fluxes in Figure 4.23 and Figure 4.24 are of a similar magnitude, consistent with the movement of the same mobile species \( i.e. \) ACN and \( \text{ClO}_4^- \). Total mass flux was close to zero at each end of the scan, but since the current was not zero in these regions, then ion flux must be balanced by solvent flux in the opposing direction.
Figure 4.25 shows the mass fluxes of anion, film, and solvent, calculated for the PEDOT homopolymer cycled in 0.1M KPF₆/ACN at 100mV/s. In contrast to the ClO₄⁻ anion, the mass flux of PF₆⁻ did not stabilise during the potential cycle. It was clear that the solvent was moving in and out of the film during the whole potential cycle. The overall effect of oxidation was the increase in the mass flux of anions within the film. On reduction, the amount of anion within the film gradually decreased. As a result, the total mass flux of solvent steadily increased during reduction. Detailed analysis of the data was limited by the resolution, as the numerical differentiation produced very noisy data.

Figure 4.25 Comparison of the mass fluxes during redox cycling (100mV/s) of PEDOT in 0.1M KPF₆/ACN. Arrows indicate the direction of the potential scan. For the CV see Figure 4.9c.

4.4 Conclusion

The behaviour (distribution of solvent and roughness) of a PEDOT homopolymer under potential control has been studied. Selective deuteration of the solvent highlighted the solvation properties of the polymer film. It was discovered that PEDOT has a high solvation in both the reduced and fully oxidised states. This may allow for the easy movement of the ions required to maintain electroneutrality during
redox cycling, without the need for any structural reorganisation, or expansion of the polymer film. This could be significant in explaining the stability of PEDOT films to extended periods of repetitive cycling, compared to many other conducting polymer systems. The film swelled by ~30% from the dry to the solvated polymer film, providing further evidence that the matrix was able to accommodate the ingress of solvent species. The large solvation of the electrodeposited PEDOT films may explain the unexpectedly small ‘mass’ changes seen in quartz crystal microbalance experiments.

The EQCM investigations of PEDOT films in different electrolytes indicate that charge was incorporated into the polymer film at the same rate, even at the extremes of potential where a mass change was not observed i.e. in the latter stages of doping (or undoping), charge was injected (or removed) with no apparent mass (frequency) change. A reversible exchange of anions and solvent was observed during redox cycling. Variation of scan rate has facilitated the exploration of the kinetic effect, including relative rates of movement of solvent and counter ion.

At 100 < \nu < 150 \text{ mV/s} \text{ the anion was the dominant mobile species with little or no solvent transfer. At } \nu < 100 \text{ mV/s} \text{ the values for } M_{\text{app}} \text{ are larger than the corresponding RMM value of the anion alone. This was interpreted as the consequence of additional solvent movement associated with the anion transfer. At faster scan rates, } \nu > 150 \text{ mV/s} \text{, a different picture emerges, giving negative values for } \alpha. \text{ This was because the rate of anion inclusion is limited on the time scale of the experiment; effectively the rate of potential scan is trapping out anion movement. Ions and large numbers of solvent molecules were not observed moving at fast scan rates because the electrode kinetics of the film was much faster than the rate of diffusion of the solvent. However, when the film was cycled at slow scan rates there was time for the mass transport reactions within the film to take place and be recorded.}

The \( M_{\text{app}} \) values representing an average across the potential range agreed with the potential dependent \( M_{\text{app}} \) values. \( M_{\text{app}} \) values for the different electrolytes generally followed the same trend, with larger values for 0.1M KPF\(_6\)/ACN, reflecting the movement of the heavier PF\(_6^-\) anion. The difference in the mass of the anion appeared...
to have no affect on the number of solvent molecules associated with it and cation substitution did not change the behaviour of the film.

The mass fluxes for 0.1M LiClO$_4$/ACN and 0.1M NBu$_4$ClO$_4$/ACN are of a similar magnitude, consistent with the movement of the same mobile species i.e. ACN and ClO$_4^-$. Total mass flux was close to zero at each end of the scan, but since the current was not zero in these regions, then ion flux must be balanced by solvent flux in the opposing direction. In contrast to the ClO$_4^-$ anion, the mass flux of PF$_6^-$ did not stabilise during the potential cycle. It was clear that solvent was moving in and out of the film during the whole potential cycle. The overall effect of oxidation was the increase in the mass flux of anions within the film. On reduction, the amount of anion within the film gradually decreased. As a result, the total mass flux of solvent steadily increased during reduction.

An in situ NR technique has been developed for dynamic electrochemical studies, allowing the simultaneous acquisition of population changes of the individual components within polymer films, as functions of time and distance. Under dynamic redox switching conditions, PVF films show hysteresis in swelling, incomplete desolvation upon reduction and temporary salt retention. These effects are more prominent at slower scan rates and therefore respond to experimental time scale.

Solvation flux was not observed in the EQCM results within the potential region of the NR experiment, confirming that PEDOT remained highly solvated in both the neutral and oxidised state. Monitoring the charge of the polymer film further reinforced the model of the easy movement of ions, as after an initial injection, charge remained constant within the polymer. The peak current did not drop after a maximum was reached, suggesting that the electrode kinetics were not mass transport limited. It has been illustrated (by the combination of NR, EQCM and CV) that in the case of the EDOT homopolymer, no exchange of solvent accompanies the incorporation of anions required to maintain electroneutrality within the film.
4.5 References

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Multilayers of EDOT and BT

The ratio in which two monomers combine to form a copolymer is determined by the composition of the feed solution and the relative reactivities of the two monomers. As discussed previously, if a monomer with a high reactivity ratio is combined with a monomer with a low reactivity ratio, the resulting copolymer will predominantly contain the monomer with the high reactivity ratio and will therefore, not exhibit the desired combination of the properties of both monomers. This poses a problem if it is imperative to combine two monomers with very different reactivity ratios.

A solution to the problem could be to construct a layered structure from the two monomers. However, it is unknown whether a layered structure will have similar properties as the desired copolymer or whether they will be completely different. Here, a 0.5 EDOT:0.5 BT copolymer system was compared with films made up of layers of EDOT and BT, in order to gain further insight into how the structure affected the properties of the film. The characteristics of the layered films were also compared to the properties of the homopolymers of BT and EDOT.

In an ideal bilayer system a conjugated polymer (polymer A) with a given oxidation potential is electrodeposited onto a substrate, and another polymer layer (polymer B) is electrodeposited directly on top of polymer A. If polymer B has a higher oxidation potential than polymer A, a peak will be observed at the oxidation potential of polymer A, followed by a peak at the oxidation potential of polymer B, with a peak current due to the sum of polymer A and B. If it is not the case that the inner polymer layer has a lower oxidation polymer than the outer layer, then the inner layer will act as an electrical insulator and prevent the oxidation of the outer layer at potentials below the oxidation potential of polymer A. Once the oxidation of the inner layer is reached a massive influx of charge due to both polymers will be witnessed. The outer film, isolated from the electrode by the inner polymer A, undergoes electron-transfer reactions with the electrode via electron-transfer mediation by redox states of the
inner film. Electron transfer is accompanied by the charge compensating flow of anionic counterions, associated with solvent, and involved in polymer chain motions. The outer layer cannot become oxidised, until the inner layer has reached its oxidation potential, as ideally, no mechanism exists for electron transport between the outer layer and the electrode at lower potentials. At potentials greater than the highest oxidation potential the flow of electrochemical charge will be equivalent to the combined total of electroactive sites in the two redox polymers.

If the inner/outer film interface is not physically sharply defined, intermingling of outer-film redox sites into the inner films carried the danger of those sites achieving contact with the electrode surface for electron flow directly to the outer film at its own oxidation potential.

Neutron Reflectivity (NR) was used to create depth profiling of the homopolymers of d₄-EDOT and BT and bilayers containing d₄-EDOT/BT and BT/d₄-EDOT (see Figure 5.1) By using the deuterated EDOT monomer instead of commercially bought EDOT, it was possible to highlight the EDOT component of the bilayer films. The same films which were deposited for neutron analysis were also characterised using spectroelectrochemistry and AFM. This allowed the thickness of the films to be recorded and compared with the values used in the model fitting procedure and for the spectroscopic properties of the bilayers to be compared with the copolymers discussed in Chapter 3.

![Figure 5.1](image)

**Figure 5.1** Structure of the d₄-EDOT and BT homopolymers along with a schematic of the layered systems.
A copolymer made from a feed solution containing 0.5 EDOT: 0.5 BT was deposited onto a quartz crystal, and compared with films made up of layers of EDOT and BT (EDOT/BT/EDOT/BT and BT/EDOT/BT/EDOT). An Electrochemical Quartz Crystal Microbalance (EQCM) was then used to acquire information on the ion and solvent movements within the films.

5.1 Spectroelectrochemistry

The in situ electrochromic properties of polymer films during doping and dedoping were characterised using spectroelectrochemistry. The homopolymers and bilayers containing d4-EDOT and BT were the same films described in the NR section of this chapter. In the following results, the homopolymers and bilayers have been potentiodynamically cycled three times from 0V to +1.2V.

The 3D plots (Figure 5.2a and b) for the BT homopolymer indicated that at 0V, a peak at 500nm was present. This dropped off quickly as the potential increased, until +1.2V was reached, where a narrow plateau was formed. A new extremely sharp peak was observed between 600 and 900 nm which only spanned the width of the narrow plateau. A further peak was also observed at 0V between 1000 and 1200nm. This was smaller than the peak at 500nm and no narrow plateau was seen. This broad feature around 1100nm in the neutral polymer was difficult to explain as a conduction band should not exist. The data presented are raw spectra as it was difficult to obtain individual background spectra for the films because of the nature of the cell. Therefore, this feature is likely to be an artefact of the background. These data were presented to highlight the changes in spectra with potential.

* Measurements were carried out on a homebuilt spectrophotometer at the Electronics Department, Glasgow University
The d$_4$-EDOT homopolymer (Figure 5.3) film tested was extremely thin. The absorbance was initially low at 0V, but this increased with potential, until +1.2V where a peak was formed, spanning between 500 and 1200nm. After +1.2V, the absorbance began to decrease and a plateau was observed at 0V. The plot for d$_4$-EDOT was different to that observed previously in Chapter 3. This is because, in hindsight, the potential range chosen for this experiment was not wide enough to incorporate the whole of the d$_4$-EDOT electrochemical p-doping response that had been witnessed before. As a result, the peak between 500 and 600nm, which would be at approximately -0.5V in this plot, is not seen, but the features of the conduction
band are highlighted. The results in Figure 5.3a and b can be attributed to the conduction band of d₄-EDOT, the beginnings of which were previously seen in Chapter 3.

![Figure 5.3](image)

**Figure 5.3** a) and b) Two views of the 3D plot of the spectra of the d₄-EDOT homopolymer cycled in 0.1M NEt₄ClO₄/ACN at a scan rate of 20mV/s.

The 3D plots of the BT/d₄-EDOT bilayer film (see Section 2.7.1), in Figure 5.4a and b, incorporated features of both the homopolymers. The peaks at 0V between 400 and 600nm were due to the BT content of the film, as it has been established that a potential lower than investigated here was required to produce a peak for d₄-EDOT around 500nm. A small ridge was seen in the BT homopolymer film at +1.2V.
spanning from 700 to 900 nm. However, in the BT/d4-EDOT bilayer there was a pronounced peak at +1.2 V spanning from 600 to 1200 nm and beyond. This feature was caused by the d4-EDOT component of the bilayer. The peaks in between the ridges after 1000 nm were from BT.

Figure 5.4 a) and b) Two views of the 3D plot of the spectra of the BT/d4-EDOT bilayer cycled in 0.1 M NEt4ClO4/ACN at a scan rate of 20 mV/s.

The spectra of the d4-EDOT/BT bilayer (Figure 5.5a and b), exhibited only small differences from that of the BT/d4-EDOT bilayer film in Figure 5.4a and b. In comparison, there was no ridge between the peaks above 1000 nm, probably because the d4-EDOT response was masked by the outer BT layer. The peaks above 1000 nm
also spanned a larger wavelength beyond the detection limits of the instrument. This feature had not previously been seen.

Figure 5.5 a) and b) Two views of the 3D plot of the spectra of the d4-EDOT/BT bilayer cycled in 0.1M NEt4ClO4/ACN at a scan rate of 20mV/s.

A 2D cross-section plot for the BT/d4-EDOT bilayer in Figure 5.4a and b, taken at two points on the wavelength scale (500 and 650nm) corresponding to the peaks $\lambda_{\text{max}}$ values attributed to the optical absorbance and the conduction band is presented in Figure 5.6. The two traces showed the absorption of the bilayer film as a function of potential taken at 500 and 650nm. The 500nm trace showed the optical transition; on
going from 0 to +1.2V, the absorption trace moved from its maximum value (blue colour) to a minimum. At this minimum the absorbance was low and the film appeared colourless as discussed in Chapter 3. In contrast, the 650nm trace showed a very rapid increase at anodic potentials close to +1V. This represented the formation of the conduction band and occurred in complementary sequence to the bleaching of the optical absorbance.

![Absorption vs. Potential](image)

**Figure 5.6** A cross-section of the 3D plot for the BT/d₄-EDOT bilayer taken at 500 and 650nm. The data has been normalised by dividing the absorbance value with the maximum absorbance value for that wavelength.

The differential of the data in **Figure 5.6** was calculated in order to observe the change in absorbance with potential at the two wavelength values. The difference in the changes of absorbance for the two wavelengths was clearly illustrated. Up until +0.4V on the potential scale, there was no change in absorbance at either wavelength. After this, the absorbance began to sharply decrease for the 500nm trace until +0.6V, where a slow increase in absorbance was observed, peaking at +1.2V. On the reduction sweep, the absorbance sharply increased until +1.0V when it began to slowly decrease. In marked contrast, the absorbance initially increased for the trace at 650nm, until +1.0V where it continued to gradually decrease until +1.0V was passed again on the return sweep. The absorbance then began to again increase, until +0.4V when it flattened out. **Figure 5.7** shows the differential absorbance for both traces (**Figure 5.6**); this demonstrated that decrease in optical absorbance was synchronised with the onset of electronic conduction.
Figure 5.7 The differential plot of the data in Figure 5.6 for the BT/d$_4$-EDOT bilayer at 500 and 650nm. The arrows depict the direction of potential.

The CVs of both homopolymers and both bilayers recorded simultaneously with the absorbance spectra can be seen in Figure 5.8. As there are no peaks observed in the trace for the d$_4$-EDOT homopolymer, it is extremely difficult to predict and discuss the CV of an ideal bilayer (two discrete layers) of d$_4$-PEDOT and polyBT. However, the current response of d$_4$-PEDOT and polyBT has been summed to give an indication of an ideal bilayer response and is presented in Figure 5.9 along with the CVs for the two bilayers.

Figure 5.8 Cyclic voltammograms of the d$_4$-EDOT and BT homopolymers and the d$_4$-EDOT/BT and BT/ d$_4$-EDOT bilayers potentiodynamically cycled from 0 to +1.2V, 20mV/s in 0.1M NEt$_4$ClO$_4$/ACN.
The magnitude of current observed for each film is very different because of the variation in thickness of the films. In order to allow direct comparison of the responses in Figure 5.9, the current has been normalised. Without any clear oxidation peaks for d₄-PEDOT it is difficult to comment on the bilayer responses, however, there appears to be no large shift in the oxidation peak for polyBT.

![Graph of current vs potential](image)

**Figure 5.9** A calculated ideal bilayer response overlaid with normalised cyclic voltammograms of the d₄-EDOT/BT and BT/d₄-EDOT bilayers potentiodynamically cycled from 0 to +1.2V at 20mV/s in 0.1M NEt₄ClO₄/ACN.

### 5.2 Atomic Force Microscopy (AFM)

The thicknesses of films deposited for NR in Section 5.3 were measured using AFM. Homopolymers and bilayers containing d₄-EDOT and BT were grown from separate solutions of the d₄-EDOT and BT monomer for NR, as described in the experimental section.

**Figure 5.10** depicts the AFM measurement taken for the BT/d₄-EDOT bilayer film. The film was scratched in order to measure the thickness of the layers with respect to the underlying substrate, a silicon block. The quartz substrate, gold layer and bilayer film were all clearly illustrated.
The AFM images were taken of all the films grown for NR and the Nanoscope 6.13 software was used to calculate the thickness of the polymer films. The thickness values in Table 5.1 agree with the values generated in the calculation of the model fits for the NR data.

<table>
<thead>
<tr>
<th>Film</th>
<th>Thickness / Å (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT Homopolymer</td>
<td>660 (66)</td>
</tr>
<tr>
<td>d₄-EDOT Homopolymer</td>
<td>570 (57)</td>
</tr>
<tr>
<td>d₄-EDOT/BT Bilayer</td>
<td>710 (71)</td>
</tr>
<tr>
<td>BT/ d₄-EDOT Bilayer</td>
<td>1000 (100)</td>
</tr>
</tbody>
</table>

Table 5.1 Thickness values for the homopolymer and bilayer films recorded using AFM.
Figure 5.11 illustrates the AFM measurements taken for the BT and d$_4$-EDOT homopolymer films. It was observed that the d$_4$-PEDOT film was much smoother and more closely packed (Figure 5.11b) than the BT homopolymer (Figure 5.11a).

Figure 5.11 AFM images of a) the BT homopolymer and b) the d$_4$-EDOT homopolymer film investigated in the NR section.
The large features observed in the AFM images are due to fragments of the polymer material that became detached from the film by scratching the sample to obtain the thickness measurement. These fragments then stuck to the surface of the polymer, close to the edge of the scratch. It has been proven in a previous experiment, that further away from the area that had been scratched, the surface of the polymer film was much smoother.

5.3 Neutron Reflectivity (NR)

For NR characterisation, a typical sequence of measurements included the collection of NR profiles for a film in the dry state; and immersed in h- and d- contrasts of solvent (e.g. h-ACN and d-ACN). In this experiment, films of d4-EDOT and BT homopolymers along with two bilayers of d4-EDOT/BT and BT/d4-EDOT were prepared by electrodepositing the monomer solutions onto a gold-coated quartz block. Full details are given in the experimental chapter.

The objective was to investigate the structure of the polymer film formed from growing the bilayer films, and to compare the distributions of solvent species within the films. By using the deuterated EDOT monomer instead of commercially bought EDOT, it was possible to highlight the EDOT component of the bilayer films. For the response of each monomer to be evident it was necessary to increase the scattering length ($N_b$) of EDOT by exchanging hydrogen for deuterium, creating a contrast with the $N_b$ of the BT monomer. Insight into the distribution of the solvent was gained by collecting the NR profiles of the films in hydrogenous and deuterated ACN. Figure 5.12 shows the reflectivity profiles overlaid with the model fits for the dry BT and d4-EDOT homopolymers, along with the BT/d4-EDOT and d4-EDOT/BT bilayers.
Figure 5.12 NR measurements (dots) and model fits (lines) for the dry films: BT (---), d$_4$-EDOT (--), d$_4$-EDOT/BT (---), and BT/d$_4$-EDOT (---). The data was offset by intervals of 100 for clarity.

Figure 5.13 shows the model N$_h$ profiles that provided the best fits to the reflectivity data. The N$_h$ of the dry BT and d$_4$-EDOT homopolymer films were 2.2e$^{-6}$ and 4.7e$^{-6}$ Å$^{-2}$ respectively. These are in good agreement with the calculated N$_h$ values for the films which were 1.9e$^{-6}$ Å$^{-2}$ (assuming $\rho = 1.2$) for BT and 4.74e$^{-6}$ Å$^{-2}$ (assuming $\rho = 1.4$) for d$_4$-EDOT.

It can be seen from Figure 5.13 that the dry BT film was approximately twice the thickness of the dry d$_4$-EDOT homopolymer. The d$_4$-EDOT polymer/air interface had a sharp gradient, illustrating that the polymer film was smooth. In contrast, the BT homopolymer film had a gradual slope at the polymer/air interface, depicting a much rougher film. The AFM results reported previously indicated that the polymer films were rougher than witnessed here in the NR results. However, it has already been stated that the surface of the polymer was expected to be smoother further away from the area of the scratch. The surfaces of the polymer films were likely to contain bumps and raised features; however, in NR the roughness of the polymer film was averaged over the whole footprint of the beam, rather than just a small section imaged in AFM.
The profile for the dry d$_4$-EDOT/BT film (Figure 5.13) contained the features expected for a bilayer film. The film appeared to have 3 regions. Close to the electrode it consisted mainly of a region of d$_4$-EDOT (≈ 200Å thick). A small amount of BT (∼ 25%) was incorporated into the band indicated by the drop in N$_b$ from that of the d$_4$-EDOT homopolymer. The next region was the interface between BT and d$_4$-EDOT; this contained approximately 50% BT and was again about 200Å thick. The last region of the film was the BT layer which was much thicker as it spanned 600Å. A small amount of d$_4$-EDOT was present in the layer as the N$_b$ was higher than expected for pure BT.

The dry BT/d$_4$-EDOT film (Figure 5.13) did not exhibit the same separation between the two layers expected in a bilayer. It appeared that the d$_4$-EDOT monomer units penetrated fairly uniformly into the whole of the BT layer. It became apparent that d$_4$-EDOT grew into BT, better than BT grew into d$_4$-EDOT. It was expected that the N$_b$ for the region of the BT/d$_4$-EDOT (see Figure 5.13) next to the Au electrode would be the same or higher than the N$_b$ value for the BT homopolymer film. However, this was not the case; the N$_b$ value actually dropped. The most likely
explanation for this was trapped h-ACN within the film, causing the Nb value to appear lower. There appeared to be a combination of BT and d_4-EDOT at the outer edge of the same film, shown by the slight elevation of the Nb above that of the BT homopolymer. However, the Nb was not as high as that expected for a region containing a high amount of d_4-EDOT, suggesting that the d_4-EDOT monomer was spread across the whole film.

**Figure 5.14** shows the solution reflectivity profiles overlaid with the model fits for the BT and d_4-EDOT homopolymers, along with the BT/d_4-EDOT and d_4-EDOT/BT bilayers, recorded in both d- and h-ACN.

![Figure 5.14](image)

*Figure 5.14* NR measurements (dots) and model fits (lines) for the films in d-ACN and h-ACN. Spectra were offset by intervals of 100 for clarity: BT (---), d_4-EDOT (--), d_4-EDOT/BT (---), and BT/d_4-EDOT (---).

The findings of the profiles for the dry films were further reinforced in the Nb profiles for the homopolymer and bilayer films in d- and h-ACN (see **Figure 5.15** and **Figure 5.16**). In the case of the d_4-EDOT/BT film (**Figure 5.15**), a distinct point was seen just above 600Å, depicting the interface between the d_4-EDOT and BT layers in the
bilayer film. The Nb had a shallow slope at the polymer/solution interface in both solvents, similar to the profile for the BT homopolymer film. It was concluded from this that the outer edge of the film was rough, due to the high BT content.

![Figure 5.15 NR profiles for BT (---), d4-EDOT (-) and d4-EDOT/BT (-) in d-ACN and h-ACN.](image)

The features associated with a bilayer film were not present in the profile for the BT/d4-EDOT bilayer (depicted in Figure 5.16). The film had a higher Nb than expected for pure BT in h-ACN, suggesting that the d4-EDOT monomer had diffused throughout the whole of the BT layer. The Nb of the film was fairly constant throughout the whole film until the polymer/solution interface. This was an unexpected result. If there was a high d4-EDOT content at the outer edge of the film, the Nb would have been much higher than was seen in the experimental results. This further confirmed that the d4-EDOT monomer was spread throughout the whole of the film. However, the polymer/solution interface was influenced by the d4-EDOT component of the film as the interface was much sharper than that of the d4-EDOT/BT bilayer film. The d4-EDOT must have formed a smooth region on the outer edge of the film.
The profile of the BT/d$_4$-EDOT film in d-ACN was different from expected. The $N_b$ of the film close to the gold coated electrode was lower than observed for the BT homopolymer in d-ACN. A probable explanation for this was trapped h-ACN within the film, which lowered the observed $N_b$ of the region. The remnants of h-ACN in the film may have been obscuring the d$_4$-EDOT component of the film which was observed when the BT/d$_4$-EDOT film was tested in h-ACN.

![NR profiles for BT (---), d$_4$-EDOT (--), and BT/d$_4$-EDOT (---) in d-ACN and h-ACN.](image)

The solvent volume fractions of the four films plotted in Figure 5.17 highlighted the difference in the two bilayer films. The percentage of solvation at the Au interface of the d$_4$-EDOT/BT bilayer film was the same as expected for the d$_4$-EDOT homopolymer. The overlap between the d$_4$-EDOT and BT layers was portrayed in the gradual decrease of solvation until there appeared to be no solvent molecules in the film. The most likely explanation for this was the tight packing of BT molecules in between those of the d$_4$-EDOT layer, restricting the expansion of the matrix, preventing solvent from ingressing into the film. The high BT content of the outer region of the film was observed by a gradual increase in solvation up to the polymer/solvent interface.
The volume solvent plot for the BT/d$_4$-EDOT film (Figure 5.17) further confirmed that d$_4$-EDOT had grown throughout the BT layer. The level of solvation was much lower than expected for either of the homopolymer films. This was again probably due to the tight packing of the d$_4$-PEDOT and BT monomers within film, leaving no holes within the polymer structure for the solvent to occupy. The solvation of the film increased as it became predominantly d$_4$-EDOT as the monomers were less tightly packed, leaving more space for the solvent molecules to occupy.

![Figure 5.17 Volume solvent fractions for BT (-), d$_4$-EDOT (--), d$_4$-EDOT/BT (---), and BT/d$_4$-EDOT (-----) in ACN.](image)

In conclusion, NR showed that the structures behaved partly as layers, but that the layers were quite diffuse. This is consistent with the similarity in behaviour of the spectroscopic properties observed for the copolymer system.
5.4 *Electrochemical Quartz Crystal Microbalance (EQCM)*

The doping/dedoping behaviour of a 0.5 EDOT: 0.5 BT (0.5E:0.5B) copolymer and two multilayers of EDOT/BT/EDOT/BT (E/B/E/B) and BT/EDOT/BT/EDOT (B/E/B/E), were investigated using the EQCM technique. The films were cycled in solutions of 0.1M LiClO$_4$/ACN and 0.1M NBu$_4$ClO$_4$/ACN, at scan rates of 5 and 20mV/s. The ion transfer reactions of the films during doping and undoping were examined and compared using EQCM.

The deposition of a film onto a quartz crystal will cause a frequency shift, $\Delta f$. From this the surface coverage, $m$, of the polymer film was calculated. Assuming a density of $\rho = 1.5$g cm$^{-3}$, a layer thickness was calculated (see Table 5.2). The films were conditioned and cycled in clean solutions of 0.1M LiClO$_4$/ACN and 0.1M NBu$_4$ClO$_4$/ACN at 5 and 20mV/s.

<table>
<thead>
<tr>
<th></th>
<th>0.5E:0.5B</th>
<th>E/B/E/B</th>
<th>B/E/B/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta f$ (kHz)</td>
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<td>5.00</td>
<td>9.24</td>
</tr>
<tr>
<td>$m$ ($\mu$g cm$^{-2}$)</td>
<td>63.37</td>
<td>23.94</td>
<td>44.18</td>
</tr>
<tr>
<td>Layer thickness (nm)</td>
<td>422</td>
<td>160</td>
<td>295</td>
</tr>
</tbody>
</table>

Table 5.2 Frequency shift, mass density and layer thickness for each of the homopolymers, copolymer and multilayer films.

5.4.1 Layered Structures. Figure 5.18 shows the current trace of the E/B/E/B multilayer film under potential control in the two electrolytes, collected while the mass of the quartz crystal was being recorded.
It was initially observed that the mass increased slowly; however, after +0.1V was reached a faster increase in mass was observed (see Figure 5.19). This mass increase slowed after +1.1V was reached and the mass change had begun to level off when +1.2V was reached. At first, after the direction of the potential had been reversed, the mass continued to increase, until +1.0V was reached. After this, mass was lost at the same rate as it was incorporated into the film. The same observations were made during the second and third cycles of the film.
The charge density of the polymer films was calculated from the CV, using Equation 4.2. Figure 5.20 is a plot of the charge density of the E/B/E/B multilayer film versus potential. Initially, the charge density of the film increased slowly, but after +0.1V was reached, the rate at which charge was incorporated into the film increased. After +1.1V, a sharp increase was seen in the rate charge was incorporated into the film. Charge continued to increase at this rate after the potential was reversed until +1.0V.
The same feature was seen in the mass versus potential plot. As charge also increased, it can be concluded that anions must still have been incorporated into the film after the scan direction had been reversed. As with Figure 5.19, charge was lost at the same rate as it was incorporated into the film, and exactly the same behaviour was seen in the second and third cycles of the film.

It can be seen in Figure 5.21 that plotting the changing mass against charge density instead of potential changed the shape of the plot. The mass of the film increased steadily as charge was incorporated into the E/B/E/B film. After 0.002 Ccm\(^{-2}\) of charge had been incorporated into the film, the increase of mass in the film began to slow down, however, the charge still increased. After 0.006 Ccm\(^{-2}\) both the charge and mass began to decrease at a steady rate. This continued until a new potential cycle was started and only 0.004 Ccm\(^{-2}\) remained in the film.

![Figure 5.21](image)

Figure 5.21 A plot of mass change versus charge for the EDOT/BT/EDOT/BT multilayer film cycled in 0.1 M LiClO\(_4\)/ACN at 5mV/s

The $\Delta M(E)$, $Q(E)$ and $\Delta M(Q)$ plots for the B/E/B/E layered film exhibited very similar features to the plots illustrated above for the E/B/E/B film (see Figure 5.19-Figure 5.21). A comparison of the apparent molar mass, the number of transferred solvent molecules and the mass fluxes for both of the layered structures is made later in this section.
5.4.2 Copolymer Film. Figure 5.22 shows the current trace of the 0.5E:0.5B copolymer film under potential control in the two electrolytes, collected while the mass of the quartz crystal was being recorded.

![Graph a)](image)

![Graph b)](image)

Figure 5.22 0.5E:0.5B copolymer film cycled in a) 0.1M LiClO₄/ACN, and b) 0.1M NBu₄ClO₄/ACN at scan rates of 5 and 20mV/s.

Figure 5.23 shows three plots for the 0.5E:0.5B copolymer film. The same trends observed for the multilayer film can be seen here. The mass and charge of the film again continued to increase for a short time after the direction of the potential had been reversed. The scales for charge and mass were much larger than in the multilayer as it was a much thicker film.
Figure 5.23  a) a plot of mass change versus potential; b) a plot of charge versus potential, and c) a plot of mass change versus charge for the 0.5 EDOT/0.5 BT copolymer film cycled in 0.1M LiClO4/ACN at 5mV/s
5.4.3 Calculation of the Apparent Molar Mass and the Number of Transferred Solvent Molecules. The apparent exchanged molar mass was calculated using Bund and Neudecks formula\(^2\), as explained in Equation 4.3. The flatter part of the mass charge plots (see Figure 5.21 and Figure 5.23c), where the mass increase slowed down, was not included in the gradient calculation. The same analysis procedure was carried out on all data for the films in both electrolytes, and at the two different scan rates.

A comparison of the apparent molar mass (\(M_{\text{app}}\)) and number of transferred solvent molecules (\(\alpha\)) (calculated as described in Chapter 4) for both the copolymer and the layered systems is presented in Table 5.3.

<table>
<thead>
<tr>
<th>Scan Rate (mV/s):</th>
<th>5</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M_{\text{app}}) (g/mol(^1))</td>
<td>(\alpha)</td>
</tr>
<tr>
<td>LiClO(_4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 E: 0.5 B</td>
<td>181</td>
<td>2</td>
</tr>
<tr>
<td>E/B/E/B</td>
<td>135</td>
<td>1</td>
</tr>
<tr>
<td>B/E/B/E</td>
<td>135</td>
<td>1</td>
</tr>
<tr>
<td>NBu(_4)ClO(_4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 E: 0.5 B</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td>E/B/E/B</td>
<td>78</td>
<td>0</td>
</tr>
<tr>
<td>B/E/B/E</td>
<td>243</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 5.3 Apparent molar mass (\(M_{\text{app}}\)) and number of transferred solvent molecules (\(\alpha\)) for the copolymer and multilayer films in 0.1M LiClO\(_4\)/ACN and 0.1M NBu\(_4\)ClO\(_4\)/ACN

If only the anion moves during redox cycling, the \(M_{\text{app}}\) and \(\alpha\) values for 0.1M LiClO\(_4\)/ACN and 0.1M NBu\(_4\)ClO\(_4\)/ACN ought to be the same. This was the case for the \(\alpha\) values when the film was cycled at 20mV/s, however, at the slower scan rate of 5mV/s they differed (see Figure 5.24).
Figure 5.24 Number of transferred solvent molecules ($\alpha$) for the copolymer and multilayer films at 5 and 20mV/s in 0.1M LiClO$_4$/ACN and 0.1M NBu$_4$ClO$_4$/ACN.

The plots for the $M_{\text{app}}$ values of the multilayers in Figure 5.25 generally exhibited the same trend. There was an inconsistent result when the film was cycled in NBu$_4$ClO$_4$ at 5mV/s, this was probably due to experimental error. The values for the copolymer film differ greatly from those of the two multilayers.

Figure 5.25 Apparent molar mass ($M_{\text{app}}$) for the copolymer and multilayer films at 5 and 20mV/s in 0.1M LiClO$_4$/ACN and 0.1M NBu$_4$ClO$_4$/ACN.
The derivative $dm/dQ$ was also used to obtain potential dependent $M_{\text{app}}$ values. To decrease the noise seen on differentiating, the data was smoothed, and a step function was applied when calculating $M_{\text{app}}$. To accurately compare the subsequent $M_{\text{app}}$ plots for different scan rates, the charge data in subsequent figures was divided by the scan rate. The difference in charge density seen for the three different films in the following $M_{\text{app}}$ plots was due to the fact that all the films were of a different thickness.

Figure 5.26 is the $M_{\text{app}}$ plot for the copolymer and the two multilayers in 0.1M LiClO$_4$/ACN, cycled at 5mV/s. The plots for the multilayers were very similar, after the initial charge injection, the $M_{\text{app}}$ values remained at 150gmol$^{-1}$, until the apparent molar mass was slowly lost. The copolymer appeared to have a much greater apparent molar mass. This began at 200gmol$^{-1}$, though mass was slowly lost as charge increased. This was most likely caused by solvent expulsion from the film.

The $M_{\text{app}}$ data for the same films, cycled at a faster scan rate of 20mV/s, are in Figure 5.27. The multilayers, followed the same trend as above, and had similar $M_{\text{app}}$ values, though these were much smaller than at the slower scan rate. However, the behaviour of the copolymer film had completely changed. Instead of having a larger $M_{\text{app}}$ than the multilayers, it had dropped to about 30gmol$^{-1}$. The trend of the plot had also changed, instead of gradually losing mass as charge density was gained, the film had roughly the same $M_{\text{app}}$ value, until mass was finally lost at the end of the potential window.
The same copolymer and multilayer films were also examined in 0.1M NBu4ClO4/ACN. Figure 5.28 shows the films cycled at 5mV/s. It was expected that the BT/EDOT/BT/EDOT film would follow the same trend as the other multilayer film; however, this was not the case. The EDOT/BT/EDOT/BT multilayer was very similar to that of the copolymer. After an initial sharp increase of mass, the $M_{app}$ steadily increased until a point halfway through charge injection, where a maximum of 100g/mol$^{-1}$ was reached, and then it slowly began to decrease. In contrast the BT/EDOT/BT/EDOT film had a sharp increase in $M_{app}$ until the midpoint point of charge injection, where a value of 260g/mol$^{-1}$ was reached. This then began to steeply decline, even though charge continued to be injected into the film.
The multilayers behaved as expected when cycled in 0.1M NBu₄ClO₄/ACN at 20mV/s (see Figure 5.29). The films again followed the same trend. There was a steady injection of mass into the film, which then levelled off at 95g mol⁻¹, and the $M_{app}$ value steadily decreased, even though charge continued to enter the film. The copolymer had a much lower $M_{app}$ at this scan rate. Initially, the $M_{app}$ value sharply increased until 50g mol⁻¹ was reached where the $M_{app}$ value continued to remain constant, even though charge was being injected into the film. The apparent molar mass of the film then sharply decreased at the edge of the potential window.

![Figure 5.29 $M_{app}$ plot for the copolymer and two multilayers cycled in 0.1M NBu₄ClO₄/ACN at 20mV/s.](image)

**5.4.4 Calculation of the Mass Fluxes.** The total mass fluxes of anion, film and solvent were calculated for all the films cycled in 0.1M LiClO₄/ACN at 20mV/s, using the method explained in Chapter 4. Figure 5.30 shows the calculated mass fluxes for the E/B/E/B multilayer film. The mass flux of the anion gradually increased until +1.0V, after this a sharp increase in the rate was observed. The total mass flux of the film followed a similar path to the mass flux of the anions until +1.0V was reached; here the film was losing mass as anions were incorporated, by the expulsion of solvent.
The mass flux plots for the copolymer film in Figure 5.31 were different to those of the two multilayer films. This was expected as the $M_{\text{app}}$ plots for the copolymer film were very different from those of the multilayers at the same scan rate. As the mass flux of the anion was increasing, the mass flux of the solvent within the film was decreasing in response. As a result, the $\frac{dm[\text{film}]}{dt}$ plot was a gentle arc during both the oxidation and reduction of the film.

Figure 5.30 Comparison of the mass fluxes during redox cycling (20mV/s) of E/B/E/B multilayer in 0.1M LiClO$_4$/ACN. Arrows indicate the direction of the potential scan.

Figure 5.31 Comparison of the mass fluxes during redox cycling (20mV/s) of 0.5E:0.5B copolymer in 0.1M LiClO$_4$/ACN. Arrows indicate the direction of the potential scan.
As expected from the previous EQCM results, the mass flux plots for the B/E/B/E multilayer were extremely similar to that of the E/B/E/B multilayer film (see Figure 5.32). The mass flux of anions began to increase rapidly after 0.6V in the oxidation cycle of the film. This was mirrored by an expulsion of the solvent after +1.0V. As the reduction cycle began at +1.2V, solvent was very rapidly incorporated into the film; this was accompanied by the rapid loss of anions.

![Figure 5.32 Comparison of the mass fluxes during redox cycling (20mV/s) of B/E/B/E multilayer in 0.1M LiClO₄/ACN. Arrows indicate the direction of the potential scan.](image)

5.5 Conclusion

The ratio in which two monomers combine to form a copolymer is determined by the composition of the feed solution and the relative reactivities of the two monomers. This poses a problem if it is imperative to combine two monomers with very different reactivity ratios. A solution could be to construct a layered structure from the two monomers.

The objective to investigate the structure of the polymer film formed from growing the bilayer films, and to compare the distributions of solvent species within the films, by means of NR, was achieved. By using the deuterated EDOT monomer instead of
commercially bought EDOT, it was possible to highlight the EDOT component of the bilayer films.

The spectra of the d₄-EDOT/BT bilayer, exhibited only small differences from that of the BT/d₄-EDOT bilayer film. In comparison, there was no ridge between the peaks above a 1000nm, probably because the d₄-EDOT response was masked by the outer BT layer. The peaks above 1000nm also spanned a larger wavelength beyond the detection limits of the instrument. This feature had not previously been seen. The 2D cross-section plot for the BT/d₄-EDOT bilayer, taken at 500 and 650nm illustrated that the conduction band occurred in complementary sequence to the bleaching of the optical absorbance. A differential plot of the data further demonstrated that blending of optical absorbance was synchronised with the onset of electronic conduction.

The structure of the polymer film formed from growing the bilayer films was investigated, the distributions of solvent species within the films were compared, and the EDOT component of the bilayer films was highlighted. The profiles of the d₄-EDOT/BT film contained the features expected for a bilayer film. The film appeared to have 3 regions. Close to the electrode it mainly consisted of a region of d₄-EDOT with a small amount of BT incorporated, indicated by the drop in N_b from that of the d₄-EDOT homopolymer. The next region was the interface between BT and d₄-EDOT; this contained approximately equal amounts of BT and d₄-EDOT. The last region of the film was predominantly made up of BT. However, the BT/d₄-EDOT film did not exhibit the same separation between the two layers expected in a bilayer. It appeared that the d₄-EDOT monomer units uniformly penetrated into the whole of the BT layer. It has become apparent that d₄-EDOT grew into BT, better than BT grew into d₄-EDOT. NR shows that the structures behave partly as layers, but that the layers are quite diffuse. This is consistent with the similarity in behaviour of the spectroscopic properties observed for the copolymer system.

A difference in the doping/dedoping behaviour of the two bilayer films was not seen in the EQCM results, even though dissimilarity was seen in the structure and solvation of the two bilayer films. The two multilayers had similar values for the apparent molar mass, and the number of transferred solvent molecules for the films cycled in the same electrolyte and at the same scan rate. In comparison, the copolymer film had
a much lower apparent mass than the multilayer films, suggesting that less solvent molecules had ingressed into the film. However, the mass flux plots for the three films followed the same pattern of behaviour.

When the films were cycled at 20mV/s the $M_{\text{app}}$ values and the number of solvent molecules transferred with the anion in 0.1M LiClO$_4$/ACN and 0.1M NBu$_4$ClO$_4$/ACN was the same, confirming that only the anion was involved in the redox process. However, at the slower scan rate of 5mV/s this was not the case. The values for the copolymer film differed greatly from those of the two multilayers. The potential dependent $M_{\text{app}}$ plots showed that in LiClO$_4$ the results for the multilayers were very similar, after the initial charge injection, the $M_{\text{app}}$ values were steady at the RMM of the anion, until the apparent molar mass was slowly lost as solvent was expelled from the film. The copolymer appeared to have a much greater apparent molar mass than the multilayers.

The mass flux plots for the two multilayer films were very similar. The only mass flux within the film up until +1.0V was due to the anion, however, above +1.0V the anion mass flux increased and solvent was expelled rapidly to compensate. However, in the case of the copolymer, both anion and solvent flux were changing across the whole of the potential window, with a rapid incorporation (or expulsion) of anion and expulsion (or incorporation) of solvent at the end (or start) of the oxidation (or reduction) cycle.

This work set out to determine whether a d$_4$-PEDOT and polyBT layered structure would have similar properties to a copolymer made up from the two monomers. It was concluded that the internal structure and solvation of the two bilayers (BT/d$_4$-EDOT and d$_4$-EDOT/BT) were completely different. However, the behaviour of mobile species within the two films did not alter during redox cycling. In comparison, the copolymer film did exhibit different electrochemical properties from those of the layered structures. A similar spectroscopic response was seen in all the films, however, a layered structure does not exhibit similar electronic properties to those of a copolymer film containing both monomers.
5.6 References

Thin films of electrodeposited polymers bearing functional groups are commonly being used as part of complex devices with applications in electrocatalysis, chemical and biological sensing, light emitting and electrochromic devices, corrosion inhibiting, and antifouling surfaces. These functionalised polymer films can be prepared by electropolymerising a synthesised monomer which already contains the desired functional group, or by electropolymerising a generic reactive monomer and then reacting the film formed with a suitable species (containing the desired group) after deposition. An advantage of the latter is that the electrodeposition conditions for the parent polymer need only to be established once, after which modification with a wide variety of different species is possible. The post-deposition modification technique can also be used to make patterned substrates suitable for use in multifunction or multi-analyte sensing devices.

It has been established that activated ester groups, bound to the backbone of a polymer matrix, act as versatile substrates for a wide variety of functional groups. In this instance, the functional group must contain an appropriate nucleophilic group (e.g. an amine or alcohol) in addition to the molecule of interest. These post-deposition reactions generally occur when the reactant and polymer bound ester come in to close proximity. Commonly, reactions with polymer bound activated ester groups are carried out by immersion of the film in a solution of the appropriate nucleophilic species.

Here, the distribution of chelated ions in polymer bound crown ether systems was probed by studying a system based on a copolymer of bithiophene with an amino 15-crown-5 functionalised pyrrole, using X-Ray Photoelectron Spectroscopy (XPS), Neutron Reflectivity (NR) and Electrochemical Quartz Crystal Microbalance (EQCM) studies. The density of chelation sites and possibly the overall solvent volume fraction within the film (and therefore the responsivity of the sensor) could be controlled by varying the ratio of thiophene and pyrrole units.
A number of copolymer films with varying compositions were grown from a solution containing a binary mixture of bithiophene (BT) and the pentafluorophenol activated ester of pyrrole-N-propionic acid (PFP), see Section 2.8. In this chapter these films are referred to as unreacted. After characterisation, the PFP monomer units within the film were functionalised with an amino 15-crown-5 group (see Figure 6.1). These films were said to be reacted. PFP is a good leaving group because the pentafluorophenol ring enables the molecule to stabilise negative charge effectively by resonance stabilisation.

![Figure 6.1 Functionalisation of the PFP unit with the amino 15-crown-5](image)

Preliminary investigations showed that high quality copolymer films could be made using either high or low mole fractions of PFP. However, if the PFP component was too large, the films swelled massively and lost mechanical integrity after reaction with the amino 15-crown-5.

### 6.1 X-Ray Photoelectron Spectroscopy (XPS)

A number of copolymer films with varying compositions were grown from a solution containing a binary mixture of BT and PFP, and both the unreacted and reacted films were characterised using XPS. The BT and PFP monomer species have many distinct features: PFP contains a large, bulky functional group; BT has double the chain length and the structures that form the polymer backbone contain a different heteroatom in the cyclic ring. Because of these large differences between the two monomer species, it is highly likely that the proportion of monomer units in the
copolymer film will considerably differ from that of the feed solution the copolymer was grown from.

The C (1s), O (1s), S (2p3/2) and F (1s) regions of the spectrum were collected for all the copolymer films. The percentage concentration of each atom in the film was then used to calculate the S/N, S/C and S/O ratios for both the unreacted and reacted copolymer films. The S/O ratio is not a reliable value to use when calculating the composition of the copolymer film. The measured amount of oxygen in the film is likely to be higher than the actual amount of oxygen in the pyrrole-N-propionic acid molecule, as the copolymers can experience surface contamination which will result in an increase of oxygen atoms being found on the surface of the copolymer. Because of this, the S/N ratio was used to calculate the amount of BT and PFP in the copolymer film, as the sulphur and nitrogen atoms are unique to the BT and PFP monomers respectively. A comparison of the mole fraction of BT ($X_{BT}$) in the feed solution and the resulting $X_{BT}$ in the copolymer film can be seen in Table 6.1. During electropolymerisation using cyclic voltammetry, PFP was incorporated into the copolymer film at a faster rate than BT. As expected, the higher the ratio of BT in the feed solution, the more BT monomer units were incorporated into the copolymer film.

<table>
<thead>
<tr>
<th>Feed Solution $X_{BT}$</th>
<th>$X_{BT}$ in Unreacted Copolymer Film</th>
<th>$X_{BT}$ in Reacted Copolymer Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>0.70</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>0.80</td>
<td>0.13</td>
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<td>0.90</td>
<td>0.28</td>
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</tr>
<tr>
<td>0.92</td>
<td>0.29</td>
<td>0.25</td>
</tr>
<tr>
<td>0.94</td>
<td>0.40</td>
<td>0.31</td>
</tr>
<tr>
<td>0.96</td>
<td>0.55</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Table 6.1 Feed solution ratios for the different copolymer compositions compared with the calculated compositions of the copolymers

The F(1s) region of the copolymer spectrum proved that after soaking the copolymer film in the ACN solution of the amino 15-crown-5, no fluorine remained in the
copolymers. If a complete exchange of the pentafluorophenol group with the 15-crown-5 group had not occurred, a change in relationship between the mole fraction of BT in the feed solution and the copolymer film would have been observed. Figure 6.2, which plots the $X_{BT}$ of the copolymer film vs. the $X_{BT}$ of the feed solution for both the unreacted and reacted copolymer films, confirm that no change in relationship was observed. It is therefore assumed that all the pentafluorophenol groups had been cleaved from the pyrrole-N-propionic acids and replaced with the amino 15-crown-5 group.

![Graph showing mole fraction of BT in copolymer film vs. mole fraction of BT in feed solution for both unreacted and reacted films.](image)

**Figure 6.2** A plot of the mole fraction of BT ($X_{BT}$) in the copolymer film versus the $X_{BT}$ in the feed solution for both the unreacted and reacted films.

After the 15-crown-5 group had been attached to the copolymer chain, and the XPS spectra of the reacted film recorded, the films were soaked in aqueous solutions of K' and Ba$^{2+}$ ions. However, after recording preliminary XPS spectra of the Ba(1s) region, it was found that no ion had chelated to the crown. It is now believed that the ions associated to the water molecules in preference to the crown. XPS analysis of a BT PFP copolymer showed that if the Ba(ClO$_4$)$_2$ and KPF$_6$ salts were dissolved in ACN, some Ba$^{2+}$ and K$^+$ ions were chelated to the crown. Because of this, a reacted copolymer film which had been soaked in an ACN solution of Ba$^{2+}$ and K$^+$ was characterised using NR.
6.2 Neutron Reflectivity (NR)

The scattering length density ($N_b$) profiles of BT:PFP copolymer films were calculated from the recorded NR data in order to investigate the polymer and solvent volume fraction profiles. By integrating these profiles, the mole fraction of monomer units in the film can be calculated. NR can be used as a vital tool in probing the distribution of chelated ions in polymer bound crown ether systems. Two ions $\text{Ba}^{2+}$ and $\text{K}^+$ were examined here. As $\text{Ba}$ ($N_b = 5.07\times10^{-6}$ $\text{Å}^{-2}$) has a very different scattering length density to that of the bulk polymer it was believed that chelation of $\text{Ba}^{2+}$ would have a strong affect on NR curves. To prove this theory, the theoretical $N_b$ values for the reacted polymer film and the film chelated by $\text{Ba}^{2+}$ and $\text{K}^+$ were calculated. These values were then inputted into the Parratt32 fitting software along with reasonable thickness and roughness values and a theoretical scattering length density profile was created (see Figure 6.3). A large change in scattering length density profiles was observed for the film from before and after chelation with $\text{Ba}^{2+}$. In contrast only a small difference was witnessed in the scattering length density profile for $\text{K}^+$, this is because the scattering length of $\text{K}$ ($N_b = 3.67\times10^{-6}$ $\text{Å}^{-2}$) is not very different from the bulk polymer.

![Theoretical scattering length profiles for a reacted 0.92:0.8 BT:PFP copolymer film and the same copolymer films containing chelated $\text{Ba}^{2+}$ and $\text{K}^+$ ions.](image)

Figure 6.3
Figure 6.4 shows the reflectivity data collected, overlaid with the model fits for dry unreacted BT and PFP copolymer films of the ratios 0.96:0.04, 0.92:0.08 and 0.89:0.11 respectively.

![Figure 6.4](image_url)

Figure 6.4 NR measurements (dots) and model fits (lines) for the dry, unreacted copolymer films: 0.96 BT:0.04 PFP (—), 0.92 BT:0.08 PFP (--), and 0.89 BT: 0.11 PFP (.—). The data was offset by intervals of 100 for clarity.

Figure 6.5 shows the model $N_b$ profiles that provided the best fits to the reflectivity data depicted in Figure 6.4. The neutron samples were made by silanising a quartz substrate and then depositing a thin layer of metal, in order to produce a working electrode onto which the copolymer films could be electrochemically deposited. The scattering length densities observed for these metal coatings were different. This is because the 0.96 BT:0.04 PFP copolymer film was grown on a platinum coated substrate whereas the 0.92 BT:0.08 PFP and 0.89 BT:0.11 PFP films were grown on gold coated substrates. The different copolymer films were all approximately the same thickness. The scattering length densities for the copolymer films differed only close to the metal layer. The large dip in scattering length density observed for the
0.92 BT:0.08 PFP copolymer film was most likely an artefact of the data modelling, and not an intrinsic feature of the film.

Figure 6.5 NR profiles for the dry, unreacted 0.96 BT:0.04 PFP (---), 0.92 BT:0.08 PFP (----), and 0.89 BT:0.11 PFP (-----) films.

After the NR profiles of the dry copolymer films had been recorded, they were soaked in a 50mM ACN solution of the amino-15-crown-5 for approximately 4 hrs. The films were then well rinsed and dried, and the dry and solution profiles of the reacted copolymers were recorded.

Figure 6.6 shows the dry reflectivity profiles of the unreacted and reacted 0.96 BT:0.04 PFP copolymer film. Attaching the amino 15-crown-5 group increased the dry thickness of the film from 530 to 575 Å. The scattering length densities also decreased from approximately \(3 \times 10^{-6}\) to \(2 \times 10^{-6}\) Å\(^{-2}\).

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\(^a\) Unlike the other two films which were deposited onto quartz blocks, the 0.92BT:0.08PFP film was deposited onto a silicon block. Silicon blocks had not been used in similar experiments before and it was found that fitting data from films grown on silicon blocks was much more complex than from those grown on quartz blocks.
Figure 6.6 NR profiles for the dry unreacted (---) and reacted (---), 0.96 BT:0.04 PFP copolymer.

The solution reflectivity data overlaid with the model fits for the unreacted and reacted 0.96 BT:0.04 PFP copolymer film can be seen in Figure 6.7.

Figure 6.7 NR measurements (dots) and model fits (lines) for the unreacted (---) and reacted (---), 0.96 BT:0.04 PFP copolymer film in solutions of d- and h-ACN. The data has been offset by intervals of 100 for clarity.
The $N_b$ profiles for the reacted and unreacted 0.96 BT: 0.04 PFP copolymer film in d- and h-ACN also depicted a drop in scattering length density after attachment of the amino 15-crown-5 (see Figure 6.8). A larger shift in $N_b$ was seen in d-ACN. The solvated thickness of the film had increased from 600 to 740 Å in d-ACN and from 640 to 700 Å in h-ACN.

![NR profiles for the unreacted and reacted 0.96 BT: 0.04 PFP copolymer in both d- and h-ACN.](image)

Figure 6.8 NR profiles for the unreacted (—) and reacted (—) 0.96 BT:0.04 PFP copolymer in both d- and h-ACN.

The solvent volume fractions for the unreacted and reacted 0.96 BT: 0.04 PFP copolymer film are plotted in Figure 6.9. A dramatic change in solvation occurred on functionalisation with the 15-crown-5 species, the average solvent content decreased from $\sim35\%$ v/v to $<5\%$. It is unusual that the immobilised 15-crown-5 moieties caused an expulsion of solvent from the polymer matrix, instead of a physical swelling of the matrix to accommodate the crown groups in a highly solvated environment. The lack of swelling on uptake of a species by the polymer matrix may be a consequence of a degree of rigidity associated with the BT monomer.
These observations could explain why in the preliminary XPS measurements, the copolymers containing a higher proportion of PFP units lost their mechanical robustness on reaction with the amino 15-crown-5. The polymer was unable to swell sufficiently to incorporate all the extra 15-crown-5 groups associated to the PFP monomer units in the films containing a higher mole fraction of PFP.

![Graph showing volume solvent fractions](image)

**Figure 6.9** Volume solvent fractions for the unreacted (---) and reacted (---) 0.96 BT:0.04 PFP copolymer in ACN.

The dry reflectivity profiles of the unreacted and reacted 0.89 BT: 0.11 PFP copolymer film can be seen in **Figure 6.10**. Attaching the amino 15-crown-5 group to a copolymer with a higher PFP content increased the dry thickness of the film from 505 to 580 Å. The scattering length density also decreased from approximately 3 x 10^{-6} to 2 x 10^{-6} Å^{-2}. The change in copolymer ratio did not cause a noticeable change in the scattering length density of either the unreacted or reacted copolymer film.
Figure 6.10 NR profiles for the dry unreacted (---) and reacted (---), 0.89 BT:0.11 PFP copolymer.

The solution reflectivity data overlaid with the model fits for the unreacted and reacted 0.89 BT:0.11 PFP copolymer film can be seen in Figure 6.11.

Figure 6.11 NR measurements (dots) and model fits (lines) for the unreacted (---) and reacted (---), 0.89 BT:0.11 PFP copolymer film in solutions of d- and h-ACN. The data has been offset by intervals of 100 for clarity.
Figure 6.12 contains the $N_b$ profiles for the reacted and unreacted 0.89 BT: 0.11 PFP copolymer film in d- and h-ACN. Again, a drop in scattering length density was seen after attachment of the amino 15-crown-5, with a larger shift in $N_b$ in d-ACN. The solvated thickness of the film increased from 620 to 680 Å in d-ACN and from 620 to 650 Å in h-ACN.

![NR profiles](image)

Figure 6.12 NR profiles for the unreacted (--) and reacted (---) 0.89 BT:0.11 PFP copolymer in both d- and h-ACN.

Figure 6.13 illustrates the solvent volume fractions for the unreacted and reacted 0.89 BT: 0.11 PFP copolymer film. As with the previous copolymers, a dramatic change in solvation occurred on functionalisation with the 15-crown-5 species, the average solvent content decreased from ~45% v/v to <5%.
The extent to which the amino 15-crown-5 functionalised films chelated $\text{Ba}^{2+}$ and $\text{K}^+$ was examined using NR. The reflectivities of two films grown from the same 0.92 BT: 0.08 PFP feed solution, and under the same conditions, were recorded before and after reaction with the amino 15-crown-5, in the same manner as the copolymers above. The films were then soaked in ACN solutions of either $\text{Ba(CIO}_4)_2$ or $\text{KPF}_6$. The reflectivity data for both films was then recorded in fresh solutions of d- and h-ACN.

Figure 6.14 shows the reflectivity data overlaid with the model fits for a 0.92 BT: 0.08 PFP copolymer film. The film was characterised dry and in d- and h-ACN. The amino 15-crown-5 was then functionalised to the film and it was again characterised in d- and h-ACN. The film was then soaked in a solution of $\text{Ba(CIO}_4)_2$, rinsed and dried and re-characterised in d- and h-ACN.
Figure 6.14 NR measurements (dots) and model fits (lines) for the 0.92 BT: 0.08 PFP copolymer film (reacted (—) and unreacted (—)) in d- and h-ACN, and in d- and h-ACN after chelation of Ba$^{2+}$ (—).

FTIR spectra taken before and after reaction of a 0.92 BT: 0.08 PFP copolymer film with the amino 15-crown-5 group can be seen in Figure 6.15. The spectra confirm the exchange of the pentafluorophenol group for the amino 15-crown-5 observed in the XPS results.

Figure 6.15 FTIR spectra of the 0.92BT:0.08 PFP copolymer film taken before and after reaction with the amino 15-crown-5.
Figure 6.16 displays the $N_b$ profiles for the reacted and unreacted 0.92 BT: 0.08 PFP copolymer film in d- and h-ACN. The solvated thickness of the film remained the same after functionalisation with the 15-crown-5. It was 700 Å and 820 Å in d- and h-ACN respectively.

The scattering length density profiles for copolymer film that contained the chelated Ba$^{2+}$ ions can also be seen in Figure 6.16. The uptake of Ba$^{2+}$ was barely discernible from the profile of the film reacted in amino 15-crown-5 in either d- or h-ACN. This may be due to either low solvation of the copolymer matrix, or the low density of crown moieties within the deposited film. The volume solvent fraction plots for these copolymers showed that after functionalisation with the amino 15-crown-5 the solvation of the copolymer films dropped dramatically to <5%. The FTIR spectra (Figure 6.15), confirmed that all of the pentafluorophenol groups had been cleaved from the film, therefore it was assumed that each molecule had been replaced with an amino 15-crown-5 group. Based on this evidence, it is probable that Ba$^{2+}$ was not readily chelated by the 15-crown-5 because of the observed poor solvation characteristics of the film.

Figure 6.16 NR model for the 0.92 BT: 0.08 PFP copolymer film (reacted (--) and unreacted (---)) in d-ACN and h-ACN, and in d-ACN and h-ACN after chelation of Ba$^{2+}$ (---).
The solvent volume fraction \((V_f)\) profiles (Figure 6.17) were calculated from the scattering length density profiles (shown in Figure 6.16), using Equation 4.1 as previously described. **Equation 4.1** is repeated below for clarity:

\[
V_f = \frac{N_b(z_{film})^{d-ACN} - N_b(z_{film})^{h-ACN}}{N_b^{d-ACN} - N_b^{h-ACN}}
\]

where \((N_b(z_{film})^{h-ACN})\) is the scattering length of the film in h-ACN, \((N_b(z_{film})^{d-ACN})\) is the scattering length of the film in d-ACN, \((N_b^{d-ACN})\) is the scattering length density of d-ACN and \((N_b^{h-ACN})\) is the scattering length density of h-ACN.

A dramatic change in solvation occurred on functionalisation with the 15-crown-5 species, causing the average solvent content to decrease from \(\sim 30\% \text{ v/v}\) to <5% (see Figure 6.17). The negative solvation calculated for the reacted film at the substrate/polymer interface is impossible. It is not a feature of the copolymer, but an artefact of the modelling process. The substrate/polymer is the hardest region of the polymer film to model because of the sharp contrast in scattering length density of the copolymer compared to the substrate; this can result in a spike within the solvation profile as the one seen in Figure 6.17.
A second 0.92 BT: 0.08 PFP copolymer film was then characterised dry and in d- and h-ACN. After this, the copolymer film was functionalised with the amino 15-crown-5 group and characterised in d- and h-ACN. The film was then soaked in an ACN solution of KPF₆, rinsed and dried and re-characterised in d- and h-ACN. **Figure 6.18** contains the reflectivity data overlaid with the model fits for the film.

![Graph showing reflectivity data](image)

**Figure 6.18** NR measurements (dots) and model fits (lines) for the 0.92 BT: 0.08 PFP copolymer film (reacted (—) and unreacted (—)) in d- and h-ACN, and in d- and h-ACN after chelation of Ba²⁺ (—).

**Figure 6.19** displays the Nₜ profiles for the reacted and unreacted 0.92 BT: 0.08 PFP copolymer film in d- and h-ACN. The thickness of the solvated film decreased from 700 to 630 Å in the reacted film in d-ACN, and remained at 640 Å in h-ACN. The uptake of K⁺ was barely discernible from the profile of the film reacted in amino 15-crown-5 in d-ACN. However, in h-ACN a substantial drop in the scattering length density of the film was observed.

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The change in the solvation behaviour of the 0.92 BT:0.08 PFP was likely to have been caused by a difference in morphology between the two films. It is probable that the second film that was investigated contained more spaces between the polymer chains, making the film more porous. This is confirmed in Figure 6.20. The volume solvent fraction of the second film was \( \sim 15\% \) after functionalisation with the amino 15-crown-5 group, as opposed to \( \sim 5\% \) in Figure 6.17. The K\(^+\) was chelated to the 15-crown-5 because the film was more highly solvated, increasing the number of K\(^+\) ions transported to the 15-crown-5. In hindsight it would have been better if this film had been chosen for the earlier experiment, as a larger change in scattering length density would have been observed when the Ba\(^{2+}\) was chelated to the crown ether substituents.
Integration of the polymer scattering length density profiles extracted from the model fits for the polymer before and after reaction with amino 15-crown-5, allowed the mole fraction of monomer units within the copolymer film to be calculated. For the 0.92 BT: 0.08 PFP copolymer system, the neutron data showed that the average mole fraction within the copolymer film was 0.89 BT:0.11 PFP. This disagrees with the ratio obtained from the XPS measurements taken of a film made from the same feed solution ratio (0.29 BT:0.71 PFP). Further experiments needed to be performed to establish the composition of the copolymer film.

### 6.3 Probing Bulk Composition of the BT:PFP Copolymer with QCM

The XPS and NR results provided contrary data for the composition of the 0.92 BT:0.08 PFP copolymer film. EQCM was employed to record the mass change of the film after hydrolysisation, and the copolymer ratio of the film was calculated. The film could either have been reacted with an amino 15-crown-5 or hydrolysed to change the mass, without altering the composition of the copolymer backbone. The film was hydrolysed in order to achieve a more accurate result, as a much bigger mass change
was accomplished by exchanging the pentafluorophenol ring for the 15-crown-5 moiety (see Figure 6.21).

![Figure 6.21](image)

The dry mass difference between the bare Au quartz crystal and the same crystal after the deposition of the 0.92 BT:0.08 PFP copolymer film was observed, and from this the surface coverage of the nonreacted film ($M_N$) was calculated, $M_N = 32055\text{ngcm}^{-2}$. The copolymer film was then hydrolysed as described in the experimental chapter and the dry mass difference between the bare Au quartz crystal and the now hydrolysed copolymer film was recorded and from this the mass density of the reacted film ($M_R$) was calculated, $M_R = 23028\text{ngcm}^{-2}$. The difference in mass between the nonreacted and reacted film ($\Delta M$) was $-9027\text{ngcm}^{-2}$. The values were substituted into the following equation to calculate the number of moles of PFP ($n_{PFP}$) within the copolymer film:

$$\Delta M = n_{PFP}(1-183) \quad \text{(Equation 6.1)}$$

where 1 and 183 represent the mass of the attached functional group of the reacted and nonreacted copolymer film respectively.

This value was then inserted into the following equation to calculate the number of moles of BT ($n_{BT}$) in the copolymer film:

$$M_N = 164n_{BT} + 303n_{PFP} \quad \text{(Equation 6.2)}$$

where 164 and 303 represent the RMM of BT and nonreacted PFP respectively.
Finally, the mole fraction of BT ($X_{BT}$) within the copolymer film was calculated using the following equation.

\[
X_{BT} = \frac{n_{BT}}{n_{BT} + n_{PFP}} \quad \text{(Equation 6.3)}
\]

The composition of the copolymer film ascertained using EQCM was 0.68 BT/0.32 PFP. The crystal with the reacted BT:PFP copolymer film deposited on the Au layer was later removed from the cell and measured using XPS. This revealed that the film was 41% S and 59% N which was equivalent to an $X_{BT}$ of 0.35. The values of $X_{BT}$ for films grown from the same feed solution composition determined by the XPS and NR techniques from the previous sections were 0.29 and 0.89 respectively. The EQCM assay was closer to the value for the neutron assay, than it was to the value for XPS. The difference in composition could have resulted from a bulk/surface effect because of the large PFP groups attached to the copolymer chain ordering at the air interface. The presence of S and N atoms within the heterocycles of the polymer backbone may have been masked by these bulky substituents as XPS is a surface technique with a low penetration depth.

### 6.4 Conclusion

In conclusion, it has been established that an activated pentafluorophenol activated ester, bound to a backbone polymer matrix of bithiophene and pyrrole could act as a versatile substrate for functional groups. The polymer bound activated ester group was successfully functionalised by immersion of the film in a solution of amino 15-crown-5. However, further investigations would need to be carried out using different functional groups.

NR can give useful insights into the changes in solvent volume fractions that occur after immobilisation reactions within a copolymer matrix. The possible relationship between the expulsion of solvent found here, and the mechanical robustness of other copolymer systems has implications for how conducting polymers are used in practical devices. Different copolymers e.g. EDOT or substituted alkyl thiophene, or electrodeposition protocols may lead to matrices that can more easily accommodate...
the immobilisation of moderate sized functional groups, providing materials with an
improved robustness, sensitivity or capacity. Chelating a K⁺ ion in the amino 15-
crown-5 group unfortunately only caused a shift of a few nm in the colour of the
copolymer, which could not be perceived by the human eye (see Appendix III). The
NR experiments have confirmed that this is most likely due to the lack of solvation of
the copolymer film after functionalisation with the amino 15-crown-5 group. As a
result, this particular system would not be viable in a sensor application.

QCM was used to provide an additional probe to bulk compositiOn
of the copolymer. This gave information consistent with the NR results, indicating that surface
composition, as determined by XPS, may differ significantly to the bulk. It may be
that comparing different film thickness or potential step deposition would indicate
whether there was a depletion or efficiency effect that would lead to a difference in
the bulk or surface compositions of the copolymer.

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Conclusion

Conjugated polymers have generated a great deal of interest as they are relatively easy to prepare, and also undergo a variety of colour changes which are a function of the doping level of the conjugated material. Altering the monomer structure or adjusting the composition of copolymers can vary the colour shade of a conjugated polymer, allowing the shade to be continuously changed as a function of the applied voltage.

BT and EDOT were found to have similar reactivities, allowing the fabrication of copolymers with a desired composition from a prescribed binary mixture of BT and EDOT monomers. A trend was found relating the ratio of BT and EDOT in the copolymer and the $\lambda_{\text{max}}$ value of the undoped copolymer, allowing the $\lambda_{\text{max}}$ value of the material to be predicted from the copolymer ratio and vice versa. Although this methodology is potentially useful, with applications in device fabrication using monomers of similar reactivity, in this case the range of $\lambda_{\text{max}}$ values were quite limited, such that the qualitative colour changes were restricted to the observed purple to pale blue transition.

Charge injection into PEDOT was rapid during redox cycling and all colour change was accomplished within the initial phase of oxidation. In contrast, the whole region of charge flux was involved in colour transition in the BT homopolymer. The electronic and optical properties of the copolymers scale stoichiometrically with the properties of the individual components. This structure-property relation is very useful for device fabrication, since it allows for the prescriptive formulation of property types.

The movement of ions and solvent during redox cycling influence both the electrochromic response and the physical properties of a polymer. The high solvation observed here for both the reduced and fully oxidised states of the PEDOT film, may have allowed the easy movement of the ions required to maintain electroneutrality during redox cycling, without the need for structural reorganisation, or expansion of
the polymer film. This is significant in explaining the unique stability of PEDOT films to extended periods of repetitive cycling, compared to many other conducting polymer systems reported in the literature.

EQCM investigations of PEDOT revealed that charge was incorporated into the polymer film at a steady rate, even at the ends of the potential window where mass (frequency) changes did not occur ("net" effect). A reversible exchange of anions and solvent was observed during redox cycling. Variation of the scan rate facilitated the exploration of the kinetic effect, including relative rates of movement of solvent and counter ions. At scan rates less than 100mV/s, additional solvent movement was associated with anion transfer within the film. At scan rates of 100 and 150mV/s, the anion was the dominant mobile species, with little or no solvent transfer. The $M_{app}$ values for the different electrolytes generally followed the same trend, with larger values for KPF$_6$, reflecting the movement of the heavier PF$_6^-$ anion. The difference in the mass of the anion appeared to have no effect on the number of solvent molecules associated with it and cation substitution did not change the behaviour of the film. The mass fluxes of LiClO$_4$ and NBu$_4$ClO$_4$ were seen to be of a similar magnitude, consistent with the movement of the same mobile species (ACN and ClO$_4^-$).

An NR method was developed, to obtain the simultaneous spatial and temporal resolution of individual components within copolymer films. The time resolution was improved to produce the first dynamic in situ electrochemical NR measurements. The individual species profiles at buried interfaces were produced subject to electrochemical control, thus providing new insights into transient population distributions. The preliminary data for the PEDOT homopolymer revealed no major changes in the structure and solvation of the film during potential cycling. However, it has been proven that in the future, dynamic in situ electrochemical NR could be a very valuable technique in the investigation of different polymer systems.

Obtaining hybrid or combinatorial properties from a binary monomer mixture where reactivity ratios are very different can be difficult, consequently the possibility of using layered structures was investigated. The structure and distribution of the mobile species in layered structures was compared to that of a copolymer. NR data illustrated that the structures behave partly as layers, but that the layers are quite
diffuse. This was reinforced by the similarity in optical behaviour of the properties observed for the copolymer system; this was consistent with random copolymer behaviour with no evidence of block separation.

Despite the differences in structure and solvation inferred from interpretation of the NR data, a difference was not witnessed in the doping/dedoping behaviour of the EDOT/BT and BT/EDOT layered structures in the EQCM results. The layered films had similar values for the apparent molar mass and the number of transferred solvent molecules, when cycled in the same electrolyte and at the same scan rate. In comparison, the mobile species within the copolymer film had a much lower apparent molar mass than the layered structures, suggesting that less solvent molecules had ingressed into the film. However, the mass flux plots for the three films followed the same pattern of behaviour. It was concluded that even though the layered film differed in structure, the observed electrochromic properties of the films and the behaviour of the mobile species within the films did not differ during redox cycling. However, the copolymer film did exhibit different electrochemical properties from the layered structures, suggesting that the same combinatorial properties desired in a copolymer cannot be reproduced in layered structures.

Following further investigations, an activated pentafluorophenol activated ester, bound to a backbone polymer matrix of bithiophene and pyrrole, could act as a versatile substrate for functional groups. NR gave a useful insight into the changes in solvent volume fractions that can occur after immobilisation reactions within a copolymer matrix. The relationship between the expulsion of solvent and the mechanical robustness of the polymer film has important implications for how conducting polymers are used in practical devices.

It has been demonstrated that NR experiments can give useful insights into the depth profile of a polymer and the changes in solvent volume fractions that can occur in a copolymer matrix during redox cycling, or after functionalisation of the polymer backbone with a nucleophilic group. The internal structure together with the charge/mass transfer dynamics of the PEDOT homopolymer and the EDOT/BT system have been studied and the results used to highlight issues that might affect the function of the colour transition such as the identity of the mobile species (solvent and
counterions) that accompany redox cycling. The rate at which mobile species moved into and were expelled from the polymer film was probed and the internal structure of copolymers and layered structures was studied. Physical changes within a polymer film were related with its electrochromic response.

One technique could not provide sufficient insight into all the electrochemical and optical properties for the polymers reported here, however combining information from all the techniques (XPS, NR, QCM, electrochemical and spectroscopic) provided a unique insight into all aspects of the properties of these polymer films.
APPENDIX I

Published Papers

Dynamic in Situ Electrochemical Neutron Reflectivity Measurements

Determining Compositional Profiles within Conducting Polymer Films Following Reaction with Vapour Phase Reagents
We report the first dynamics in situ electrochemical neutron reflectivity measurements on electroactive films. The improved time resolution yields individual species profiles at buried interfaces subject to time-variant electrochemical control, providing new insights into transient population distributions.

Assembly of controlled interfacial architectures is a primary goal of interfacial electrochemistry. A generic issue is the extent to which the real interfacial structure and composition correspond to the design. A vast array of surface-sensitive spectroscopies, imaging, and chemical, and acoustic probes have been coupled with electrochemistry to characterize the structure, composition, and dynamics of modified electrodes as functions of time and space. An underexplored aspect is the spatial distribution of species at the interface, which may have greater impact on properties than chemical composition. Generally, spectroscopic measurements provide spatially integrated signals. Imaging methods provide lateral mapping of the exterior surface of a film but do not explore the interior, where most of the functionality lies. Ellipsometry can provide internal composition, but despite superb temporal resolution, it is limited by insufficient measurements to ensure unique fits to complex interfacial structures.

A recent technique for characterizing "well" interfaces is neutron reflectivity (NR). It has many parallels with its optical counterpart, ellipsometry, but with the additional feature of isotope sensitivity. This "contrast variation" allows one to alter the "visibility" of a selected species. Commonly, the technique exploits H/D substitution, for which the effect is large, we use H2O/D2O switching to locate the solvent.

Development of NR to study "buried" interfaces under potential control has distinguished composite and bilayer polymer films, revealed permeating solvent in electroactive polymers, and metal hydroxide films, identified permselectivity failure at high electrolyte concentrations, and revealed 1D profiling of diffusion and reaction within a film of a solution phase mediator. These and related NR studies have data acquisition time scales of 1–2 h, so one can observe equilibrated films as a function of potential (charge) but not the dynamics of interconversion.

The generic objective is simultaneous spatial and temporal resolution of individual components (polymer, solvent, and ions) within film interiors. For the polyvinylferrocene (PVF) system studied here, this requires NR data leading to counterion and solvent population changes as functions of time and distance within a redox switching film on a time scale of seconds. This demands an improvement in time resolution of 2–3 orders of magnitude.

There is no prospect of accomplishing this via an increase in incident flux or detector efficiency. We use a different strategy, boson integration within continuous multiple linear potential cycles, to yield the first dynamics in situ electrochemical NR measurements, with an effective time scale of ca. 2 s. Spin-coated PVF films on 20 nm Au working electrode films (on polished quartz blocks) were exposed to aqueous NaClO4 in a three-electrode cell. NR profiles, R(Q), were obtained during voltammetric cycling (at scan rates, v = 1, 5, and 10 mV s−1) using the CRISP and D17 reflectometers at the ISIS Facility and Institut Laue Langevin, respectively. NR data acquired over multiple potential cycles were sequentially stored in bins associated with 20 mV potential (D) windows and were presented here as a function of momentum transfer, Q (nm−1) = (4π2A sin θ/λ), in each potential window accumulated over multiple cycles. At a sweep rate v (mV s−1), the effective time resolution in seconds is 20v.

Figure 1 shows E- (r-) resolved R(Q) profiles for two films of different surface coverage and at different scan rates to accentuate the effective time-scale differences. End views of the final profiles (R=Q projections) show the familiar pattern of fringes superposed on the Q=0 (Gauss law) decay. The signal quality is clearly adequate to discern fringes of different periodicity, representing the Au electrode and PVF film thicknesses. Thus, the immediate goal of the study is accomplished, we can acquire high-quality NR profiles in situ for electroactive films subject to a time-variant electrochemical control function. Subsequent discussion relates to what can be learned from these results.

To determine relative ion and solvent transfer rates during redox switching requires comparison of the present data with static NR responses. In H2O, the relative increases in solvent and ClO4− populations accompanying film oxidation are such that their opposing contributions to the total film scattering length density roughly cancel. Long time-scale NR experiments are thus virtually blind to absolute solvent and counterion film population changes. However, transient differential exorcisms of the relative populations from this compensatory stoichiometry are highlighted. Conversely, the positive scattering lengths of D2O and ClO4− reinforce each other, so experiments in D2O are optimal for following integrated population changes.

The first quantitative outcome is the variation of E with film thickness (b), for a single film, b = 2π/Q (bQ = fringe periodicity). Figure 1 is more complex due to the superposition of fringes for the polymer film and the metal electrode. Features due to the PVF layer are most apparent at low Q (<0.5 nm−1). At higher Q, fringes lose magnitude 2 dampen the PVF contributory, and fringes due to the underlying metal electrode dominate the profile. Variations in the fringe pattern with E are readily seen via the position of the first maximum in R(Q) films.
oxidation (reduction) results in fringe compression (expansion); since $Q$ represents inverse space, one is observing film swelling upon oxidation and shrinkage upon reduction. This is chemically reversible on the time scale of a complete redox cycle, but on the time scale of the individual profiles, swelling occurs over a narrower region of potential than does shrinkage.

The second issue is the extent to which changes in $h$ correlate with electrochemical charge ($Q$). Simplistically, one might view this as equivalent to plots of film mass change, $\Delta m$ versus $t$, in an ECQM experiment. However, the complexities of chain and mobile species packing under transient conditions mean that the two are not necessarily equivalent. Figure 2 shows a 3D plot of $h$ and $Q$ as functions of $t$; this is a dynamic compositional map of the system, in which $h$ is dominated by solvent level and $Q$ exclusively represents ion content. Two-dimensional $h(Q)$ and $Q(h)$ projections of the 3D compositional vector show that solvation is equilibrated with the redox state, but that the latter is kinetically controlled.

Third, dynamic capability allows exploration of experimental time-scale (here, $Q$) effects. Analogues of Figure 2 at different scan rates show the interplay of electrochemical and (de)solvation kinetics.

Finally, we seek the transient ion and solvent depth profiles within the film that underlie the simplistic overview of “film thickness”. Fuller analyses of $Q(h)$ profiles for films bathed in solvent media of different contrast show that the film comprises an interior zone and compositionally distinct interfacial regions near the electrode and the solution. The interior region has spatially uniform composition when the film is fully reduced but has a solvent-rich center when the film is partially oxidized.
Determining Compositional Profiles within Conducting Polymer Films Following Reaction with Vapor Phase Reagents


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A combination of XPS, reflectance infrared spectroscopy, and neutron reflectivity measurements has been used to probe the spatial and global extents to which carboxylic acid motifs in electrodeposited conducting polymer films can be functionalized by reaction with vapor phase reagents (a carbodiimide together with trifluoroethanol) with the goal of controlling hydrophobicity. Across a range of polymer depositions and reaction temperatures, neutron reflectivity showed that, surprisingly, functionalization of the polymer matrix at depths >5–10 nm into the polymer film was always significantly lower than at the exposed surface. The most efficient functionalization was found to occur when a low-density polymer matrix was prepared by elution of motifs cleaved from the polymer by base hydrolysis. Finally, when trifluoroethanol functionalization was performed, the macroscopic property of hydrophobicity was related to the thickness and internal microstructure, and composition of the reacted films was elucidated by the above combination of probes.

Introduction

Creating interfaces functionalized with specific motifs is often seen as a tractable route to the development of materials for incorporation in devices or applications associated with catalysis, sensing, chromatography, energy conversion/storage, and display technologies. Obviously, the goal of assembling sophisticated molecular interfacial architectures required for such applications necessitates a series of chemical synthesis and physical fabrication steps. It is often less appreciated, however, that characterizing both the presence and spatial distribution of species at a functionalized solid interface can be significantly more challenging than characterizing the target of a “reaction pot” molecular synthesis (i) the “product” is inseparable from its location (the solid surface), (ii) certain features of the location (e.g., electrochemical potential or illumination of the substrate) may be a structural driver, (iii) spatial organization of components can be crucial to the functionality, and (iv) the sample size is many orders of magnitude smaller than for ‘reaction pot’ syntheses. As a consequence, it is not uncommon to find schematic cartoons of interfacial assemblies that represent design and inspiration, rather than demonstrable fact. While some exemplary exceptions to this generalization do exist for monolayer or ultrathin films, more typically, for thin polymer films, many interfacial characterization methods suffer from an inability to unambiguously determine the depth profile of different species within the film matrix.

As part of a wider program aimed at developing functional polymer interfaces, with a view to creating a patterned hydrophobic surface, here we probe the trifluoroethanol (TFC) functionalization (performed using vapor phase reagents) of carboxylic acid motifs in an electrodeposited conducting polymer (poly(pyrrole-N-propionic acid)). Commonly, coupling or substitution reactions to append motifs to a polymer support are bought about either by (i) immersion of the polymer in a solution containing a reagent that activates the carboxylic acid group, together with a species containing the desired functional motif, or by (ii) deposition of an activated polymer, followed by a solution based nucleophilic substitution reaction. Classical examples include peptide and oligonucleotide syntheses on solid-phase resins. While performing these reactions in a solution medium is often most appropriate, there are instances where this is less desirable and here we investigate the use of vapor phase reactants. To put the less widely used vapor phase reaction scheme in context, it is advantageous when (i) the polymer occupies a small area on a complex substrate containing materials or components that would dissolve or be compromised (e.g., elements of an electronic circuit) by immersion in a solvent, (ii) solvent molecules undergo competitive or side reactions with the activated polymer; (iii) the molecule to be immobilized react with solvent species, changing the character of the motifs before immobilization has had time to occur (e.g., the propensity of silane derivatives to form oligomers in solvents containing trace water), or (iv) solvent access may be difficult (e.g., in capillary chromatography or lab-on-a-chip microfluidic systems).

Despite the conceptual simplicity of using the strategy of postdeposition modification of a parent polymer to create a desired functional interface, two important aspects that are not known a priori are (i) the overall extent of the intended
Modification and (ii) the spatial distribution of the appended species within the functionalized film. A cartoon depicting two idealized scenarios for the progression of a postdeposition modification reaction is shown in Figure 1. On the left-hand side, the reaction front proceeds uniformly perpendicular to the film interface, leading to a strongly depth dependent functionalization profile. In contrast, on the right-hand side, the polymer contains fissures or alternate percolation pathways (exaggerated in the cartoon), which leads to the reaction occurring more uniformly throughout the thickness of the film. While at the macro scale the former scheme may appear the more intuitive, the granular structure of many electrodeposited polymer films indicated by AFM images (for examples, see Supporting Information) could suggest features of the latter scheme could contribute to the reaction profile, particularly in thin films.

For the case of the vapor-phase TFE functionalization investigated here, previous studies using a method or systems that bear some similarities to that investigated here do not give a clear-cut indication as to the extent or profile of the functionalization that might be expected. For example, it has been reported that when the vapor phase functionalization of plasma treated films cast from a chemically synthesized polymer, the surface modification is relatively inefficient and possibly limited to the surface layers.\(^\text{12,13}\) In contrast, when using electrochemically deposited films containing activated ester groups, functionalization with small molecules in solution proceeds efficiently throughout the thickness of the film.\(^\text{14}\) Furthermore, for electrochemically deposited conducting polymers, transport of ions and solvent throughout the polymer during electrochemical oxidation and reduction processes is relatively easy.\(^\text{15}\) The difference between these observations may be that the electrochemical deposition of the polymer can lead to a more open matrix than in a cast film due to a branched/budding growth mechanism.

To address the characterization issues associated with the chemical derivatization of thin films or surfaces, two widely used techniques are reflectance-absorbance infrared spectroscopy (RAIRS) and XPS assaying. The former technique can indicate the overall extent of functionalization through examination of vibrational bonds associated with the appended motifs, or bond formation/destruction. The latter, XPS, technique can be used to determine speciation at the exposed interface; however, in the context of a thin polymer film, it has a limited penetration depth (ca. 3–5 nm). N.B.: Although depth profile information can be obtained from XPS measurements by using either takeoff angle measurements or ablation methods, in the first instance the profile is limited to the outer 1–3 nm, and in the second instance, as with SIMS, uncertainties exist both because of the possibility of different components being removed at different rates and because of difficulties in controlling the depth of material removed (on the nm scale).

Previously we have used in situ neutron reflectivity to characterize the internal structures of single and binary electroactive films in the "vertical" (i.e., perpendicular to the interface) direction.\(^\text{16–18}\) Neutron reflectivity (NR)\(^\text{9}\) is one of the few tools that can probe significant depths below the surface in a spatially resolved manner and is sensitive to the chemical speciation. Furthermore, through measurements of the volume occupied by solvent molecules when the polymer is immersed in isotopically different solvents, the internal microstructure can be probed. This allows an evaluation of the extent to which the physical, or void, space within the matrix could limit entry of the reactant species. Therefore, below we use this sophisticated technique and augment it with measurements from other spectroscopic and physical probes to determine both the overall populations and spatial locations of TFE motifs incorporated into the film by reaction with vapor phase reagents. We go on to use this information to guide optimization of the interfacial modification protocols to create a "product" film in which the chemical functionalization corresponds more closely to the design objective, and so can be tested against the required physical functional criteria (in this case the creation of a hydrophobic interface).

It is notable that NR has been widely used over the past decade to characterize the structure and interactions of molecules at solid and liquid interfaces.\(^\text{20–22}\) Here, however, because the material is undergoing a gross change in composition due to a chemical reaction, the "model" fitting methods used to extract compositional, or scattering density (Nb) profiles from the NR data, require additional RAIRS and XPS characterization assays for reliable interpretation. To illustrate the importance of complementary measurements, if data from these probes were analyzed individually, or in pairs, the information extracted would leave unanswered questions. For example, whereas the infrared and XPS measurements provide a global assay of chemical bonds and an elemental analysis close to the exposed surface respectively, the NR technique allows a spatial evaluation of the compositional (and solvation) profile below the exposed interface of the polymer. Neutron reflectivity alone, however, does not yield direct information about chemical bonding or species identity and thus there can be ambiguity in the assignment of neutron derived density profiles to the distribution of particular species. By assigning the chemical species present, RAIRS and XPS provide the boundary conditions and checks for scattering length density models. This is particularly important when studying multicomponent systems of indeterminate composition.

It should be noted that while the detail of the spatial functionalization profiles described are specific to the system studied here, the methodology described is generic for systems where the character of thin films are modified by reaction with functional motifs. Thus, while this multiprobe approach incor-
porating NR characterization can still be considered as an emerging technique for characterizing functional modifications to polymer films that are driven by chemical reactions, when coupled with the inherent communing or developments of high flux neutron sources (SNS, ISIS-TR3, ESS), it provides an accessible and adaptable means to examine structure–composition–function paradigms found in a wide variety of systems studied for either basic science understanding or technological applications.

**Experimental**

**Electrodeposition of Polymer Films.** Films of poly-(PyCO₂H)H₃, poly(FPP)₃ and poly(PyCO₂-TFE) were deposited by repetitive potential cycling in solutions of 10 mM monomer in 0.2 M tetramethylammonium perchlorate/McCN. A scan rate of 20 mV/s was used and potential cycling between 0 and 1.15 V versus SCE was used until the current density at polymer redox peak was ~10 µA/cm². Poly(PyPP) films were hydrolyzed by immersion in 0.1 M NaOH in DMDO H₂O (85 15 v/v) for 5 h. Soaking in 0.1 M HCl and then H₂O was used to elute the Na⁺. Confirmation of the complete hydrolysis was obtained from XPS and infrared measurements.

**Synthesis of the TFE Ester of PyCO₂H (PyCO₂-TFE).** A 28 mmol (4 g) sample of PyCO₂H was reacted with 31 mmol diethyl ether in DCC and 31 mmol TFE (3.1 g) in 50 cm₃ dry dioxane. After stirring at 0°C for 8 h and filtration, dioxane was removed by distillation at reduced pressure. The resulting low melting point yellow solid was purified on a silica column, eluting with a solution of 80% dichloromethane, 20% hexane. After removal of the solvent, the PyCO₂–TFE was found to be a colorless liquid.

**Vapor Phase Reaction of Poly(PyCO₂H) with TFE.** Polymeric films were placed in an evacuable descator together with a vial containing a solution of TFE, pyrene and PcPDI in the ratio 9:3:4 (total volume ~10 cm³). The descator was then evacuated to 1 mTorr. For reactions at 50°C, the descator was placed in a fan assisted oven at 50°C. The liquid in the vial was inspected at the end of the reaction period to confirm there had been no leakage of the descator.

**X-Ray Photoelectron Spectroscopy (XPS).** XPS measurements were performed using a Scintag ESCA 300 at the National Centre for Electron Spectroscopy, CCLRC, Daresbury Laboratory, U.K. Monochromated Al Kα radiation was used with a takeoff angle of 90°. An analyzer entrance slit of 0.8 mm and a flood gun energy of 2 eV (to compensate for the films being on insulating glass substrates). The energy scales of spectra were shifted so that the major C 1s peak was positioned at 285 eV.

**Laboratory Characterization Measurements.** RAIR measurements were performed using a Spectra-Tech reflectance accessory mounted on a Bomem MB120 infrared machine. A reflectance angle of 55° and p-polarized radiation were used. AFM measurements were made on a Digital Instruments Dimension 3100 instrument working in tapping mode. Contact angle measurements were made using a Krüss DSA100 camera and analyzed using in-house software. The tabulated results correspond to a mean of measurements taken from 8 drops on different areas of each sample.

**Neutron Reflectivity (NR).** For NR measurements, the polymer films were deposited on large area (50 mm x 100 mm) thin film (20 nm) gold electrodes supported on single-crystal quartz or silicon substrates, as described previously. When measuring poly(PyCO₂H) films in water, the pH was adjusted to 2 using dilute HCl to ensure protonation of the carboxylate groups.

NR measurements were performed on either the D17 time-of-flight reflectometer at the Institute Laue-Langevin (ILL), France, or the CRISP time-of-flight reflectometer at the ISIS facility (RAL), U.K. Typically three reflection angles were used, and reflectivity in the range 0.2–1.5 nm (D17) or 0.05–0.65 nm (CRISP) was collected. These measurements were then transformed to reflectivity as a function of momentum transfer, Q, using the usual formula and R(Q) profiles from different angles were combined to generate R(Q) spanning the range Q = 0.65–1.5 nm⁻¹. Chopper and slit settings were such that the Q resolution was 3.5%.

Model fitting of NR profiles to obtain scattering length density (NB) profiles was performed using the Parat32 software and the methodology described in detail elsewhere. In general, iterative model fitting was performed until χ² values for best fit models were in the range 0.7–1.45 for measurements in solution (measurements in air had higher χ² values due to the errors estimated by counting statistics being exceptionally low).

**Specular Neutron Reflectivity (NR) Theory and Equations Used to Evaluate Composition and Volume Fractions from Model Neutron Scattering Length Density (NB) Profiles.** Descriptions of both the information that can be gained from NR measurements and a practical way in which experiments are performed can be found in a number of text books. In brief, the specular NR experiments are performed using grazing incidence angle illumination of the electrode/polymer film interface with a collimated neutron beam. The incident and reflected beam pass through either the substrate (quartz), or air Tranmission and reflectivity at the polymer-substrate, polymer-air, or polymer-solvent interfaces are governed by the Fresnel equations using the neutron, rather than optical, refractive index of the various materials. Commonly, the neutron scattering properties of the various media are expressed in terms of an NB value of the material, which is determined by its density and atomic composition (eq 1). This can be related to the neutron refractive index in a similar way that the optical refractive index is related to the optical dielectric constant.

In order to extract quantitative information from NB profiles we need to manipulate the general equations that describes the NB profiles in terms of volume fractions (φ) and NBs of the various component materials (e.g., that of the material in a pure phase containing no air or solvent), eqs 1 and 2.

\[ NB = \Sigma \phi_i NB_i \]  
\[ NB_{film} = \phi_1 NB_1 + \phi_2 NB_2 + \phi_3 NB_3 \]  

where \( \phi_i \) and \( NB_i \) are the scattering lengths of the various atoms, density and molecular weight of the material respectively. For purposes of generality, the 'medium' in eq 2 can be air or a solvent. The surface coverage \( \Gamma = (\phi_{surf}/\rho_{surf}) \) of the various components in the film can be calculated by integration of eq 1 across the thickness of the polymer film, \( d \)

\[ \int (NP/N_a) \, d d = \int \phi_1 \rho_1 \rho_{surf} \rho_{surf} \, d d + \int \phi_2 \rho_2 \rho_{surf} \, d d + \int \phi_3 \rho_3 \rho_{surf} \, d d \]

Derivations of additional equations used to extract the volume fractions and profiles of the various components in the films are given in the Supporting Information.
The measurements and results below are divided into three sets. In outline, the first set describes the functionalization and aqueous solvation profiles following reaction between TFE and electropolymerised films of the PyCO$_2$H monomer. To examine the influence of reactant concentration (partial pressure) on the vapor phase reaction, both room temperature and elevated temperature (50 °C) reaction conditions were used. (Gas cell infrared measurements indicated that the concentration of vapor phase species at 50 °C is ~6x that at RT.) The functionalization and solvation profiles of the resultant films are also compared with those found in films prepared either by TFE functionalization using solution based reagents or by polymerization of the PyCO$_2$-TFE monomer. The second set of measurements examines the influence of the internal microstructure of the base polymer matrix on the functionalization and solvation profiles. This is achieved by using hydrolys of the pentafluorophenyl activated ester group and electropolymerized poly(PEP) to leave a poly(PyCO$_2$H) matrix in which free space has been created by the departing pentafluorophenyl groups. Finally, the third set of measurements compares the surface wetting (the design goal of the TFE functionalization), of the variously prepared TFE modified films and relates the observations to the preceding structural characterization.

1.1. XPS Characterization of Vapor Phase Reaction with Electrodeposited Poly(PyCO$_2$H). Figure 2 shows typical C (1s) XPS spectra for a se-deposited poly(PyCO$_2$H) film before (black trace) and after reaction in the vapor generated from a 9:4:3 solution of TFE, pyridine, and iPCDi at either room temperature (red trace) or 50 °C (green trace). The spectrum of the unreacted film (black trace) is simple, containing only two peaks, one at ca. 283.5 eV (C–H and C–C groups) and the other at 289.5 eV (the CO$_2$H group). Two additional peaks are found in the spectra of the reacted films. The peak at ca. 293 eV corresponds to the carbon atom in the CF$_3$ group of the trifluoromethyl substituent and the one at 283 eV corresponds to the carbon atom in the C–O ester linkage. The peak at ca. 289.5 eV is still present in the spectrum of the reacted film because of the similarity in binding energy of carbon in –CO$_2$H and –CO$_2$R groups and the presence of unreacted PyCO$_2$H) groups in these films (RAIRS spectra presented later, Figure 5, show bands for both carboxylic acid and ester groups).

Clearly the magnitude of the CF$_3$ and C–O C (1s) peaks in Figure 2 are larger when the reaction is performed using the saturated vapor generated at 50 °C (green trace), indicating a greater extent of reaction. To quantify this, integration of the peaks in the F (1s) and N (1s) regions of the XPS spectra (not shown) gave F:N atom ratios of ~7:1 and ~5:1 for RT and 50 °C conditions respectively. In both cases this is much lower than the 3:1 that would be expected had every carboxylic group in the poly(PyCO$_2$H) film been derivatized with TFE. Although typical film thicknesses were in the range 20–30 nm, due to the limited penetration depth of XPS, these reaction efficiencies of 23% and 50% for RT and 50 °C conditions correspond to a “depth weighted” average over ~5 nm from the exposed interface.

It was found that the above reaction efficiencies represent close to the practical maximum value for these two sets of vapor generating conditions. For example, the reaction in TFE in the vapor generating solution and reaction time were doubled to 16 h, the derivatization efficiency (at 50 °C) only increased to 63%, RT reactions for a period of days did not lead to a significantly larger extent of reaction either.

To get a qualitative indication of whether the derivatization reaction had taken place homogeneously throughout the polymer or whether there was any indication of a depth dependence (cf. Figure 1), we detached films from the underlying Au electrode substrate by peeling off with adhesive tape and collected XPS spectra from the newly exposed interface. It was found that the extent of reaction at this interface varied from 0% to ~50%, being least with short reaction times and thick films. For the 16 h, 50 °C reacted film above, the F (1s) and N (1s) ratio indicated that the extent of derivatization at the inner, Au/polymer, interface was 52%, still noticeably less than at the outer, polymer/vapor interface.

Possible reasons for the (unexpected) limited extent of reaction could include (i) the low concentration of reactants in the vapor phase, (ii) the lack of a suitable medium (solvent), (iii) an activation energy barrier, (iv) diffusion effects, or (v) the lack of available free volume within the polymer (i.e., a steric effect). To investigate the latter, we attempted to carry out the reaction by immersion polymer films in both acetone and DMSO solutions of the reactants (at up to 0.5 M TFE concentration). Surprisingly, both XPS and RAIRS measurements indicated that the extent of reaction was similar to that when 50 °C vapor phase conditions were used. Notwithstanding the influence of solvent, the possibility of there being a high intrinsic energy barrier is not likely to be a cause of the low extent of reaction since the PyCO$_2$–TFE monomer synthesis proceeds readily at room temperature. This suggests that the most likely cause of the incomplete reaction may be diffusion and/or steric effects both of which are influenced by the interfacial and internal microstructure of the polymer film.

Thus, to probe the TFE functionalization within the film, as indicated in the introduction section, we have used neutron reflectivity (NR), to (i) determine the degree of homogeneity of the TFE functionalization throughout the film, i.e., whether there is a gradual decrease in functionalization, or a marked abrupt interface, between functionalized and unfunctionalized regions of the polymer and (ii) examine how the internal microstructure and solvation of the derivatized films relates to the efficacy of the functionalization reaction and the design objective of creating a hydrophobic interface.

1.2. Neutron Reflectivity Measurements of Electropolymerised PyCO$_2$H Films. Usefully, when probing the PyCO$_2$H–TFE ester system using NR, it is possible to use deuterated or hydrogenous TFE. The presence of such isotopically different components in different films gives rise to differences in their scattering length density (SLD) profiles in regions where the TFE moieties are located. These differences are manifested in the measured NR profiles and are analogous to those which would
Figure 3. Reflectivity profiles (dots and error bars) and model fits (lines) for two poly(PyCO2H) films before (black and green traces) and after reaction with either h'-TFE (red) or d'-TFE (dark yellow).

occur in the (angle dependent) optical reflectivity of a multilayer film if the refractive index of one of the layers were changed. However, it is important to appreciate that in order to maximize the accuracy of deductions made by comparison of Nb profiles from separate h'-TFE- and d'-TFE- films, it is necessary for the thickness, internal structure and degree of functionalization of the films to be as similar as possible. Consequently, among the first set of NR results we describe below are measured NR profiles and model Nb fits that demonstrate that we have been able to refine our electrochemical techniques to deposit films that are closely similar in thickness and density profiles.

1.2.1. NR Characterization Electropolymized PyCO2H Functionalized at 50°C Measurements of films in the dry state. Separate films were exposed to the vapor generated at 50 °C containing either h'-TFE or d'-TFE and Figure 3 shows the NR profiles (collected in air) for the films before and after reaction. Our ability to experimentally prepare identical films referred to above, is indicated by the similarity of the fringe pattern in the NR profiles and the model Nb fits for the two unreacted films (black and green traces, Figures 3 and 4a).

Figure 3 also shows the NR profiles of two films after reaction in the h'- or d'-TFE-based vapors (red and yellow traces). These are noticeably different to the unreacted profiles, particularly in the regions of ~0.55 nm⁻¹ (h'-TFE, *red trace*) and ~0.2 nm⁻¹ & 0.55 nm⁻¹ (d'-TFE, *yellow trace*). The difference in fringe pattern from that of an unreacted film is largest for the d'-TFE derivatized film due to the higher Nb of the CD₂ group compared to that of the CH₃ group present in the TFE component.

The model Nb profiles for the reacted films are shown in Figure 4a (red and yellow traces), and it can be seen that both reacted films are thicker and have a higher Nb, as expected, than the precursor poly(PyCO₂H). Furthermore, the Nb profiles show that the unreacted films appear to be uniformly dense (black and green lines) whereas in both reacted films, the Nb gradually decreases toward the polymer/Au interface. (Note: The Supporting Information shows that the γ values for fits using a single homogenous layer are significantly greater than the graded profiles shown in the main text.) This is consistent with a gradual in the functionalization profile from being most functionalized at the outer interface and least functionalized at the Au interface, and is explored in more detail below.

Evaluating the composition films reacted at 50 °C. As described in the Supporting Information, the overall extent of reaction can be calculated by integration of the Nb profiles of a dry film, before and after reaction (Supp. Eqs. 5). Doing this for the h'-TFE and d'-TFE films of Figure 4 gives an overall reaction efficiency of 33% and 31% respectively.

Figure 4. (a) Model Nb fits to data of Figure 3. Unreacted films, black and green traces; reacted with h'-TFE, yellow trace; reacted with d'-TFE, red trace. (b) Estimation of volume fraction for PyCO₂TFE component in poly(PyCO₂H) film reacted with TFE; see later for details. y-axis corresponds to the volume fraction of poly(PyCO₂TFE) x Nb, Poly- TFE.

Figure 5. RAIRS spectra of poly(PyCO₂H) before (dark yellow) and after reaction with d'-TFE (red) together with spectra of films discussed later in text: hydrolyzed poly(PFP) reacted with d'-TFE (black); electropolymized presynthesized PyCO₂TFE (blue) and poly-(PyCO₂H) reacted with iPCDI (green). Spectra offset along the absorbance axis for clarity.

Since an NR-derived assay depends on model fitting to the measured NR data, RAIRS spectra (Figure 5) were also collected to support, or refute, the model fits by requiring the changes in magnitude of IR bands characteristic of the different components to be consistent with the integrated Nb profile assay. For the PyCO₂H- TFE system, bands at 1715 and 1760 cm⁻¹ in the reacted film spectrum (red trace, Figure 5) are indicative of both unreacted PyCO₂H (yellow trace) and PyCO₂TFE ester (blue trace) groups being in the reacted films (and also consistent with the XPS assay of Figure 2). Here, the change in the area under the PyCO₂H peak (after deconvolution) provides an estimate of the reaction efficiency (31%) that is consistent with the NR derived values.

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Combining forms of eq 2 that are appropriate to the PyCO\textsubscript{3} and \(d^2\)-TFE and PyCO\textsubscript{3}A-TFE systems, the reacted dry film Nb profiles of Figure 4a can be manipulated to give the PyCO\textsubscript{3} and PyCO\textsubscript{3}A volume fractions in a reacted film (see Supporting Information) Similar manipulations are commonplace when measurements of a single film are made in different contrasts of a solvent, in order to extract the solvent volume fraction within a polymer matrix. Here, however, since the numerical manipulations involve measurements on physically different films some caveats apply: the films should have identical microstructures, thicknesses and functionalization profiles. In the present case, the reliability of this approach is supported by the similarity in the global extent of reaction for the two films (both in the NR and RAIRS assays), the similarity in density and thickness of the two as deposited poly(PyCO\textsubscript{3}) films before reaction, and the similarity in the thickness change on reaction. Thus, Figure 4b shows the variation in volume fraction of the PyCO\textsubscript{3}A component multiplied by the NbPyco\textsubscript{2}A as a function of depth within the polymer film. The general trend seen is one in which the PyCO\textsubscript{3}A-TFE volume fraction \(\phi_{PycoA-TFE}\) decreases at distances further from the exposed air/polymer interface (NB). Since the number of layers used in the model fitting of the polymer layers is not constrained, undulations may arise in profiles derived from combining the models of different films. Although not shown, there is a converse variation in the PyCO\textsubscript{3}H volume fraction. Using an estimate for NbPyco\textsubscript{2}A of \(29 \times 10^{-3} \text{cm}^{-2}\) (derived from measurements of a film prepared by polymerization of the synthesized PyCO\textsubscript{3}A-TFE monomer and monomer density measurements, see later and Supporting Information), the profile of Figure 4b indicates that \(\phi_{PycoA-TFE}\) falls from a maximum of \(>80\%\) at the interface to \(\sim 35\%\) at distances \(5-10\) nm into the film. Although these are volume fraction measurements, they are consistent with mole fraction XPS results described earlier.

A further quantity that is of particular interest in the context of the vapor phase reaction method is the free volume (i.e., air) within the dry polymer films—this can give a guide as to whether vapor phase molecules can enter the matrix. Although a neutron "contrast" is not available for air for use in eq 1, \(\phi_{air}\) can be calculated by difference from unity of \(\phi_{PycoA} + \phi_{PycoH}\) As above, these latter two quantities can be calculated from the dry profiles using NbPyco\textsubscript{2}A and NbPyco\textsubscript{2}H estimates obtained from measurements described later. Thus, it can be estimated that \(\phi_{air}\) was 17% in the unreacted poly(PyCO\textsubscript{3}) films and \(\sim 10\% \pm 5\%\) in the bulk of the reacted poly(PyCO\textsubscript{3}-TFE) films (Note: The relatively large error associated with the \(\phi_{air}\) estimate in the poly(PyCO\textsubscript{3}A-TFE) films is due to it being obtained from combination of four quantities, each of which is derived from model fitting to experimental data).

NR measurements in water of poly(PyCO\textsubscript{3}) reacted at 50 \(^\circ\text{C}\). Since the objective of performing the TFE derivatization reaction was to attempt to prepare a hydrophobic interface, we collected a series of NR profiles for the variously reacted films immersed in water. Knowledge of the degree of water penetration into the matrix could then be considered alongside the surface topography (from AFM images) in order to account for observed variations in contact angles (see later). Furthermore, the presence of a medium inside the polymer film for which a neutron contrast was available can serve to indicate changes in density (and hence functionalization) that occur at different distances from the film interface.

Due to the multicomponent nature of the TFE derivatized films and anticipated (from XPS measurements) lack of functional uniformity, to provide comparative data, NR profiles were collected of films corresponding to the unreacted state and a fully TFE-functionalized polymer. Thus, panels a and b of Figure 6 show the Nb profiles (in water) of an as deposited poly(PyCO\textsubscript{3}) film and of a film prepared by polymerization of pre-synthesized PyCO\textsubscript{3}A-TFE monomer respectively. To interpret these figures at a qualitative level, the larger the difference between the polymer film Nb when measured in two isotropically different solvents, the larger the amount of solvent in the film. Conversely, if the measured Nb of the polymer film is the same regardless of the Nb of the solvent, then there is no solvent in the matrix. Further details of how to calculate the solvent volume fractions are given in the Supporting Information. Thus, Figure 6a shows that there is a significant amount of water (19%), uniformly distributed throughout the thickness of the poly(PyCO\textsubscript{3}) film. Figure 6b shows that there is a minimal amount of water in the region of the poly(PyCO\textsubscript{3}A-TFE) film near to the gold electrode substrate and that the film gradually becomes more solvated toward the exposed interface, the average solvation is \(\sim 5\%\) (NB). Any trapped air that may be present in the poly(PyCO\textsubscript{3}A-TFE) film adjacent to the gold electrode would not be apparent from these measurements. Usefully, from these measurements, NbPyco\textsubscript{2}A and NbPyco\textsubscript{2}H values can be obtained if it can be assumed that the water effectively "wets" the polymer—contact angle measurements suggest that whereas this is likely for the poly(PyCO\textsubscript{3}) film, some residual air may remain in the interior of poly(PyCO\textsubscript{3}A-TFE) matrix when it is immersed in water and that NbPyco\textsubscript{2}A would be underestimated. A comparison of the calculated solvent volume fractions of these angle component films with those of the reacted films is given later, in Table 1, after discussion of the variously reacted films.

The data and model fits corresponding to NR measurements (in water) of poly(PyCO\textsubscript{3}) films reacted at 50 \(^\circ\text{C}\) with \(d\)-TFE or \(d^2\)-TFE are given in Supplementary Figures with the best-fit model Nb profiles being shown in Figure 6c,d. An indication that the TFE functionalization at 50 \(^\circ\text{C}\) has occurred to some extent throughout the film comes from the observation that the Nb values for the solvated polymer near to the Au electrode are different to those of the unreacted film (region marked "1") in Figure 6a–d. The H/D exchange associated with the carbonyl groups in D_{2}O is not observed in the systems, the largest differences in polymer Nb are between (i) NbPyco\textsubscript{2}A-4a and NbPyco\textsubscript{2}A and (ii) NbPyco\textsubscript{2}A-4a and NbPyco\textsubscript{2}H (NbPyco\textsubscript{2}A-4a-TFE is similar to NbPyco\textsubscript{2}A and NbPyco\textsubscript{2}H-4a-TFE is similar to NbPyco\textsubscript{2}H). Thus, TFE functionalization is most notable in an Nb profile for the \(d\)-TFE reacted film measured in D_{2}O (NbPyco\textsubscript{2}A-4a in lower than NbPyco\textsubscript{2}H).

The above differences in polymer Nb also mean that the influence of greater functionalization at the outer interface (as seen in the dry Nb profiles) can be seen more clearly on the Nb profiles of the PyCO\textsubscript{3}A-4a-TFE/H\textsubscript{2}O and PyCO\textsubscript{3}A-4a-TFE/D\textsubscript{2}O systems here, at the solvent interface, the difference in Nb between the polymer layer and the solvent is greater than the difference in Nb between the polymer at the electrode interface.
and the solvent. In particular, the replacement of the H/D exchangeable carboxylate groups by h^2-TFE moieties at the polymer interface leads to a noticeable dip in the Nb profile measured in D_2O (region marked "-" in Figure 6d).

The presence of the H/D exchangeable PyCO,H moieties (whose spatial distribution is a priori unknown) in the reacted film matrix complicates quantitative interpretation of the Nb profiles. However, using a knowledge of the overall film composition, it is possible to calculate (see Supporting Information for method) the average volume fraction of water within the derivatized films from these profiles. For both the h^2-TFE and d^2-TFE films this is ~10%, a level significantly lower than in the unreacted film, but significantly higher than in the film prepared from pre-synthesized PyCO2-TFE. This decrease in water content, however, is similar to that which would occur based on the extra volume occupied by the TFE groups alone suggesting that interactions with the residual carboxylic acid groups may still play a role in determining the overall solution.

A method to evaluate the Nb profile that avoids the complications of carboxylic acid H/D exchange involves comparison of the Nb profile of the film after reaction in the dry state (e.g., red trace in Figure 4a) with that for the polymer immersed in H_2O (e.g., red trace in Figure 6d). This approach can be used in this instance because both the dry and hydrated film are the same and consequently the difference between these profiles is proportional to the degree of aqueous solution. Performing such numerical manipulations indicates that variation in solvation across the bulk of the film between the Au electrode and solution interface is small. Indeed, when inserting various arbitrarily constructed Nb profiles into eq 1, it was found that in order for the PyCO_2-TFE:PyCO,H ratio at the solution interface to be larger than that than at the Au electrode interface (as also indicated by the XPS measurements) the solvation near the solution interface needed to be only slightly below that at the polymer/Au electrode interface.

TABLE 1: Volume Fractions and Reaction Efficiencies for Unreacted and Reacted Poly(PyCO,H) Films

<table>
<thead>
<tr>
<th>polymer</th>
<th>average (\phi_{water}) ((\phi_{water, dry}))</th>
<th>average (\phi_{PyCO}_2)</th>
<th>average (\phi_{PyCO, H})</th>
<th>average reaction efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>as deposited poly(PyCO,H)</td>
<td>19% (16%)</td>
<td>60% (~50%)</td>
<td>30% (~35%)</td>
<td>19%</td>
</tr>
<tr>
<td>hydrolyzed poly(PFP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly(PyCO_2-TFE) from PyCO_2-TFE monomer</td>
<td>5% (~5%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly(PyCO_2H) reacted at RT</td>
<td>16%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly(PyCO,H) reacted at 50°C</td>
<td>10% (10%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydrolyzed Poly(PFP) reacted at 50°C</td>
<td>45% (~50%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 7 shows the reflectivity profiles and fits for electropolymerised PyCO,H films (in water) after reaction with h^3- or d^4-TFE at room temperature. Simple inspection reveals that near to the Au electrode (region marked "-+" in Figure 7) the Nb profiles of the reacted films are similar to those of the unreacted poly(PyCO,H) film (region marked "-+" in Figure 6a) and that at the solution interface (region marked "++" in Figure 7) the Nb values are markedly different than those in the bulk. Two possible variations in structural or compositional profile that could account for the polymer phase Nb near the solution interface...
interface being different to that in the bulk are (i) a lower solvent volume fraction within the polymer and/or (ii) a smaller proportion of carboxylic acid groups with their associated exchangeable protons near the polymer/solution interface. Both of these explanations are consistent with a variation in compositional profile in which the extent of TFE derivatization is greater at the solution interface. Thus, these observations provide a further clear indication that, even for films that are only 15–20 nm thick and have been exposed to reactant vapor for a significant period of time (8 h), the functionalization is restricted to a region of the polymer film close to the exposed interface.

As noted in the discussion of the 50 °C reaction, the differences in Nb profiles are most noticeable in the profiles for the PyCO₂H-h⁻¹TFE/D₂O and PyCO₂⁻d⁻¹TFE/H₂O systems.

Although, if both reacted films had identical microstructures, thickness and functionalization profiles, except for the H/D substitution of the ester moieties, there would be sufficient data in Figure 7a to extract the volume fraction profiles for water and the two polymer components, such manipulations should be treated cautiously. This is because small variations between the two films can bias such results in an unknown manner, especially when constraint-free model fitting is used. Nevertheless, using manipulations of eq 2 applied to the measurements shown in Figure 7 suggests that the volume fraction of water in the reacted films falls from ~17% at the Au interface to ~8% at the solution interface (see supplementary data for equations and supplementary Figure 1 for details). Furthermore, PyCO₂⁻TFE extracted from these manipulations support the qualitative observation that, under these reaction conditions, the ester functionalization has been limited to the outer part of the polymer films (Supplementary Figure 2).

1.3 Characterization of Solution-Phase Reaction with Electrodeposited Poly(PyCO₂H). To investigate whether the overall extent of the vapor phase reaction was limited by either a lack of solvent medium or low reactant concentration, films of electrodeposited poly(PyCO₂H) were reacted with TFE/pyridine/PCDI mixtures in acetonitrile and DMSO. From RABBIT measurements, it was found that even when the TFE concentration was 0.5 M and a reaction time of 3 h was used, the extent of reaction was only ~33%, similar to that found for the vapor phase reaction at 50 °C. XPS measurements also confirmed this limited reaction and NR characterization yielded similar Nb profiles (Supplementary Figure 3) to those for the 50 °C vapor phase reacted films. This is a striking observation when set alongside the ready and rapid transport of counterions throughout the film during electrochemical oxidation and reduction.

1.4 Component Volume Fractions within Poly(PyCO₂H) before and after RT Reaction. Earlier a method was described by which the spatial variation in volume fractions of the various components could be extracted from profiles of two films, one reacted with h⁻¹TFE and the other with d⁻¹TFE (see also the Supporting Information). Here a method to calculate the average volume fractions based on the Nb profiles of a single film is formulated. This is done by integrating eq 1 for the D₂O and H₂O based Nb profiles and combining these equations with a "mass balance" type expression for the overall composition of the film based on the dry state Nb measurements (which indicated 33% of the PyCO₂H moieties had been functionalized with TFE, see supplementary eq 5, 10–12). Using this method, Table 1 details the volume fractions of the components in the various films studied.

Interestingly, the nonpolymer volume in the dry films is only slightly less than that when the films are immersed in water, i.e., immersion in solvent only slightly swells the polymer. For instance, ~16% of the volume in the dry unreacted polymer is air and in when immersed in water the solvent volume fraction increases to ~19% as a result of the film swelling uniformly by ~15%. However, the significant decrease in the amount of water within the film after functionalization may be a consequence of both the hydrophobic nature of the TFE moieties and the film polymer chains/microstructure not being able to undergo further swelling-type reorganization after they have reacted with TFE. Indeed, it is notable that although the dry film thickness increases by ~15% after the vapor phase reaction, there is negligible further swelling on immersion in water.

1.5 Discussion of Structural Profiles for Electropolymerized PyCO₂H Reacted under Different Conditions. The results from the three sets of characterization measurements described above shed light on whether the reactant phase (solution or vapor), concentration or diffusion are the prime cause of the limited overall extent of reaction (after reaction times of several hours). The similarity of the solution-phase reaction profile to that of the vapor phase reaction at 50 °C shows that the lack of solvent does not impede the vapor phase reaction. This, coupled with the lack of complete functionalization at the high concentrations used in the solution reaction, suggests that the ultimate limitation on functionalization may be due to the inaccessibility of certain of the carboxylic acid motifs.

The composite Figure 8 overlays selected Nb profiles from Figures 6 and 7. These provide a clear proof that the vapor phase functionalization reaction is initially confined to the exposed interface, after which a more homogeneous functionalization occurs deeper into the film. Nevertheless, as with the solution reaction, even the outer regions of the film do not become fully functionalized. In terms of the cartoons of Figure 1, the progress of the reaction could be viewed as initially being similar to the left-side cartoon, with a reactant transport profile similar to that in the right-side cartoon prevailing at later stages (although
regions containing a dense polymer matrix surrounded by a less dense matrix, rather than actual fissures may exist.

A postulated limitation on the extent of functionalization due to constraints on access of reactant molecules to some regions of the polymer matrix should be viewed in the context of volume fractions determined from Nb profiles of the reacted films. These suggest there is still ‘free’ volume available within the reacted polymer matrix. It may be, however, that the polymer chains cannot unfurl and so make use of this volume as the film is progressively functionalized (N.B.: electropolymerisation of the PyCO2H-TFE film is another monomer is straightforward implying there is no intrinsic steric impediment to a fully functionalised film).

To investigate whether making a polymer film with a more open internal microstructure could influence the overall extent of reaction, variations in the poly(PyCO2H) deposition protocol were explored. These included (i) the use of faster growth conditions18 and (ii) formation of a poly(PyCO2H) film by hydrolysis of the pentafluorophenol ester in pre-grown poly(PFP) films. XPS and RAIRS measurements indicated that the latter approach was most successful and thus, as described below, NR characterization of the hydrolyzed poly(PFP) system was carried out to probe the film microstructure and solvation.

2.1. Reaction of TFE Vapor with Poly(PyCO2H) Prepared from Hydrolysis of Poly(PFP). XPS measurements showed that when 50 °C reaction conditions were used, the functionalization of the exposed interface of a hydrolyzed poly(PFP) film was 100%. In contrast, RAIRS measurements on 20 nm thick films (Figure 5, black trace) showed that there still remained some unreacted PyCO2H groups. $Ar^+$ ablation of the polymer used to probe beneath the surface using XPS since repeated attempts to remove the reacted polymers from the substrate using sellotape were unsuccessful. The XPS assay suggested that the extent of reaction fell to ~20% toward the electrode interface (although we note that this depth profiling method is problematic because of the unknown ablation depth and ablation rates of different species).

The Nb fits of Figure 9 show that hydrolysis of the initially deposited poly(PFP) film leads to a large decrease in the overall film thickness (black and red traces, Figure 9). Furthermore, the density profiles of the co deposited and hydrolyzed poly(PFP) films suggest that their outer interface is significantly more diffuse than as deposited poly(PyCO2H) films (black and green traces, Figure 4a). Significantly, no off-specular scattering was seen, indicating that the hydrolysis of the film did not lead to a break up of the film or micron scale surface roughening.

These differences in interfacial morphology between the as grown poly(PFP) and poly(PyCO2H) films are corroborated by AFM measurements (Supplementary Figure 4). These show that the clusters of polymer in poly(PyCO2H) are much smaller and more densely packed than in the poly(PFP) films, both before and after reaction with TFE.

Despite the greater diffuseness of the hydrolyzed polymer, comparison of the Nb profiles before and after reaction (red and green traces, Figure 9) indicate that the film still swells when TFE is incorporated into the film. The observation that it does not reach the same thickness as the initial, unhydrolyzed poly(PFP) film suggests that there is potential for further functionalization under different reaction conditions.

Integration of the dry Nb profiles of Figure 9 indicates that the overall extent of reaction is 49%, significantly larger than the 33% for the poly(PyCO2H) films (Table 1). Again, this value is consistent with the reflectance infrared assay shown in Figure 5 (black trace).

The greater diffuseness of the exposed interface of hydrolyzed poly(PFP) films, compared to those of poly(PyCO2H) is also evident in the Nb profiles of the films immersed in H2O and D2O (Figure 10a). While the solvation at the Au electrode is similar to the value throughout the thickness of the as deposited poly(PyCO2H) films (Figure 6a), the bulk and solution interface are much more solvated. The average value for $\delta_{TFE}$ is ~60% (Table 1).

Clearly from Figure 10b,c, the solvent volume fractions within the reacted films are similarly nonuniform. This gradation between the Au/polymer and polymer/solvent interfaces is much greater than for the as-deposited poly(PyCO2H) system (Figures 6 and 7) and it can be concluded that on reaction, the average $\delta_{TFE}$ falls from ~60% to ~55%. Using the same method as for the poly(PyCO2H) system above, the average fractions of the polymer components are estimated to be ~20% and ~35%
This showed (see that hal not possible to made using DMSO exploration -100 PyCO₂⁻ TFE :O PyCO₁H at the available NR reaction with II- TFE reaction different film.

To conclude the NR structural studies, a brief investigation using DMSO was carried out to see whether the functionalized film was similarly solvated by an organic solvent as by water. This showed (see supplementary Figures 5 and 6) that there was little difference in solvation in the two media, an observation that is consistent with deductions made about the hydrophobicity of the reacted, hydrolyzed poly(PFP) films from contact angle measurements described below.

3.1. Contact Angle Measurements. Finally, as a brief exploration of the composition-structure-property relationships for this system, water droplet contact angle measurements were made on the variously prepared and reacted films. These are summarized in Table 2 and while the advancing angles show that all the reacted films have a degree of hydrophobicity, the receding angles indicate this is a nonequilibrium state, i.e., the polymer surfaces are 'wetted' following a short period of exposure to water. This difference may be a consequence of the TFE functionality being confined to the outer surface of the polymer and thus only able to provide a transient barrier to the wetting and solvation of the underlying, unreacted poly-(PyCO₂H).

TABLE 2: Advancing and Receding Contact Angles for Droplets of Water Placed on Unreacted and Reacted Poly(PyCO₂H) Films

<table>
<thead>
<tr>
<th>polymer</th>
<th>advancing</th>
<th>receding</th>
</tr>
</thead>
<tbody>
<tr>
<td>unreacted poly(PyCO₂H)</td>
<td>31°</td>
<td>none</td>
</tr>
<tr>
<td>poly(PyCO₂H) reacted at RT</td>
<td>99°</td>
<td>45°</td>
</tr>
<tr>
<td>poly(PyCO₂H) reacted at 50 °C</td>
<td>98°</td>
<td>57°</td>
</tr>
<tr>
<td>hydrolyzed poly(PFP) reacted at 50 °C</td>
<td>91°</td>
<td>22°</td>
</tr>
<tr>
<td>polymerized PyCO₂⁻ TFE</td>
<td>101°</td>
<td>64°</td>
</tr>
</tbody>
</table>

Conclusions

A combination of XPS and RAIRS measurements has shown that the extent of reaction of thin poly(PyCO₂H) films with TFE is limited to ~33%, whether the reaction is performed using vapor phase reagents at an elevated temperature or in solution. NR measurements of films prepared by performing the vapor phase reaction at room temperature, showed that the initial stage of this reaction is confined to the outer interface before progressing toward the substrate. This suggests that the "grain boundary" like features seen in the AFM images of the polymer films do not correspond to fissures or percolation pathways that provide a significant transport pathway during the early stages of the functionalization reaction.

NR shows that after reaction, although the void space within the polymer noticeably decreases, there is still a significant volume that could be occupied by other species (solvent and/or reactant vapor molecules). Furthermore, an increase in the vapor concentration by a factor of ~6 only results in a 50% increase in the extent of reaction. This suggests that a reaction limit is imposed by a need for buried polymer chains to unfurl in order to accommodate the volume occupied by TFE adduct and/or regions of the polymer being too dense to accommodate the diffusion of reactant species.

NR, RAIRS, and XPS show that a significantly greater extent of TFE functionalization can be obtained by preparing more diffuse (as shown by NR measurements) poly(PyCO₂H) films through hydrolysis of pre-deposited poly(PFP). However, the more open structure of these films means that these films have a higher degree of solvation and poorer hydrophobicity properties than found for the TFE-functionalized, as-deposited poly-(PyCO₂H). This is an illustration of how a detailed system...
Compositional Profiles within Conducting Polymer Films

can explain why, even though the material preparation conditions can be varied to give a system that chemically closer to the target material, the overall functional performance is less than optimal. For the vapor phase modified films, the resolution of the neutron beam angles are significantly less than the advancing angles may be due to the dominating effect of the residual hydrophilic PyPCO2H motifs preventing water from being excluded from the film

Finally, having found that different sets of reaction conditions and polymer preparation methods control the spatial distribution of functional motifs inhomogeneous within polymer films, two applications in which these may be useful are (i) in preparing stratified polymers and (ii) providing insights into how water molecules may be adsorbed by polymers fabricated by different methods for use in sensor applications Notably, the demonstrated utility of combining infrared and XPS measurements with neutron reflectivity could be extended to probe both the spatial distribution of motifs introduced to polymer matrices by means of a subsequent (vapor or solution phase) chemical reaction, and the surrounding polymer microstructure which could influence the accessibility of the motifs toward, for example, interactions with analyte species, in the case of a sensor, e.g. polymer-DNA sensors

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Supporting Information Available Manipulation of NR equations, NR profiles, AFM images. This information is available free of charge via the Internet at http://pubs.acs.org

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(25) Paarl 32 software developed by the KMI, Berlin


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APPENDIX II

*Characterisation of d$_4$-EDOT*

The d$_4$-EDOT was extracted in ether, dried with magnesium sulfate and the solvent removed. After analysis of the spectra below, it was deemed that the compound did not require further purification.

$^{13}$C NMR (Figure 7.1) confirms the presence of only one species, identifiable by three individual resonance peaks in the spectrum:

- $\delta$ vs. TMS = 140.78 ($\beta$-C coupling)
- 98.58 ($\alpha$-C coupling adjacent to the S atom)
- 62.89 (methylene C atoms)

The methylene C atoms were additionally identifiable by the $^{13}$C-$^2$D coupling (Figure 7.2) and it was inferred from these data that d$_4$-EDOT was in excess of 95% pure.

$^2$D NMR (Figure 7.3) reveals a single broad peak ($\delta$ vs. D$_2$O = 3.99). Additionally, the molecular ion was seen as the most intense peak in the mass spectrum (Figure 7.4). M/z of 146.8 compares with RMM of 146.21.

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$^a$ Spectra supplied by Dr. J Young and Dr G Weaver, Loughborough University
Figure 7.1 $^{13}$C NMR of d$_4$-EDOT

Figure 7.2 Expansion of $^{13}$C NMR of d$_4$-EDOT
Figure 7.3 $^2$D NMR of $d_4$-EDOT.

Figure 7.4 Mass spectrum of $d_4$-EDOT
APPENDIX III

Spectroscopic data illustrating wavelength shift after chelation of $K^+$

Figure 7.5 A comparison of the UV-vis spectra of the 0.04 PFP:0.96 BT copolymer before and after soaking in a 25mM KPF$_6$/ACN solution. A shift of 8nm in $\lambda_{max}$ was seen.