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Synthesis and characterisation of chiral conducting polymers

Ian Norris

University of Wollongong

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SYNTHESIS AND CHARACTERISATION OF CHIRAL CONDUCTING POLYMERS

A thesis submitted in fulfillment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

IAN NORRIS, B.E (Chem)

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ABSTRACT

This thesis describes circular dichroism (CD) and uv-visible-near infrared studies on optically active polyaniline salts doped with (+)- or (-)-camphorsulfonic acid (HCSA), which provide new insights into conformation changes in the polymers caused by the synthetic route, temperature and solvent. The chiroptical properties of optically active PAN.(+)-HCSA films prepared electrochemically were found to be distinctly different to those of films prepared chemically via the acid doping of emeraldine base with (+)-HCSA. The results indicated two different conformations for the polyaniline chains, assigned as “extended coil” and “compact coil”, respectively. This is the first time that different conformations have been unequivocally demonstrated for the polymer chains of electrochemically and chemically prepared polyaniline.

A striking thermochromic effect was induced by heating an electrochemically deposited PAN.(+)-HCSA film to 140°C for 10 min. The conformation of the polyaniline chains was shown from CD and uv-visible-near infrared spectral studies to convert from an “extended coil” to a “compact coil” conformation. This change in conformation was accompanied by a decrease in the electrical conductivity of the film. These effects were not reversed upon cooling. Further heating the electrochemically deposited (or chemically cast) optically active PAN.(+)-HCSA films beyond their glass transition temperature resulted in progressive thermal de-doping to form racemic emeraldine base.

The PAN.(+)-HCSA emeraldine salts formed by doping emeraldine base with (+)-HCSA in a range of organic solvents (NMP, DMSO, DMF and chloroform) have been shown to adopt a “compact coil” conformation. The position of the high wavelength, localized
polaron absorption band and the corresponding bisignate CD bands underwent a significant red shift, which has been attributed to the slow de-aggregation of the polyaniline chains in solution. In contrast, the dissolution of electrochemically deposited PAn.(+)-HCSA films in these organic solvents or benzyl alcohol resulted in the polymers largely retaining their original solid-state “extended coil” conformation.

The conductivity of chemically cast PAn.(+)-HCSA films was found to increase by one and two orders of magnitude, respectively, after exposure to thymol and carvacrol vapour. This was accompanied by the development of a free carrier tail in the near-infrared region, which supports the “secondary doping” of the polyaniline chains by both thymol and carvacrol vapours. These new “secondary dopants” have the advantage of being less toxic than the previously studied m-cresol. The alternative doping of emeraldine base with (+)-HCSA using molten thymol or liquid carvacrol as solvent also resulted in the “secondary doping” of the PAn.(+)-HCSA salts formed. Their uv-visible-near infrared spectra suggested that the polymer adopted a partial “extended coil” conformation. However, their CD spectra indicated that the majority of the polyaniline chains was still in the “compact coil” conformation. Related studies with the dye Thymol Blue showed that while its sulfonate group readily doped emeraldine base dissolved in NMP, DMSO and DMF, the dye did not cause “secondary doping” despite the presence of the thymol group in its structure.

The preparation and chiroptical properties of optically active polyaniline in each of its five accessible redox and pH states have been reported for the first time, namely: leucoemeraldine base, emeraldine base, emeraldine salt, pernigraniline base and pernigraniline salt. The new chiral materials were obtained via the chemical reduction
or oxidation of optically active PAn.(+)-HCSA or via its de-doping with NH₄OH. The chiroptical properties of the optically active polymers so derived depended on the conformation of the precursor emeraldine salt employed, with different behaviour being found with electrochemically deposited ("extended coil") and chemically deposited ("compact coil") PAn.(+)-HCSA precursor films.

This thesis also describes three new synthetic routes to improve the processability of the optically active polyanilines, which has been one of the limitations restricting their applications to date.

(i) A simple, new method for the *in situ* deposition of optically active PAn.(+)-HCSA and PAn.(-)-HCSA films from aqueous solutions of aniline undergoing oxidative polymerization with ammonium persulfate in the presence of (+)- and (-)-camphorsulfonic acid has been developed. The chiroptical properties of these *in situ* deposited emeraldine salt films indicated that they possess neither a pure "compact coil" nor a pure "extended coil" conformation, but may have an intermediate conformation. De-doping of the *in situ* deposited films with aqueous 0.1 M NH₄OH gave optically active emeraldine base films, which could be re-doped with HCl vapour or aqueous 1.0 M HCl to generate optically active PAn.HCl films with retention of polymer configuration.

(ii) Novel chiral polyaniline colloids have been generated via the electrohydrodynamic polymerization of aniline in aqueous (+)- or (-)-HCSA using polystyrene sulfonate (PSS) as a steric stabilizer and co-dopant. The chiroptical properties of these effectively "water soluble", colloidal polyaniline dispersions indicated that the
polymer was synthesized largely in the "compact coil" conformation. The optical activity of the colloidal dispersions increased markedly upon standing for 24 hr, indicating that the asymmetric rearrangement of the polyaniline chains induced by the chiral HCSA dopant occurs much more slowly than the initial doping process. Interestingly, the optically active fractions of polyaniline colloids PAn.(+)-HCSA/PSS were remarkably inert to chemical oxidation or reduction and alkaline de-doping. Related studies using polyethylene oxide as an alternative steric stabilizer showed that it was inferior to PSS', with significant over-oxidation of the polyaniline apparent.

(iii) The first reported synthesis of optically active poly(o-methoxyaniline) has been achieved via the enantioselective polymerization of o-methoxyaniline from aqueous solutions containing (+)- or (-)-camphorsulfonic acid. The dark green films of the POMA.(+)-HCSA and POMA.(-)-HCSA emeraldine salts exhibited mirror imaged CD bands in the visible region, confirming macroasymmetry of the polymer chains and enantioselectivity in the chiral induction. The steric influence of the methoxy substituent caused the POMA.(+)-HCSA and POMA.(-)-HCSA films to adopt a "compact coil" conformation, in contrast to the "extended coil" conformation for similarly deposited parent PAn.(+)-HCSA salts. Significantly, for processing purposes, these electrochemically prepared POMA.HCSA salts are highly soluble in a range of organic solvents such as DMF, DMSO, NMP, CHCl₃ and methanol. They adopt the same conformation in each of these different solvents, but a large red shift in the high wavelength polaron absorption band suggests an increase in the conjugation length of the polymer chain along the solvent series NMP < CHCl₃ < DMSO, DMF < methanol.
Deprotonation of the electrochemically deposited POMA.(+)-HCSA film using 1 M NH$_4$OH resulted in the formation of an optically active methoxy-substituted emeraldine base film, which could be re-doped with aqueous 1.0 M HCl to generate optically active POMA.HCl films with retention of the main chain chirality of the polymer backbone.

Optically active poly(o-methoxyaniline) could also be synthesized in solution via the acid doping of methoxy-substituted emeraldine base with (+)-HCSA in DMSO solvent. However, the generation of optical activity in the polymer was substantially slower than for the corresponding parent polyaniline, taking several days to fully develop. The extent of aggregation of the doped POMA.(+)-HCSA salts in solution was highly dependent on the molecular weight of the methoxy-substituted emeraldine base.
DECLARATION

This is to certify that the work described in this thesis has not been submitted for a higher degree at any other University or Institution.

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PUBLICATIONS

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CHAPTER 1
General Introduction

1.1 Conducting Polymers

Intrinsically conducting polymers are a relative new class of organic polymers with the remarkable ability to conduct electrical current. For a polymer to become intrinsically conducting, the polymer must contain overlapping π molecular orbitals and a high degree of π-bond conjugation. When the highly conjugated polymer is in its neutral state it is essentially an insulating material. It is only upon removal of a π-bond electron from the conjugated polymer backbone to form a radical cation defect (called a polaron) that the insulating polymer becomes conductive. Removal of the π-bond electron causes the remaining electrons in the π orbitals to become delocalized along the length of the conjugated polymer backbone, thereby enabling free mobility of the polaron to move along the chain. The formation of the positively charged polymer backbone is accompanied by the incorporation of a dopant anion which has the effect of electrostatically balancing the positive charges.

The major breakthrough in conducting polymer research was in 1977 with the discovery by Shirakawa, MacDiarmid and Heeger\(^1\) that the partial oxidation of polyacetylene films with gaseous bromine or iodine resulted in a dramatic increase in the electrical conductivity of the polymer with values in the metallic region. Although polyacetylene is the most characterized and conductive (up to \(10^5\) S/cm) conducting polymer, its poor environmental stability has limited its commercial potential. The most conducting form of polyacetylene is the \textit{trans} isomer, as it is highly crystalline after being doped with iodine.
In 1979 conducting polypyrrole films were first synthesized by Diaz et al.\textsuperscript{2} These were prepared via the anodic oxidation of pyrrole in acetonitrile while using tetraethylammonium tetrafluoroborate as the supporting electrolyte. The conductivity of the polypyrrole films was as high as 100 S/cm and, while significantly lower than polyacetylene, the polypyrrole films were thermally and environmentally stable. Later Diaz et al\textsuperscript{3} found that conducting polyaniline films could also be synthesized using electrochemical polymerization route. Since then numerous conducting polymers have been prepared, with the chemical structure of the most researched examples shown in Table 1.1.

**Table 1.1. Common Conducting Polymers and their Preparative Method**

<table>
<thead>
<tr>
<th>Conducting Polymer</th>
<th>Structure</th>
<th>Preparative Method</th>
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<tbody>
<tr>
<td>trans-Polyacetylene</td>
<td><img src="image" alt="Structure" /></td>
<td>CP</td>
</tr>
<tr>
<td>Polypyrrole</td>
<td><img src="image" alt="Structure" /></td>
<td>CP/EP</td>
</tr>
<tr>
<td>Polythiophene</td>
<td><img src="image" alt="Structure" /></td>
<td>CP/EP</td>
</tr>
<tr>
<td>Polyaniline</td>
<td><img src="image" alt="Structure" /></td>
<td>CP/EP</td>
</tr>
<tr>
<td>Poly(para-phenylene vinylene)</td>
<td><img src="image" alt="Structure" /></td>
<td>CP</td>
</tr>
</tbody>
</table>

CP – chemical polymerization, EP – electrochemical polymerization
While the majority of applications for conducting polymers are based on the bulk conductivity and electroactivity of the polymer, for some applications the morphology of the polymer is also important. A wide range of potential applications currently being explored include their use as electrochromic devices, rechargeable batteries, sensors, electromagnetic radiation shielding, electrochemical actuators and anti-corrosion agents, as well as use in electrochromatography and membrane separations.

1.2 Polyaniline

Due to its high environmental stability, facile redox and pH switching between differently coloured states, relatively high conductivity and low cost, polyaniline is recognized as one of the most promising organic conducting polymers for future commercialization. Unlike most conducting polymers, polyaniline exists in a variety of forms that differ in the degree of oxidation of the polymer backbone and the degree of protonation of the imine nitrogen atoms. The oxidation state in the base (unprotonated) form can vary from the fully oxidized polymer (pernigraniline) to the half oxidized polymer (emeraldine) to that of the fully reduced polymer (leucoemeraldine), as shown in Scheme 1.1.
However, the only conducting form of polyaniline arises from the complete protonation with acids (HA) of the imine nitrogen atoms in emeraldine base to form emeraldine salt PAN.HA. This results in the generation of a delocalized polysemiquinone radical cation 1 and is accompanied by an increase in conductivity of ca. $10^{10}$.

Polyaniline is synthesized by the oxidation of aniline with an appropriate chemical oxidant or by electrochemical polymerization on an inert electrode substrate. Genies et
al and Lux have suggested that the polymer produced by these two different polymerization routes may have different structures. For the electrochemical oxidation of aniline, the mechanism would be related to radicals adsorbed at the surface of the electrode, whereas chemical oxidation of aniline would involve radicals distributed in solution. Therefore, electrochemical oxidation might allow different coupling reactions between the monomer, the intermediate products and the resulting aniline oligomers and polymers.

1.2.1 Electrochemical Polymerization

The electropolymerization of aniline must be carried out in acidic solutions in order to deposit conducting emeraldine salt PAn.HA films on inert electrodes. Acidic solutions are necessary as the monomer is most soluble in water under acidic conditions and it is well known that the conducting form of polyaniline only forms when the pH is less than 3.14

A wide range of electrodes films have been employed, including platinum, indium-tin-oxide (ITO) coated glass and vitreous carbon for the deposition of polyaniline. The electrochemical methods for the polymerization of aniline are galvanostatic (constant current), potentiostatic (constant potential) and potentiodynamic (potential cycling). Aniline is usually polymerized using potentiostatic or potentiodynamic techniques because the monomer oxidation potential is close to that required to over-oxidize the polymer. Over-oxidation causes the degradation of the polymer backbone that results in inferior electronic and mechanical properties for the polymer.20
A variety of acids including HCl, H2SO4, HNO3, HClO4 and HF has been successfully incorporated into polyaniline. The anion incorporated has a considerable effect on the rate of the nucleation step and the rate of polymer deposition. Kitani et al. have shown that aniline polymerizes 2.7 times faster in H2SO4 than from HCl, HNO3 and especially HClO4. The difference in polymer growth rates is reflected in the morphology of polyaniline films. Polyaniline films deposited from H2SO4 and HCl have an open and porous structure, while films deposited from HClO4 have a compact and pore-free structure.

The generally accepted mechanism for the synthesis of polyaniline by electrochemical polymerization is shown in Scheme 1.2. This process has been described as an E(CE)n process. This means that the polymerization is initiated by an electrochemical (E) process, and is propagated by the repetition of a chemical (C) process followed by an electrochemical (E) process. The initiation (step 1) and rate-determining step is formation of the radical cation of aniline, which is independent of the pH of the electrolyte. This is usually described as the oxidation product of aniline and has three different resonance forms.

The resonance forms with the radical on the N and in the ring para position are most likely to react in a coupling reaction (step 2) to give a dimer, by eliminating two protons. The dimer formed undergoes rearomatization to its neutral state. However, the radical cations in the ortho position are commonly observed, but are not likely to participate in the polymerization reaction due to electrostatic repulsion of the adjacent positively charged amine group. However, ortho coupling can still proceed to a limited extent, which results in the formation a corrupted polymer.
Chain propagation (step 3) requires the oxidation of the oligomer to form a radical cation. At the potential to oxidize the aniline, the oligomer is also oxidized to form its radical cation, which is delocalized over the aniline at the end of the chain, and thus can react with an aniline radical cation in the para resonance structure to increase the chain length. The growth of the polyaniline chains has been shown to be autocatalytic, where the rate of polymer formation increases as the mass of polymer deposited on the electrode increases. The autocatalytic growth of the polymer is a function of applied potential, monomer concentration and pH. The polymer is formed in the conducting emeraldine salt form that arises from the simultaneous doping of the polymer by protonation (step 4) during chain propagation.

**Step 1: Initiation**

\[
\text{NH}_2 + \text{HA} \rightarrow \text{HA-N}^+ \text{A}^{-} \text{H} \\
\text{N} \quad \text{ortho} \quad \text{para}
\]

resonance forms of the radical cation

**Step 2: Coupling**

\[
\text{HA-N}^+ \text{A}^{-} \text{H} + \text{HA-N}^+ \text{A}^{-} \text{H} \rightarrow \text{HA-N}^+ \text{A}^{-} \text{H}
\]
1.2.2 Chemical Polymerization

The chemical oxidation of aniline in aqueous acid media by a variety of oxidizing agents results in the formation of the green emeraldine salt PAn.HA as a precipitate. Although the most commonly used oxidizing agent is ammonium persulfate\textsuperscript{28,29}, other chemical oxidants successfully used for the polymerization of aniline include potassium dichromate\textsuperscript{30}, iron chloride\textsuperscript{31} and hydrogen peroxide.\textsuperscript{32} This oxidation reaction is usually carried out in hydrochloric acid or sulfuric acid at a pH between 0 and 2.

A study by Jozefowicz et al\textsuperscript{33} of the oxidation of aniline using ammonium persulfate as the oxidizing agent indicated that the rate of reaction is dependent on the temperature in the range 0-80°C. The enthalpy of the reaction is high ($\Delta H^0 = -372$ kJ/mol) and does not vary with the initial temperature between 0° and 80°C nor with the concentration of aniline, but does vary with the concentration of the oxidant.
The optimal oxidizing conditions for aniline with ammonium persulfate have been reported in the literature with respect to molecular weight, conductivity and reaction yield.\textsuperscript{34,35,36} More recently it has been reported\textsuperscript{37-40} that significantly higher molecular weight polyaniline can be synthesized at temperatures between $-30^\circ$ and $-40^\circ$C, using lithium chloride as an inert solute to keep the reaction mixture mobile. According to these authors, the lower temperature reduces the time of the initiation step (monomer oxidation) in solution and increases the rate of the chain propagation step, which are responsible for the formation of high molecular weight polyaniline chains.

The reaction mechanism now generally accepted for the synthesis of polyaniline with ammonium persulfate as the oxidizing agent, shown in Scheme 1.3, has been proposed by Lux\textsuperscript{15} and Strejskal et al.\textsuperscript{41} The initiation step (step 1) in this chemical oxidation is again the formation of the radical cation of aniline, which has three resonance structures. The aniline cation radicals with the radical on the N and in the para position participate in a coupling reaction (step 2) to form a dimer, by eliminating two protons.

Chain propagation results from the coupling reaction of the oligomer radicals and the aniline cation. As the polymerization proceeds, the reaction mixture becomes deep blue. The deep blue colouration observed is associated with the formation of protonated pernigraniline (step 3). MacDiarmid et al.\textsuperscript{42,43} monitored the reaction open circuit potential and reported that the polyaniline intermediate was pernigraniline before the oxidant was completely consumed. This was later confirmed by spectroscopic studies of the polymerization process.\textsuperscript{41,44}
Once all of the ammonium persulfate has been consumed while unreacted aniline is still present, pernigraniline is a sufficiently strong oxidizing agent to oxidize the remaining aniline. During this stage, the colour of the reaction mixture quickly turns to green indicating the formation of emeraldine salt, i.e. the pernigraniline becomes reduced by aniline to the emeraldine oxidation state (step 4), while aniline is polymerized as shown in steps 1, 2 and 3. Therefore, the emeraldine salt precipitate, PAn.HA 1, is obtained by the reduction of pernigraniline initially formed and the oxidative polymerization of aniline by pernigraniline.

**Step 1: Initiation**

\[
\text{N} \quad \text{ortho} \quad \text{para}
\]

resonance forms of the radical cation

**Step 2: Coupling**
1.2.3 Doping Mechanism in Polyaniline

Polyaniline has a conduction mechanism that is unique among conducting polymers in that its most highly conducting doped form can be reached by two different processes: protonic acid doping of emeraldine base and oxidative p-type doping of leucoemeraldine. Doping of other p-type conducting polymers, e.g. polypyrrole, polyacetylene and polythiophene results in the formation of a carbonium ion, but the doping of polyaniline results in the formation of a nitrogen based salt.

Polyaniline can exist in a range of oxidation states that are associated with the ratio of amine and imine sites in the polymer chains. The oxidation state that can be doped to the highly conducting form of polyaniline is the emeraldine state which has an equal number of amine and imine sites. The protonic doping of emeraldine base, shown in Scheme 1.4, results in the complete protonation of the imine nitrogen atoms to give the fully protonated emeraldine salt, PAn.HA, initially in the bipolaron (dication salt) form.
This protonation is accompanied by a nine to ten magnitude increase in the conductivity of the polymer to 1-10 S/cm.
Magnetic studies of emeraldine salts, PAN.HA, have shown that they are paramagnetic, which indicates that the bipolarons formed undergo dissociation and protonation to give a delocalized polaron lattice, with a polysemiquinone radical cation salt (Scheme 1.4). If the emeraldine salt had bipolarons present, it would be diamagnetic. It can be seen from the alternative resonance forms where the charge and spin are placed on the other nitrogen atoms, that the overall structure is expected to have extensive spin and charge delocalization which results in a half-filled polaron band.

The conducting emeraldine salt can also be obtained by the electrochemical or chemical oxidation (p-type doping) of the fully reduced leucoemeraldine. This actually involves the oxidation of the $\sigma/\pi$ system rather than the $\pi$ system of the polymer as is the case for p-type doping for other conducting polymers. The resulting doped polymer is formed as the polysemiquinone radical cation salt.

The relationship between protonic acid doping and oxidative doping of the different forms of polyaniline to give the conducting emeraldine salt form of polyaniline is illustrated in Scheme 1.5.
1.2.4 Solubility of Polyaniline

An important factor that has to date limited some of the potential commercial applications of conducting polymers is their intractability, being insoluble in common solvents and infusible (making thermal processing also impossible). Their intractability arises from the highly conjugated nature of the polyaniline chains and the interchain interactions, which are important factors for the electrical conductivity of the polymers. However, Angelopoulos et al.\textsuperscript{46} demonstrated that polyaniline in the emeraldine base form is soluble in a range of organic solvents, including N-methylpyrrolidinone (NMP), acetic acid, formic acid, dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). The dissolution of emeraldine base in NMP has been the most widely practiced route for
processing polyaniline into films and fibres. These emeraldine base films can then be doped in acidic solutions to produce conducting emeraldine salt films.

It has been recently shown by Cao et al that processing of polyaniline in the conducting emeraldine salt form can be achieved by doping emeraldine base with an acidic counterion with “surfactant like” properties. Camphorsulfonic acid (HCSA) and dodecylbenzenesulfonic acid (DBSA) have proven to be successful “surfactant like” dopants to render polyaniline soluble in NMP, DMSO and m-cresol. Films of PAn.(±)-HCSA cast from m-cresol are of considerable interest due to the combined effect of high conductivity (100-400 S/cm) and optical transparency.

1.2.5 Factors Effecting the Conformation of Polyaniline

MacDiarmid et al have recently shown that polyaniline salt films prepared by the chemical doping of emeraldine base with racemic (±)-HCSA in a variety of organic solvents under identical conditions can have markedly different conductivities. The amorphous free-standing films cast from chloroform have a conductivity of 2 S/cm, whereas those cast from m-cresol are partially crystalline and exhibit a conductivity of 200 S/cm. A similar increase in conductivity was observed for racemic PAn.(±)-HCSA films cast from chloroform and then exposed to m-cresol vapour. This increase in the conductivity and crystallinity of the emeraldine salt film caused by an “inert” substance has been labeled “secondary doping”.

Based on these observations, MacDiarmid et al proposed that polyaniline can exist in two distinct conformations: “extended coil” (highly conducting) and “compact coil” (less conducting). The conformation of the solvated polyaniline chains is dependent on
the interactions between the solvent and the polymer backbone. When the polymer-
polymer interactions between different segments on the same chain are greater than the polymer-solvent interactions, then the polymer chain segments will tend to interact strongly with each other leading to a “compact coil” conformation. However, when the polymer-solvent interaction is greater than the polymer-polymer interaction the polymer will prefer the “extended coil” conformation to maximize the interactions between the polymer and the solvent. As the polymer is promoted to the “extended coil” conformation, the defects in the \( \pi \)-conjugation in the polyaniline backbone due to chain twisting tend to be eliminated. Thus, electron delocalization along the polymer backbone is increased, thereby increasing the conductivity and crystallinity of the polymer.

A distinctive spectroscopic feature associated with the change from a “compact coil” to an “extended coil” conformation is the disappearance of the localized polaron band in the visible spectrum at 750 - 850 nm, characteristic of the “compact coil” conformation, and the appearance of a strong, broad free-carrier tail in the near infrared (1000-2500 nm).\(^{54,55}\) The presence of a free-carrier tail is consistent with delocalized electrons in the polaron band. Solutions of racemic PAn.(±)-HCSA in \( m \)-cresol also exhibit markedly higher reduced viscosity compared to chloroform solutions, arising from an increase in the hydrodynamic volume of the polyaniline chains.\(^{55}\) Liquid crystalline behaviour has also been observed for concentrated solutions of PAn.(±)-HCSA in \( m \)-cresol.\(^{56}\) The existence of a liquid crystalline phase implies that the polymer possesses a rather rigid chain structure in \( m \)-cresol.
Theoretical studies\textsuperscript{57,58} suggest that these effects associated with \textit{m}-cresol arise from a synergistic combination of interactions between the \textit{m}-cresol, HCSA and the polyaniline chains. These involve H-bonding between the phenolic OH group of the \textit{m}-cresol and the carbonyl group of the HCSA and \pi-stack of phenyl rings in the secondary dopant and the polyaniline chain.

The concept of "secondary doping" is not just restricted to emeraldine base doped with camphorsulfonic acid in \textit{m}-cresol. Casting PAN.(\pm)-HCSA films from various substituted phenols including \textit{p}-cresol, 3-ethylphenol and 2-chlorophenol results in the polymer adopting an "extended coil" conformation, as reflected by an increase in the conductivity and crystallinity and the appearance of a free-carrier tail absorption in the near infrared.\textsuperscript{52,59} Also the doping of emeraldine base in \textit{m}-cresol with a wide range of other dopants, such as methanesulfonic acid, \textit{p}-toluenesulfonic acid and dodecylbenzenesulfonic acid, results in the polymer adopting an "extended coil" conformation.\textsuperscript{52,59}

\section*{1.3 Chirality}

In chemistry, a compound is said to be chiral, if the two mirror images of the compound are not superimposable. These mirror images of a chiral molecule are called enantiomers. Chirality and the associated optical activity observed in such molecules are an important characteristic of many biological compounds such as amino acids, proteins and carbohydrates.

Enantiomers have identical chemical and physical properties in the absence of any external chiral influence. This means that enantiomers have the same melting point,
solubility and FTIR, uv-visible and NMR spectra. One physical property in which enantiomers differ is their interaction with plane-polarized light. Equimolar solutions of two separate enantiomers rotate plane-polarized light in opposite directions, but by the same magnitude. The direction in which an enantiomer rotates plane-polarized light is used in its nomenclature: the enantiomer that rotates plane-polarized light in a clockwise direction is labeled the dextrorotatory (denoted (+)) isomer, while the enantiomer causing anticlockwise rotation is labeled the laevorotatory (denoted (-)) isomer. Enantiomers also absorb left- and right-hand circularly polarized light to different extents, a property which is exploited in circular dichroism spectroscopy, which is used extensively in this thesis to characterize the optical activity of the novel chiral polyanilines (see Section 2.4.2 for further discussion of this technique).

However, enantiomers frequently exhibit markedly different behaviour when placed in chiral environments, such as those found in biological systems. Consequently, when a biologically active chiral compound, such as a drug, interacts with a chiral receptor site, the two enantiomers of the drug may lead to different biological effects. For this reason, chiral molecules are becoming increasingly important in the pharmaceutical and agricultural industries.

1.4 Chiral Conducting Polymers

In contrast to the extensive literature on the synthesis, properties and applications of conducting polymers, there have been very few reports of optically active examples possessing main chain chirality. In 1985 Baughman et al. proposed that optical activity in the \( \pi-\pi^* \) absorption band of conjugated polymers could be induced by the presence of enantiomerically pure side chains or the incorporation of a chiral dopant into the
polymer backbone. Subsequent studies have largely concentrated on polypyrrole and polythiophene in which a chiral substituent has been covalently attached to either the 3-position of the heterocyclic ring or the pyrrole N atom. However, an optically active side chain or the presence of a chiral dopant will not necessarily lead to main chain chirality.

1.4.1 Optically Active Polypyrroles

The first reported synthesis of electropolymerization of pyrrole derivatives with various chiral substituents on the nitrogen atom was reported by Baughman et al.\textsuperscript{60} The electrochemical polymerization of the chiral monomers resulted in the deposition of polymers 2, 3 and 4, with the polymers showing a markedly reduced conductivity compared to the unsubstituted polypyrrole film. The authors commented that the large substituents attached to the nitrogen atom probably forced the adjacent pyrrole rings out of the co-planar arrangement required for high conductivity. Unfortunately, no studies on the chiroptical properties of these polymers were made.

\[
\begin{align*}
2-4 \\
\text{Polymer} \\
\text{Rubbery, non-conductive} \\
P\text{owder in solution, no deposit on electrode} \\
\text{Film, } \sigma = 10^6 \text{ S/cm}
\end{align*}
\]
Salmon et al.\textsuperscript{61,62} similarly attached various chiral substituents based on (+)-camphorsulfonate esters with an alkyl spacer to the pyrrole N atom. The electrochemical polymerization of these monomers, 5 and 6, resulted in the deposition of polypyrroles on Pt and ITO-coated glass electrodes. However, the circular dichroism (CD) spectra of these polymers showed that the chiral substituents on the polypyrrole rings did not induce main chain chirality, only CD bands at 295 nm associated with the (+)-camphorsulfonate group were observed.

![Image of monomers 5 and 6]

While all previously studied chiral pyrrole monomers had the chiral substituent attached to the pyrrole N atom, Garnier et al.\textsuperscript{63} synthesized various pyrrole monomers that contained chiral amino acids at the ring 3-position. The electrochemical polymerization of these monomers on Pt and ITO-coated glass electrodes resulted in the deposition of the corresponding polymers 7-9. The conductivity of these polymers was ca. 1 S/cm, which was significantly lower than the parent polypyrrole. This is presumably due to steric crowding by the chiral amino acid substituents forming the polymer backbone to
deviate from an idealized co-planar arrangement. The uv-visible spectrum of polymer 8 deposited on ITO-coated glass showed a maximum absorption at 465 nm. This absorption corresponds to the bipolaronic transition of the conjugated polypyrrole backbone. The CD spectrum of the doped polymer exhibited a well-defined positive Cotton effect ($\Delta\varepsilon = 0.95 \text{ M}^{-1}\text{cm}^{-1}$) centred at 465 nm associated with this absorption band. The CD spectrum of the corresponding monomer showed no visible CD bands, as the monomer did not have any absorption in the visible region. Based on these observations, they concluded that the chiral amino acid groups at the 3-position of the pyrrole ring induced main chain helical chirality in the conjugated polymer backbone.

![Chemical structure of polymers 7-9](image)

An alternate approach to synthesizing chiral polypyrrole films by using a chiral dopant has been reported by Kato et al. Their approach was to electrochemically polymerize pyrrole in the presence of the chiral polyamide 10 to produce a black free-standing film on a Pt electrode. The polypyrrole composite film consisted of 0.35 chiral polyamide groups per pyrrole repeat unit, and had a conductivity of 0.5 S/cm. However, the only CD bands present were associated with the exciton-coupled bands for the $\pi-\pi^*$ transition
of the polyamide dopant. It was therefore concluded that the chiral polyamide does not induce main chain chirality in the polypyrrole chains.

Saint-Aman et al. recently prepared a pyrrole monomer substituted with an optically active β-D-glucose derivative attached to the pyrrole N atom. Interestingly, the electrochemical polymerization of the monomer on a vitreous carbon electrode could easily be achieved in acetonitrile containing (-)-camphorsulfonic acid (HCSA) and Bu₄NClO₄, but was completely inhibited using (+)-HCSA or racemic (±)-HCSA. The resulting polymer film showed high optical rotation ([α]D = +500°). They attributed this optical rotation to the polypyrrole backbone adopting an asymmetric conformation, although no CD spectrum of the polymer was measured to confirm this. Significantly, cyclic voltammograms in the presence of (+)- or (-)-HCSA in water and acetonitrile showed that the doping level was substantially higher with (-)-HCSA than with (+)-HCSA in both solvents, indicating that the chiral polypyrrole film exhibits significant enantioselection during the redox cycles.
Recently, Pleus et al.\textsuperscript{66,67} reported the synthesis and electropolymerization of the chiral pyrrole monomers 12-15 containing (-)-ethyl L-lactate as a chiral functional group. The steric and electronic influence of the chiral substituent prevented the polymerization of monomers 13 and 15 on a platinum electrode. Although the chiroptical properties of these polymers were not measured, cyclic voltammograms for poly-12 and poly-14 in the presence of (+)- or (-)-HCSA dissolved in acetonitrile revealed that these polymers also possess enantioselective recognition properties.
1.4.2 Optically Active Polythiophenes

Lemaire et al. reported the synthesis of a thiophene monomer containing propyl-2-phenylbutyl ether as the chiral substituent at the 3-position. Electropolymerization resulted in the deposition of a compact, free-standing film of 16. The undoped polymer showed a very large optical rotation for (S)-16 ([α]_D = +3000°), while the corresponding optical rotation of the monomer was only [α]_D = +21.5°. The high optical rotation of the polymer suggests that a helical main chain conformation is induced by the chiral substituent, but the CD spectrum of 16 was not reported. Cyclic voltammograms of (S)-16 in (+)- and (-)-HCSA dissolved in acetonitrile showed that the doping level was 50%
higher when the electrolyte contained (+)-HCSA compared to (-)-HCSA. Similarly, the opposite selectivity was observed when (R)-16 was similarly studied. The conductivity of the free-standing film was 1 S/cm.

Subsequent work by Lemaire et al.\textsuperscript{69,70} showed that changing the chiral substituent in the 3-position in the polymers 17-20 had a dramatic effect on the conductivity of the chiral polythiophene films (10\textsuperscript{3} to 15 S/cm).

\[ \sigma = 15 \text{ S/cm} \quad \sigma = 10 \text{ S/cm} \quad \sigma = 10^3 \text{ S/cm} \quad \sigma = 0.5 \text{ S/cm} \]

Hjertberg et al.\textsuperscript{71} have reported the synthesis of a water-soluble polythiophene 21 with an amino acid side chain, using ferric chloride as the oxidizing agent. The polymer is insoluble in non-polar solvents, but is soluble in water, methanol and dimethyl sulfoxide. Interestingly, the chiroptical properties of this polythiophene are markedly different when dissolved in water and methanol. Changing the solvent from methanol to
water results in a blue shift of the $\pi-\pi^*$ absorption band at 410 nm. Similarly, the optical rotation of the polymer dissolved in water is very large ($[\alpha]_D = +3800^\circ$), but is reduced dramatically in methanol. The CD spectra of the aqueous and methanol solutions of the polythiophene reveal two different conformations of the polymer. The aqueous solution exhibits one pair of exciton-coupled CD bands in the visible region that are associated with the $\pi-\pi^*$ transition of the thiophene rings, indicating that the chiral side chain induces the polymer backbone to adopt a helical conformation. However, there are no CD bands present for the methanol solution. They proposed a conformational change or possibly a change in aggregation when the solvent is changed from water to methanol. For example, partial interconversion between syn conformers of the chiral side chains present in water to anti conformers in methanol may be involved, with the syn conformers causing the polymer to adopt a helical conformation while the anti conformers lead to a planar arrangement for the polymer backbone.

![Chemical Structure](image)

The synthesis of the regioregular head-to-tail polythiophene 22 by polymerizing the chiral monomer using a nickel (II) catalyst was recently developed by Meijer et al.\textsuperscript{72,73} The uv-visible spectrum of 22 cast from chloroform shows three absorption bands at 512, 540 and 592 nm that are assigned as the $\pi-\pi^*$ absorption bands. Although the
polymer dissolved in chloroform is optically inactive, the CD spectra of the cast film shows bisignate Cotton effects associated with the above \( \pi-\pi^* \) absorption bands, indicating that the chiral side chain induces main chain chirality in the polymer backbone. The gradual addition of methanol to the chloroform solution results in the evolution of CD bands in identical positions to those observed for the cast film. Based on these results, they proposed that induced chirality is observed if polythiophene is either in the solid state or when aggregated in a "poor" solvent.

Thermal studies of films of \( \text{22} \) cast from chloroform show that the polymer loses optical activity at temperatures above 160°C while the polymer melts. Interestingly, the conformation of the film is highly dependent on the rate of cooling. Upon slow cooling, the original optical activity of the film is recovered. However, rapid cooling of the film results in a complete stereomutation of the main chain, as evidenced by the appearance of a mirror image of the original CD spectrum. Similar thermochromic and solvatochromic effects were observed by Meijer et al\textsuperscript{74,75} in another chiral polythiophene \( \text{23} \). In addition they found that the photoluminescence of \( \text{23} \) in the aggregated phase was circularly polarized.
1.4.3 Optically Active Polyanilines

The above routes to induce main chain chirality by attaching a chiral substituent to the pyrrole and thiophene rings are generally synthetically tedious and the size and/or electronic properties of the chiral substituents can have a detrimental effect on the conductivity and mechanical properties of the chiral polymer. The alternate approach of incorporating a chiral dopant anion in order to induce macroasymmetry to the polymer chains may therefore have significant advantages.

This latter approach was employed by Majidi et al.\textsuperscript{76} in 1994 for the first reported synthesis of an optically active polyaniline. They described the electropolymerization of aniline in the presence of the chiral dopants (+)- and (-)-camphorsulfonic acid on ITO-coated glass, resulting in the deposition of the optically active emeraldine salt films.\textsuperscript{24} The PAn.(+)-HCSA and PAn.(-)-HCSA films exhibited CD bands at 295, 330, 450 nm and a band that extends past 800 nm, with mirror imaged CD spectra for the enantiomeric salts. The CD band at 295 nm is associated with the HCSA incorporated into the polymer, while the strong CD bands in the visible region confirm macroasymmetry in the polymer backbone. This was ascribed to the formation of helical chains that were maintained in a preferential one-screw-sense via binding to the chiral CSA$^-$ anions.

Subsequent studies\textsuperscript{77,78} showed that optically active salts\textsuperscript{24} can also be synthesized by the enantioselective doping of neutral emeraldine base with (+)- or (-)-HCSA in a range of organic solvents. Interestingly, Meijer et al.\textsuperscript{79} observed that while the doping of emeraldine base with (+)-HCSA in $m$-cresol showed no visible region CD bands in solution, polyaniline films obtained by spin-casting from the above solution exhibited...
strong CD bands in the visible region. They proposed that optical activity for the polyaniline chain is only observed in the solid state or upon aggregation in a “poor” solvent. Related studies by Majidi et al\(^7\) suggested that changing the solvent from chloroform to \(m\)-cresol caused the polymer chains in PAN.(+)HCSA to convert from a helical cisoid conformation to a planar zigzag transoid conformation.

\[
\begin{align*}
\text{HCSA} &= \text{CH}_2\text{SO}_3\text{H} \\
&\quad \text{(1S)-(+)10-camphorsulfonic acid} \\
&\quad \text{or} \\
&\quad \text{(1R)(-)-10-camphorsulfonic acid}
\end{align*}
\]

### 1.5 Potential Applications for Chiral Conducting Polymers

The majority of pharmaceuticals contain at least one chiral centre, but until recently the majority were marketed as racemic mixtures.\(^8\),\(^9\) Homochiral drugs offer a means to increase the specificity of drug action by providing optimal orientation or functionality of the drug. However, the conventional synthetic routes to producing such compounds generally result in the formation of racemic mixtures of the two enantiomers. Historically, chiral drugs were developed and marketed as racemates because the
technology to synthesize only the desired enantiomer was lacking. Unfortunately, the administration of racemic drug mixtures can have tragic consequences. A well-documented example is the drug thalidomide, which was administered as a racemic mixture to pregnant women in the late 1950's as a sedative. While the R isomer had the desired biologically effect, the S isomer was found to be teratogenic and embryo toxic, leading to serious birth defects.\textsuperscript{82}

Having recognized the danger and economic waste of delivering drugs as racemic mixtures, the US Food and Drug Administration\textsuperscript{80} highlighted the importance of developing new synthetic routes for the production of chemicals in enantiomerically pure form. For this reason, interest in chiral conducting polymers has grown considerably in recent years due to their perceived potential in areas such as chiral electrodes for asymmetric synthesis and as materials for the chiral separation of enantiomeric chemicals. These polymers offer potential advantages for these applications as they are relatively low cost materials, their synthesis is relatively simple and they can be deposited on a wide range of substrates.

1.5.1 Asymmetric Electrochemical Synthesis

Asymmetric synthesis, in principle, is the most cost-effective method for producing single enantiomers, because the entire precursor is converted to the desired isomer. The use of electrochemical asymmetric synthesis for the preparation of optically active chemicals was first reported in 1967.\textsuperscript{83} Although electrochemical asymmetric synthesis has been little studied since then, it has some practical advantages over more conventional chemical\textsuperscript{84} and enzymatic\textsuperscript{85} methods. For example, synthetic steps such as the attachment of and removal of chiral auxiliaries would not be required and the
synthesis may be possible in a wider range of solvents than for enzyme-based systems. Several different approaches for asymmetric electrochemical synthesis have been investigated, including the use of chiral solvents, chiral supporting electrolytes and chiral chemically modified electrodes.

However, no experimental studies have been reported to date using chiral conducting polymers as asymmetric inductors for the electrochemical oxidation and reduction of prochiral organic molecules. Nevertheless, Nonaka et al. have reported the potential of using conducting polymer modified electrodes for asymmetric synthesis. They described the fabrication of a platinum electrode that was sequentially coated with achiral polypyrrole (for electrical conductivity) and poly(L-valine) or poly(L-glutamate) (for chirality). These chemically modified electrodes achieved partial asymmetric synthesis of prochiral organic molecules, especially in the oxidation of sterically crowded aryl alkyl sulfides to chiral organosulfoxides.

The electrochemical deposition of optically active conducting polymers provides a facile route for the direct coating of these polymers onto an electrode surface for the preparation of chiral, chemically modified electrodes. This approach has several advantages over the route described above by Nonaka et al. The electrochemical synthesis leads to the direct grafting onto the electrode surface, while maintaining high conductivity that results in fast charge transfer, allowing the preparation of electrodes with a large surface-to-volume ratio and a maximum density of chiral active sites.
1.5.2 Chiral Separations

As enantiomers have identical physical properties, they are consequently difficult to separate and analyze. Traditionally, the resolution of enantiomeric compounds has involved the conversion of enantiomers into diastereomers using chiral reagents. Unlike enantiomers, diastereomers have different physical properties and can be separated using, for example, TLC and HPLC with achiral stationary phases.

The separation and subsequent analysis of racemic mixtures has been markedly enhanced by the development of HPLC with chiral stationary phases. A large number of chiral stationary phases are commercially available; all are fairly expensive and, in some cases, have poor stability and reproducibility. Most chiral stationary phases have quite specific structural requirements for successful enantiomeric separation and therefore apply to a limited range of compounds.

One of the most promising advances in chiral stationary phases has been the development of helical synthetic polymers, as they generally show high chiral recognition properties. For example, helical polymers such as cellulose esters and poly(triphenylmethyl methacrylate) as chiral stationary phases have shown the ability to resolve racemic compounds including esters, amides and alcohols. However, the majority of these helical polymer chiral stationary phases are limited in their low loading capacity due to pressure limitations, making scale-up difficult. Tedious preparative routes, high column costs and the requirement of an organic solvent to enhance chiral discrimination (which may denature biological compounds) are other limitations.
Achiral conducting polymer stationary phases based on polypyrrole have been successfully developed as chromatographic stationary phases for HPLC. The interactions in the column can be adjusted by the incorporation of appropriate counterions into polypyrrole\textsuperscript{97} or by applying a potential to the stationary phase during chromatographic separation.\textsuperscript{98,99} This work suggests that chiral conducting polymer stationary phases may have the potential for electro-chromatographic separation of chiral compounds, since the stationary phase can be tuned after synthesis.

Another successful approach investigated for the separation of enantiomers involves the use of enantioselective polymer membranes. These membranes usually consist of a non-selective porous support coated with a thin layer of a chiral polymer for selectivity. The selectivity of these membranes is determined by enantiospecific interactions between the enantiomer to be separated and the top layer of the chiral polymer, resulting in one enantiomer being preferentially diffused through the membrane. Recently it has been demonstrated that chiral poly(amino acid) membranes are able to separate amino acids.\textsuperscript{100,101} For example, poly(L-glutamate) with amphiphilic side chains has shown good selectivity in the enantioselective transport of both tryptophan and tryosine. The good enantioselectivity is believed to be associated with the polymer backbone adopting an ordered $\alpha$-helical conformation. Although these membranes achieve high selectivity, they are limited by their poor flux rates.

Ogata et al\textsuperscript{102,103} reported the first separation of enantiomeric amino acids using chiral conducting polymer membranes. The chiral membrane was prepared by electrochemically depositing polypyrrole in the presence of dextran sulfate (an anionic polysaccharide) or poly(L-glutamic acid) on a platinum-coated poly(vinyl difluoride)
membrane. L-tryptophan permeated preferentially through these polypyrrole membranes as compared to D-tryptophan. They believe that the good chiral discrimination observed is related to the high ordered α-helix in the dextran sulfate and poly(L-glutamic acid) dopants incorporated into the polypyrrole membrane.

1.6 Aims of the Project

Due to its ease of synthesis, high conductivity and low cost, one of the most exciting conducting polymers showing main chain chirality is polyaniline doped with (+)- or (-)-camphorsulfonic acid. However, compared to optically active polythiophenes, there have been few reports on the factors that effect the conformation and chiroptical properties of chiral polyanilines, which are important fundamental questions for the commercial development of the polymer. The first part of this thesis (Chapters 3-6) attempts to address this issue, by examining the effect of synthetic route, temperature, solvent, secondary doping and oxidation state on the conformation and chiroptical properties for both electrochemically deposited and chemically cast polyaniline doped with (+)-camphorsulfonic acid.

The second part of the thesis (Chapters 7-9) is devoted to the development of new synthetic routes to improve the processability of these optically active polyanilines, which has been one of the limitations to their applications to date. The first method investigated involves the in situ chemical deposition of optically active polyaniline films onto a glass substrate, without the use of an organic solvent (Chapter 7). The second method involves the electrochemical synthesis of optically active polyaniline colloids using a flow-through cell developed in these laboratories (Chapter 8). The final method investigates the first synthesis of optically active poly(o-methoxyaniline) salts
which, due to the methoxy substituent on the aniline ring, are expected to show high solubility in a range of organic solvents.

The successful achievement of the above targets and the fundamental insights thereby provided should, it is believed, provide a strong foundation for future exploitation of the potential of these novel chiral conducting polymers in applications such as electrochemical asymmetric synthesis and chiral separations.
CHAPTER 2
General Experimental

2.1 Introduction
This chapter summarizes the source of all the materials employed in this thesis. It also describes the synthetic routes for producing optically active polyaniline films and solutions used in the investigations of the factors effecting the conformation of polyaniline in Chapters 3-6. These routes are based on those developed recently by Majidi et al. Further details on the particular experimental procedures are provided at the start of each chapter.

Also described in this chapter are the analytical techniques used to characterize the optically active polymers prepared in this study.

2.2 Materials

2.2.1 Monomer Preparation
Aniline and o-methoxyaniline, purchased from Aldrich Chemical Co., were distilled and then stored under nitrogen below \(-10^\circ\text{C}\) in a freezer prior to use.

2.2.2 Reagents

(1S)-(+) and (1R)(-)10-camphorsulfonic acid (HCSA), poly(styrenesulfonic acid) (PSS) (sodium salt, MW 70,000), polyethylene oxide (PEO) (MW 300,000), hydrazine dihydrate, phenylhydrazine, thymol, Thymol Blue, carvacrol, aminopropyltriethoxy silane and octadecyltriﬂorosilane were purchased from Aldrich Chemical Co. and used as supplied. Sodium nitrate, ammonium persulfate, hydrogen peroxide, concentrated
hydrochloric acid, concentrated sulfuric acid and concentrated ammonia were purchased from Ajax Ltd and used as supplied.

2.2.3 Solvents
Spectroscopic grade dimethyl sulphoxide (DMSO), 1-methyl-2-pyrrolidinone (NMP) and dimethylformamide (DMF) were purchased from Aldrich Chemical Co. and used as supplied. Spectroscopic grade chloroform and HPLC grade methanol were purchased from Ajax Chemicals and used as supplied. Aqueous solutions were prepared using Milli-Q water.

2.2.4 Electrode Substrates
Indium-tin-oxide (ITO) coated glass electrodes (40Ω/ ) were obtained from Delta Technology Ltd., while reticulated vitreous carbon (RVC) electrodes (with a porosity of 100 pores per inch (PPI) and an effective surface area of 65.6 cm²/cm³) were purchased from ERG Materials and Aerospace Corporation.

2.3 Synthesis of Optically Active Polyanilines
2.3.1 Electrochemical Deposition of Optically Active Polyanilines
The electrochemical polymerization of aniline was carried in a three-electrode electrochemical cell shown in Figure 2.1. The optically active emeraldine salt, PAn.(+)-HCSA, was deposited from a 20 mL aqueous solution containing 1.0 M (+)-HCSA and 0.2 M aniline, which was purged with nitrogen gas before commencing electropolymerization. Depending on the nature of the experiment, ITO-coated glass or platinum working electrodes were employed. The electrochemical cell also consisted of
a Ag/AgCl reference electrode (3 M NaCl salt bridge) and a platinum gauze or RVC auxiliary electrode, as illustrated in Figure 2.1.

![Figure 2.1. Electrochemical Cell for the Polymerization of Aniline](image)

Unless otherwise stated, the polymer was deposited on the working electrode using potentiostatic polymerization, in which a constant potential was applied to initiate polymerization. This approach was employed to prevent possible over-oxidation of the polymer, discussed earlier in Chapter 1. For this reason galvanostatic polymerization is unsuitable. The emeraldine salt films were deposited by applying a potential of +0.8 V (vs Ag/AgCl) for the Pt working electrode and +1.1 V (vs Ag/AgCl) for the ITO-coated glass electrode using a charge density of 120 mC/cm$^2$. The potential was applied to the working electrode using a BAS CV-27 or a Princeton Applied Research 363. Data acquisition for the potential, current and charge was made using a MacLab 4e (AD Instruments) interfaced with a Macintosh computer using Chart 3.3.5 software.
2.3.2 Chemical Synthesis of Optically Active Polyanilines

This alternative route to optically active polyaniline involved the doping of emeraldine base (EB) with the chiral acids (+)- and (-)-HCSA in a variety of organic solvents. The emeraldine base was synthesized using a previously reported procedure: 104

Aniline (20 mL) was dissolved in 250 mL of 1.0 M aqueous HCl solution and the solution then cooled to 0-2°C using an ice bath. A solution of 45.6 g ammonium persulfate dissolved in 250 mL of 1.0 M aqueous HCl solution was prepared and then added dropwise to the monomer solution using a burette over a period of 60 min with vigorous stirring. The reaction was allowed to proceed for a further 3 hours. The PAN.HCl precipitate was collected on a Buchner funnel and washed with four portions of 1.0 M HCl solution until the filtrate was colourless. The precipitate was then washed with three 100 mL portions of a 1:1 methanol/water mixture to remove any oligomeric impurities.

The green emeraldine salt was converted into neutral emeraldine base (EB) by stirring the precipitate in 500 mL of 1.0 M NH₄OH solution for 8 hours. The blue product was collected on a Buchner funnel and washed with 1.0 M NH₄OH until the filtrate become colourless. The emeraldine base powder was dried under vacuum for 24 hours at room temperature and stored in a freezer prior to use.

Optically active PAN.(+)-HCSA and PAN.(-)-HCSA solutions were prepared by dissolving 0.5 mg of the EB in 5 mL of the desired organic solvent (NMP, DMSO, DMF or CHCl₃). The EB solution was then doped to the emeraldine salt form with 116 mg of (+)- or (-)-HCSA (giving 0.1 M HCSA).
Chapter 2: General Experimental

Optically active PAn.(+)-HCSA and PAn.(-)-HCSA films were prepared by evaporative casting from concentrated solutions of PAn.(+)-HCSA and PAn.(-)-HCSA. These concentrated solutions were prepared by dissolving 100 mg of EB in 10 mL of the organic solvent (NMP, DMSO and DMF) to form a 1 wt% solution, that was subsequently doped with the stoichiometric amount of (+)- or (-)-HCSA (253 mg) to fully dope the EB. The solution was magnetically stirred for 4 hours before being filtered through a Whatman No. 42 filter paper. Thin films were then cast onto microscope glass slides and the solvent removed by heating in an oven at 80°C overnight at atmospheric pressure.

2.4 Polymer Characterization

2.4.1 Uv-visible-NIR Spectroscopy

The conformation and oxidation state of the polyanilines in solution and as films deposited on transparent substrates were examined using uv-visible-NIR spectroscopy.

The uv-visible spectra of the polyaniline films or solutions were recorded between 300 or 1100 nm using a Shimadzu UV-1601 spectrophotometer or between 300 and 2600 nm using a Perkin-Elmer Lambda 9 uv-visible-NIR spectrometer. NIR spectra were also measured in a few cases between 833 and 2500 nm using the NIR lamp on a Bomen MB-154 Fourier transform IR spectrophotometer. Solution spectra were recorded in a 1 cm pathlength quartz cell after they were filtered using a 0.45 μm syringe filter. It was not possible to obtain the uv-visible spectra of the polyanilines below 300 nm due to the strong absorption of the ITO coated glass substrate and the HCSA incorporated into the polymer.
2.4.2 Circular Dichroism Spectroscopy

The most powerful technique for the measurement of optically activity in chiral molecules is circular dichroism (CD) spectroscopy. Circular dichroism has also proved to be a very sensitive spectroscopic probe for conformational changes in optically active polymers. For example, with peptides, CD spectroscopy is commonly employed to estimate the proportion of the chain present in solution as the alternative α-helix, β-sheet and random coil conformations. Circular dichroism spectroscopy involves measuring the difference in molar extinction coefficients (Δε) of left- and right-circularly polarized light passing through the compound as a function of wavelength, as shown in equation (2.1).

\[
\Delta \varepsilon = \varepsilon_L - \varepsilon_R
\]  

(2.1)

In general, the CD spectrum of an optically active compound exhibits bands at the same wavelength as the absorption bands in its uv-visible spectrum. If left hand circularly polarized light is absorbed to a greater extent than right hand circularly polarized light, Δε is positive and this CD band is called a positive circular dichroism Cotton effect. If right hand circularly polarized light is preferentially absorbed, Δε is negative and this CD band is called a negative circular dichroism Cotton effect.

However, when two (or more) chromophores located on the same molecule constitute a chiral system, the energy level of the excited state splits. In the uv-visible spectrum this usually results in a single, broad absorption band, while the high sensitivity of the CD spectroscopy results in the formation of split CD bands. These split bands are often
opposite in sign (bisignate), as found with optically active polythiophenes.\textsuperscript{72-74} That is, if the first CD band is positive, the second band must be negative, with these bands centred on the absorption band observed in the uv-visible spectrum. In the chiral polyanilines prepared in this thesis, the chromophore is continuously repeated along the polymer chain, so bisignate CD signals are therefore anticipated for each visible absorption band.

The CD spectra of the polyaniline films or solutions were recorded using a Jobin Yvon Dichrograph 6. Solution spectra were recorded in a 1 cm pathlength quartz cell after they were filtered using a 0.45 μm syringe filter.

\subsection*{2.4.3 Electrical Conductivity}

Depending on the experiment, the DC conductivity measurements of the optically active polyanilines in the emeraldine salt form were determined using the four-point probe method or the Van der Pauw method.

\subsubsection*{2.4.3.1 Four Point Probe Method}

The four-point probe method was employed to measure the volume resistivity of polyaniline films using the procedure outlined in ASTM (D4496-87)\textsuperscript{105}, with the conductivity being the inverse of the volume resistivity. This apparatus consists of four electrodes - two external electrodes through which a current is passed, and two inner electrodes where the potential drop is measured. The design of the rig used for measuring the volume resistivity of polyaniline films is shown in Figure 2.2.
To calculate the volume resistivity, $R_v$, of the polyaniline film, the following equation (2.2) was applied:

$$R_v = \frac{x \cdot y}{z} \times \frac{\Delta E}{I} \quad \text{Ω cm} \quad (2.2)$$

where:

$x$ = thickness of the polyaniline film (cm)

$y$ = width of the polyaniline film (cm)

$z$ = distance between the inner electrodes (cm)

$I$ = current applied between the outer electrodes (mA)

$\Delta E$ = potential difference between the inner electrodes (mV)

The conductivity of the film can be calculated using equation (2.3).

$$\sigma = \frac{1}{R_v} \quad \text{S/cm} \quad (2.3)$$
In this work, polyaniline films were cast onto microscope glass slides from the concentrated emeraldine salt solution to produce films with a thickness of ca. 50 µm, length of 30 mm and a width of 3 mm. The thickness of the film was measured using a digital micrometer (Mitutoyo) with a resolution of 1 µm. A current of 1 mA was applied between the outer electrodes using a PAR 363 and the resulting potential drop between the inner electrodes was measured with a HP34401A multimeter.

2.4.3.2 Van der Pauw Method
The technique employed for measuring the volume resistivity of pressed pellets of polyaniline powders was the Van der Pauw method. This technique consists of attaching four equally spaced points of electrical contact to the periphery of the polyaniline disc. A current is passed through two adjacent contacts (A and B) and the resulting potential drop is measured between the two contact points (C and D), as shown in Figure 2.3. Then the same current is passed through A and D and the potential drop is recorded between B and C. For a circular disc, the two voltages should be equal in value.

Figure 2.3. Van der Pauw assembly
To calculate the volume resistivity, $R_v$, of the polyaniline disc, when $V_{CD}/V_{BC} = 1$, the following equation (2.4) was applied:

$$R_v = \frac{\pi d}{\ln 2} \times \frac{V_{CD} + V_{BC}}{2I} \Omega \text{ cm} \quad (2.4)$$

where:

$d$ = thickness of the polyaniline disc (cm)

$I$ = current applied (mA)

$V_{AB}$ = potential difference between C and D (mV)

$V_{CD}$ = potential difference between C and D (mV)

The conductivity of the polyaniline pellet can then be calculated using equation (2.3).

In this study, polyaniline powders were compressed into a pellet using a KBr press and the thickness of the pellet measured using the digital micrometer. A current of 1 mA was applied using a PAR 363 and the resulting potential drop was measured with a HP34401A multimeter.

2.4.4 Cyclic Voltammetry

Cyclic voltammetry experiments on polyaniline are frequently used to obtain information on the mechanism of polymer growth as well as the redox behaviour of the polymer. These experiments involve scanning the potential at a fixed scan rate from a potential more negative than the reduction potential to a potential higher than the oxidation potential, and plotting the current response as a function of the potential applied.
In the present work, the optimal monomer oxidation potential for potentiostatic polymerization for any new monomer/working electrode substrate combination was determined using cyclic voltammetry. Potentiodynamic polymerization of aniline or o-methoxyaniline in the presence of 0.2 M (+)-HCSA was carried out by cycling the potential between −0.2 and +1.0 V (vs Ag/AgCl) at a scan rate of 20 mV/s, the final scan being stopped with the potential at its extreme positive value. Characterization of the electroactivity of the deposited polyaniline and poly(o-methoxyaniline) films on a Pt electrode was carried out by cycling the potential between −0.2 and +0.9 V (vs Ag/AgCl) at a scan rate of 50 mV/s in a 1.0 M HCSA aqueous solution. The cell design and electrochemical instrumentation used in these latter experiments are described in Section 2.3.1.

2.4.5 Thermogravimetric Analysis

Thermogravimetric analysis is used to determine changes in the weight of a sample, resulting from chemical or physical transformations as a function of temperature or time. For the thermal analysis of polyaniline samples, this technique is commonly used to determine the weight of solvent incorporated into the polymer, the onset of thermal de-doping of emeraldine salt due to the loss of the dopant acid, and the decomposition of the polymer backbone. The limitation of this technique is that it does not provide information as to the nature of the products evolved.

Thermogravimetric analyses were carried out on optically active polyaniline powders using a Perkin-Elmer Model TGA7 thermogravimetric analyzer. A temperature range
from 20-800 °C was examined using a heating rate of 40 °C/min, under a nitrogen atmosphere.

2.4.6 Differential Scanning Calorimetry

Differential scanning calorimetry is used to provide quantitative information on the thermal behaviour of materials as they undergo physical and chemical changes during heat treatment. This technique measures the amount of heat that is involved as a material undergoes an exothermic or endothermic transition as the material is heated at a controlled heating rate. From DSC studies of polyaniline, the heat loss associated with the removal of solvent from the polymer film, the glass transition temperature and the onset of melting or evaporation of the dopant acid can be easily determined. This technique is complimentary to thermogravimetric analysis of the polyaniline samples.

DSC studies were carried out on optically active polyaniline powders using a Perkin-Elmer DSC 7. A temperature range from -10 to 420°C was examined using a heating rate of 5 °C/min, under a nitrogen atmosphere.
CHAPTER 3
Effect of Synthetic Route and Temperature on the Conformation of Optically Active Polyanilines

3.1 Introduction

MacDiarmid et al.\textsuperscript{52,53} have established that polyaniline salts, PAn(±)-HCSA, synthesized by doping emeraldine base (EB) with racemic (±)-HCSA in various solvents (equation 3.1) can exist in two molecular conformations which are solvent dependent.

\[
\text{EB} + \text{HCSA} \rightarrow [\text{\begin{array}{c}
\text{H} \\
\text{N} \\
\text{CSA}' \\
\text{H}
\end{array}}]_n \quad (3.1)
\]

The racemic PAn(±)-HCSA films cast from NMP, CHCl\textsubscript{3} and DMSO solvents were reported to possess a “compact coil” conformation characterized by a localized polaron band at approximately 800 nm in the uv-visible spectrum.\textsuperscript{54,55} They also exhibit absorption bands at ca. 350 and 420 nm attributed to a benzenoid $\pi-\pi^*$ transition and a second polaron transition, respectively. In contrast, an “extended coil” conformation was assigned to PAn(±)-HCSA films cast from $m$-cresol. For these latter films, the two low wavelength absorption bands merge into a broad peak in the 300-450 nm region. However, the most striking characteristic of the “extended coil” conformation is the replacement of the long wavelength localized polaron band by an intense free carrier tail in the near-infrared. This is indicative of increased delocalization of charge carriers along the polymer chains.
There have been few investigations of thermochromism in polyanilines, despite the numerous studies into the thermal properties of polyaniline.\textsuperscript{107-110} Several papers have noted a moderate blue shift of the exciton absorption peak of emeraldine base\textsuperscript{111,112} and ring-substituted EB\textsuperscript{113} films or solutions upon heating. However, there have been no reports to date for thermochromism in the emeraldine salt oxidation state.

In contrast, thermochromism has been extensively studied in substituted polythiophenes.\textsuperscript{73,74,114-116} Heating of these films or solutions leads to a marked blue shift of the highest wavelength absorption band, that has been attributed to a twisting of the polymer backbone from an essentially planar to a less ordered non-planar conformation. The temperature-dependent circular dichroism spectra of optically active examples of such polymers have provided further insights into the nature of the thermochromism in polythiophenes.\textsuperscript{73,74}

The recent synthesis of optically active polyanilines, via the enantioselective electropolymerization of aniline in the presence of aqueous (+)-HCSA\textsuperscript{76} or the enantioselective doping of EB with (+)-HCSA in a range of organic solvents,\textsuperscript{77} provides the opportunity to use the powerful tool of circular dichroism (CD) spectroscopy to probe the factors that influence the conformation of these polymers. The present chapter investigates the influence of the following factors on the conformation of the emeraldine salt PAn.(+)-HCSA:

(i) synthetic route, and

(ii) temperature.

Subsequent chapters will explore the influence of solvent (Chapter 4) and novel secondary dopants (Chapter 5) on the conformation of optically active polyanilines.
3.2 Experimental

3.2.1 Film Preparation

Electrochemically deposited films of PAN.(+)-HCSA were obtained on 4 cm² ITO-coated glass using the procedure described in Chapter 2 (applied potential of +1.1 V vs Ag/AgCl; 120 mC/cm² charge passed). Analogous powder samples of PAN.(+)-HCSA for conductivity, TGA and DSC studies were similarly prepared via electrodeposition on a Pt working electrode using a potential of +0.8V vs Ag/AgCl. After scraping from the Pt electrode, the powders were dried for several days in a desiccator prior to physical measurements.

Chemically prepared PAN.(+)-HCSA films were obtained by casting a concentrated solution of emeraldine base doped with (+)-HCSA in DMSO onto a microscope glass slide, as described in Chapter 2.

3.2.2 Thermal Studies

After recording their room temperature CD and uv-visible spectra, the above films were exposed for 10 min periods to successively higher temperatures from 50°-240°C in an oven under atmospheric conditions. After each 10 min treatment, the films were cooled to room temperature before measuring their CD and uv-visible spectra.

Thermogravimetric analysis (TGA) was carried out on both electrochemically deposited and chemically cast PAN.(+)-HCSA under a nitrogen atmosphere. The electrochemically deposited PAN.(+)-HCSA powder was also characterized by differential scanning calorimetry (DSC).
3.2.3 Conductivity Studies

A powder sample of electrochemically prepared PAn.(+)-HCSA was pressed into a pellet (thickness 0.806 nm) and the conductivity measured both at room temperature and after heating at 140°C for 30 min using the van der Pauw method (see Chapter 2).

3.3 Results and Discussion

3.3.1 Effect of Synthetic Route

It is frequently assumed that chemically and electrochemically synthesized forms of polyaniline have the same conformation, although no definitive study has yet been performed to determine whether this is correct.\textsuperscript{117} However, recent solvatochromism studies of electrochemically deposited racemic PAn.(±)-HCSA by Mattoso et al\textsuperscript{118} suggested that the conformation of polyanilines may be partially dependent on the synthetic route. The presence of a free carrier tail for the polymer dissolved in NMP and chloroform solvents suggested that the electrochemically deposited polyaniline was partially synthesized in the "extended coil" conformation, while no free carrier tail was observed when the EB was doped with racemic (±)-HCSA in either NMP or chloroform.

By employing the optically active (+)-HCSA dopant, the present study takes advantage of the high sensitivity of circular dichroism spectroscopy to investigate the conformation of the emeraldine salt, PAn.(+)HCSA, synthesized by either (i) the electrochemical polymerization of aniline (+1.1 V \textit{vs} Ag/AgCl) or (ii) the chemically doping of EB with (+)-HCSA in DMSO. Both types of PAn.(+)HCSA films used in this study were synthesized with approximately equal thickness (2-3 \textmu m) for spectroscopic analysis.
The UV-visible spectra of PAN.(+)-HCSA films obtained via electrochemical polymerization of aniline and alternatively by the chemically doping of EB with (+)-HCSA in DMSO are shown in Figure 3.1. These reveal distinct differences, indicating different conformations for the polyaniline chains in the two emeraldine salt films. The chemically doped PAN.(+)-HCSA film cast from DMSO exhibited an intense, well-defined polaron band at ca. 825 nm, characteristic of a "compact coil" conformation for the polyaniline chain. The spectrum also showed two lower wavelength absorption bands at 425 nm and 350 nm, assigned as a second polaron band and a benzenoid $\pi-\pi^*$ transition, respectively. Similar UV-visible spectra were obtained for EB doped with (+)-HCSA in DMF, chloroform and NMP, with only slight differences in the location of the high wavelength polaron band suggesting different conjugation lengths for the polyaniline chains in these solvents. These spectra for the chemically produced PAN.(+)-HCSA films were identical to those reported previously by MacDiarmid et al\textsuperscript{54} for racemic PAN.(±)-HCSA films cast from these solvents.

In contrast, the electrochemically deposited PAN.(+)-HCSA film exhibited only a single broad absorption peak in the 350-450 nm region, while the high wavelength polaron band now appeared as a weak shoulder at ca. 800 nm superimposed on a strong free-carrier tail in the near-infrared. This indicates significant delocalization of charge carriers along the polymer chains, suggesting an "extended coil" type conformation for the polyaniline backbone. However, the near infra-red absorption of this electrochemically deposited PAN.(+)-HCSA film was much less dominant than that observed previously for PAN.(±)-HCSA films cast from m-cresol.\textsuperscript{52,53}
Figure 3.1. Uv-visible spectra of PAn.(+)-HCSA films prepared by electrochemical polymerization of aniline or chemical doping of EB

The different conformations for these PAn.(+)-HCSA films are strikingly evident from their respective CD spectra, which are shown in Figure 3.2. The more complex low wavelength CD spectrum for the chemically doped film is consistent with the presence of two absorption bands in this region. The CD bands at 405 and 460 nm may be tentatively assigned as the bisignate, exciton-coupled bands associated with the polaron absorption band observed for this salt at ca. 425 nm (Figure 3.1). Partly overlapping with these is another probable pair of bisignate exciton-coupled CD bands (one of which is evident at 345 nm), associated with the benzenoid $\pi-\pi^*$ absorption band seen at ca. 350 nm. The other expected CD band associated with the 350 nm absorption peak is masked by the 295 nm band for the (+)-HCSA dopant incorporated into the polymer backbone.
Figure 3.2. CD spectra of PAn.(+)-HCSA films prepared by electrochemical polymerization of aniline or chemical doping of EB

In contrast, the CD spectrum of the electrochemically deposited PAn.(+)-HCSA film (Figure 3.2) exhibited only one pair of bisignate, exciton-coupled bands at 360 and 450 nm, as anticipated from the presence of only one broad absorption band in the region at ca. 400 nm (Figure 3.1). Interestingly, unlike the chemically doped film, it showed significant CD ellipticity in the region 500-700 nm. More detailed examination (see Chapter 9, Figure 9.6) did not reveal a CD maximum before the instrument limit (780 nm), but rather a continuous increase in ellipticity. This is consistent with the presence of only a weak polaron absorption shoulder at ca. 780 nm and a dominant strong free carrier tail in the NIR (see above).

The above results provide strong evidence that electrochemically and chemically produced polyaniline salts possess different conformations for their polymer chains. It
has been previously considered that polyanilines doped with HCSA synthesized via these two routes had similar chemical structures, although differences in molecular weights and reaction mechanisms have been reported. The lower molecular weights reported for electrochemically prepared polyaniline salts may be responsible for their different conformations compared to chemically doped salts. However, an alternative possible explanation for the different chiroptical properties of the electrochemically and chemically prepared PAn.(+)-HCSA salts is the presence of different configurational or regio-isomers. In either case, these structural differences will need to be borne in mind when comparisons are made between electrochemically and chemically prepared polyanilines.

3.3.2 Effect of Temperature on PAn.(+)-HCSA Films

The majority of thermal studies on polyaniline films to date have focussed on the effect of temperature on the conductivity, stability and electroactivity of emeraldine salt PAn.HA films. Depending on the dopant acid, HA, these generally show good thermal stability and progressive de-doping to produce the neutral emeraldine base form at elevated temperatures (e.g. ≥ 150°C for PAn.HCl and ≥ 180°C for PAn.H₂SO₄). General thermal decomposition of the polyaniline chains does not generally occur until the temperature is raised beyond 400°C.

3.3.2.1 Thermochromism in Electrochemically Deposited PAn.(+)-HCSA Films

The present thermochromism studies on electrochemically deposited PAn.(+)-HCSA involved heating a film to the desired temperature for 10 min and then measuring the chiroptical properties once the film had returned to room temperature. Therefore, any
changes in the polymer conformation observed in this study are irreversible changes resulting from the thermal treatment of the PAn.(+)-HCSA.

The room temperature uv-visible and CD spectra of the PAn.(+)-HCSA film (Figures 3.3 and 3.4) were consistent with a predominantly “extended coil” conformation for the polyaniline chains, e.g. showing a strong free carrier tail absorption band in the near-infrared. There was little change observed in the chiroptical properties of the PAn.(+)-HCSA film over the temperature range 20°-80°C. However, at temperatures progressively above 80°C, the uv-visible and especially the CD spectra of these films underwent a series of marked changes. These culminated with the appearance at 140°C of uv-visible and CD spectra (Figure 3.3 and 3.4) identical to those previously found for chemical produced PAn.(+)-HCSA salts (see Section 3.3.1).

Figure 3.3. Uv-visible spectra of an electrochemically deposited PAn.(+)-HCSA film at room temperature and 140°C
A series of intermediate UV-visible and CD spectra were observed for the electrochemically prepared PAn.(+)-HCSA film at temperatures between 90°-130°C. For example, the CD spectrum obtained after heating at 120°C for 10 min is shown in Figure 3.4b. Interestingly, after allowing this latter heated film to stand for 30 min at room temperature, the CD spectrum reverted to the original room temperature spectrum. This may arise from reversible structural changes associated with the thermal loss of water from the polymer film and its subsequent re-adsorption with time at room temperature, as PAn.(+)-HCSA was observed to be a hygroscopic compound. The TGA for PAn.(+)-HCSA, described later in more detail (see Figure 3.8), showed a significant weight loss between 80-150°C, which provides further evidence that the spectral

Figure 3.4. CD spectrum of an electrochemically prepared PAn.(+)-HCSA film at room temperature, after heating at 120°C for 10 min and after heating at 140°C for 10 min
changes observed up to 130°C are related to the reversible loss of water from the polymer.

In contrast, the uv-visible and CD spectra of the PAN.(+)-HCSA film heated to 140°C indicated that the polymer underwent an irreversible conformational change from the original "extended coil" conformation to a "compact coil" conformation. The uv-visible spectrum (Figure 3.3) exhibited a well-defined polaron band at 835 nm as well as two lower wavelength absorption bands at 425 nm and 355 nm, assigned as a second polaron band and a benzeniod π-π* transition, respectively. The near-infrared spectrum showed that the free carrier tail for the film at room temperature was absent for the spectrum at 140°C, which provides further evidence that the polyaniline chains convert to the "compact coil" conformation at this elevated temperature.

The CD spectrum of the PAN.(+)-HCSA film heated to 140°C (Figure 3.4) showed two bands at 405 and 455 nm, which are assigned as the bisignate, exciton-coupled bands associated with the 425 nm absorption band. Also, the spectrum exhibited a CD band at 355 nm associated with the benzeniod π-π* transition, as well as the tail of the (+)-HCSA circular dichroism signal (λ_max = 295 nm).

That is, unexpectedly, the polyaniline chains have undergone a transition from an "extended coil" conformation to a "compact coil" conformation at this temperature. This unprecedented temperature-induced structural change in polyanilines above 140°C suggests that the "compact coil" conformation is the more thermodynamically stable for PAN.(+)-HCSA salts. It is not reversed on cooling, unlike the thermochromic effects previously observed73,74 in optically active polythiophenes. This behaviour should
therefore be more strictly defined as a thermal rearrangement rather than thermochromism.

The thermally induced structural changes observed above for electrochemically deposited PAn.(+)-HCSA may have significant implications when other physical and mechanical properties of such salts are examined at temperatures above 140°C.

Exposure of the PAn.(+)-HCSA films to temperatures beyond 140°C resulted in irreversible changes that were progressively observed in the uv-visible and CD spectra, shown in Figures 3.5 and 3.6, respectively.

![Figure 3.5](image-url)  
**Figure 3.5.** Effect of heat treatment (140°-240°C) on the uv-visible spectrum of an electrochemically deposited PAn.(+)-HCSA film
Figure 3.6. Effect of heat treatment on the CD spectrum of an electrochemically prepared PAn.(+)-HCSA film: (a) 160°C, (b) 180°C, (c) 200°C, (d) 220°C, (e) 240°C

The electrochemically deposited PAn.(+)-HCSA film gradually lost the localized polaron absorption band at 840 nm, while a new peak grew at lower wavelengths (Figure 3.5). These changes, and the observation of isosbestic points at 440 and 710 nm, are consistent with thermally induced de-doping of the PAn.(+)-HCSA to give emeraldine base. The uv-visible spectral changes were accompanied by a large mass loss (refer to Figure 3.8), which is attributed to the loss of the dopant HCSA from the polymer backbone. The melting of the dopant at 198°C, and its subsequent decomposition at temperatures above 230°C, may facilitate the loss of HCSA observed at temperatures above 200°C.

The associated CD spectral changes shown in Figure 3.6 are also consistent with the progressive loss of the chiral (+)-HCSA dopant at temperatures > 180°C. The strong CD
bands for the initial "compact coil" PAN.(+)-HCSA diminished with increasing temperature, until the film was almost optically inactive after heating at 240°C for 10 min. The observation of an isodichroic point at 440 nm is consistent with the conversion of PAN.(+)-HCSA to racemic emeraldine base. The failure to observe CD bands for the emeraldine base confirms the importance of the (+)-CSA⁻ dopant anion in maintaining the macroasymmetry of the polyaniline chains at elevated temperatures. It is significant to note, however, that the alternative room-temperature de-doping of PAN.(+)-HCSA films with NH₄OH has been shown¹²⁰ to give optically active EB. Presumably at room temperature, unlike the elevated temperatures in this study (above the polymer glass transition temperature, Tₙ, of 190°C, as determined in Section 3.3.2.2 using DSC), the polymer chains do not have sufficient mobility to undergo the inversions required for racemization.

It is worth noting that similar thermal treatment of a poly(methyl methacrylate) blend with an "expanded coil" form of PAN.(+)-HCSA (cast from m-cresol), revealed no change to a "compact coil" chain conformation even at 180°C.¹²¹ Instead, thermal de-doping (loss of HCSA) occurred directly from the "expanded coil" conformation of the PAN.(+)-HCSA to give neutral emeraldine base.

3.3.2.2 Thermogravimetric Analysis and Differential Scanning Calorimetry Study of Electrochemically Deposited Polyaniline

In an attempt to further explain the spectroscopic/conformational changes observed for the electrochemically deposited PAN.(+)-HCSA film above 140°C, both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies of the polymer were performed.
(i) **TGA Study**

The TGA curve for the electrochemically deposited polymer is shown in Figure 3.8. It revealed three separate stages of weight loss under a nitrogen atmosphere. The first weight loss between 80°-150°C may be attributed to the loss of water and unreacted monomer from the polymer. Similar losses were observed by Monkman et al.\(^{122}\) for a chemically derived, racemic PAn(±)-HCSA sample obtained from m-cresol. Matveeva\(^{123}\) has suggested that water molecules are bound to the N atoms of polyanilines via strong H-bonding interactions. Their thermal loss from the polymer should generate increased free volume between the polymer chains, facilitating conformational changes.

The second weight loss between 220°C and 330°C is attributed to the loss of (+)-HCSA from the polyaniline chains, as (+)-HCSA has a melting point of 198°C. The weight loss associated with (+)-HCSA was somewhat higher than that calculated for fully doped polyanilines (as determined by the weight loss above 330°C), due to the presence of some surface (+)-HCSA remaining on the polymer film after electrochemically synthesis. The third weight loss stage above 330°C, in common with that observed previously for other polyaniline samples,\(^{107-109,119}\) is attributed to the degradation of the polymer backbone.
Figure 3.8. TGA (20°-800°C) for electrochemically prepared PAN.(+)-HCSA powder under nitrogen gas. Initial weight = 8.025 mg.

The general shape of the TGA curve is similar to the result obtained by Ansari\textsuperscript{119} for electrochemically deposited PAN.HCl, the only difference being the temperature at which the dopant is removed from the polymer. As HCl is highly volatile, it is removed from the polymer at approx. 150°C, i.e. PAN.(+)-HCSA is more thermally stable. The TGA is consistent with the three-step decomposition model of emeraldine salt proposed by Wei and Hsueh\textsuperscript{124} They suggested that the initial weight loss is due to the volatilization of water molecules, followed by loss of the dopant at higher temperatures and at even higher temperatures the degradation of the polymer backbone that can lead to the production of acetylene and ammonia gases.
(iii) **DSC Study**

The DSC curve for the electrochemically deposited polymer is shown in Figure 3.9. It exhibited three endothermic peaks. The first peak between 80°-130°C is related to the removal of water from the polymer that corresponds to the weight loss observed in the TGA. The second endothermic peak at 190°C presumably corresponds to the glass transition temperature of the polymer, as no weight loss was observed at this temperature. As the change in conformation discussed above occurs well below the glass transition temperature, this implies that the increased flexibility of the polyaniline chains in the amorphous region at the $T_g$ was not responsible for the conformational change observed at 140°C.

![DSC curve for electrochemically prepared PAn.(+)-HCSA powder](image)

**Figure 3.9.** DSC (-10°-420°C) for electrochemically prepared PAn.(+)-HCSA powder

However, above the glass transition temperature the PAn.(+)-HCSA film loses optical activity (see Figure 3.6), the polyaniline chains then have sufficient mobility to undergo racemization. The endothermic band above 200°C is associated with the melting of the
Chapter 3. Effect of Synthetic Route and Temperature

(+)-HCSA and its subsequent decomposition, as reflected by the second weight loss stage in the TGA.

3.3.2.3 Effect of Temperature on the Conductivity of Electrochemically Deposited PAN.(+)-HCSA

The "extended coil" conformation of racemic PAN.(±)-HCSA has been reported\textsuperscript{52,53} to be more conductive than the "compact coil" conformation. The conductivity of an optically active, electrochemically deposited PAN.(+)-HCSA pellet was therefore measured at room temperature and after heating to 140°C to determine whether a decrease in conductivity occurred, as might be anticipated from the change in conformation at 140°C proposed above.

The conductivity of the optically active PAN.(+)-HCSA pellet at room temperature was 20 S/cm, which is much higher than the conductivity reported\textsuperscript{118} for electrochemically deposited racemic PAN.(±)-HCSA of 1 S/cm. Minto and Vaughan\textsuperscript{125} recently observed a similar phenomenon in which a film of optically active PAN.(+)-HCSA salt cast from m-cresol exhibited significantly higher conductivity than the corresponding salt doped with racemic (±)-HCSA. X-ray diffraction data indicated enhanced stereoregularity and crystallinity in the salt containing the homochiral (+)-HCSA dopant, suggesting that this enhanced structural order was the cause of the increased electrical conductivity.

Thermal treatment of the PAN.(+)-HCSA pellet at 140°C for 10 min reduced its conductivity to 12 S/cm. The latter conductivity is in the range expected\textsuperscript{52} for "compact coil" polyaniline salts, which provides further evidence that a conformational change occurred. However, the only moderately higher conductivity observed for the untreated
(room temperature) PAN.(+)-HCSA indicated that it does not possess an extreme “extended coil” conformation, for which conductivity values greater than 100 S cm\(^{-1}\) have been reported.\(^{52,53}\) This is consistent with the room temperature uv-visible spectrum of electrochemically deposited PAN.(+)-HCSA in Figure 3.1, that also suggested only partial delocalization of the charge carriers in this salt and a partially “expanded” polymer chain.

3.3.2.4 Thermochromism in Chemically Doped PAN.(+)-HCSA Films

For chemically cast PAN.(+)-HCSA films, no changes in their chiroptical properties were observed between room temperature and 80°C, as this latter temperature was used to remove the solvent from the cast film. Very little change occurred on further heating to 160°C. However, at temperatures progressively above 180°C, the uv-visible and especially the CD spectra of these films underwent a series of irreversible changes that are shown in Figures 3.10 and 3.11, respectively.

A gradual decrease was observed in the intensity of the localized polaron absorption band at 840 nm, while a new peak grew at lower wavelengths (Figure 3.10). The observation of isosbestic points at 450 and 710 nm was consistent with the clean conversion of PAN.(+)-HCSA to emeraldine base, via the thermally induced de-doping of the PAN.(+)-HCSA and the loss of the dopant HCSA from the polymer backbone.
Figure 3.10. Effect of heat treatment (RT-240°C) on the uv-visible spectrum of a chemically cast Pan.(+)-HCSA film

Figure 3.11. Effect of heat treatment on the CD spectrum of a chemically cast Pan.(+)-HCSA film: (1) room temp., (2) 160°C, (3) 180°C, (4) 220°C, (5) 240°C
The associated CD spectral changes shown in Figure 3.11 were again consistent with the progressive loss of the chiral (+)-HCSA dopant from the polymer at temperatures > 180°C. The strong CD bands for the PAn.(+)-HCSA diminished with increasing temperature, as expected for de-doping to give racemic emeraldine base. The failure to observe CD bands for the EB formed again indicates that the polymer chains have sufficient mobility to undergo the inversions required for racemization when heated past the polymer glass transition temperature. This has been tentatively assigned as 150°C for chemically doped PAn.(±)-HCSA by Monkman et al.122

It may be noted that the chemically prepared PAn.(+)-HCSA film retained a higher degree of optical activity than the corresponding electrochemically deposited PAn.(+)-HCSA film when heated to 240°C, suggesting that the former is more stable to thermal de-doping.

3.3.2.5 Thermogravimetric Analysis of Chemically Doped Polyaniline

To provide more information on the thermal stability of the above chemically prepared PAn.(+)-HCSA, thermogravimetric analysis of the polymer powder was performed under a nitrogen atmosphere. The TGA for the chemically doped polyaniline is shown in Figure 3.12. This showed three separate stages of weight loss.
Figure 3.12. TGA (20°-800°C) for chemically doped PAN.(+)·HCSA powder under nitrogen gas.

The first weight loss between 90 and 180°C can be attributed to the removal of water and then solvent from the amorphous region of the polymer. The glass transition for this polymer is expected to be near 150°C, based on work by Monkman et al\textsuperscript{122} for chemically cast racemic PAN.(±)-HCSA. Above the glass transition temperature, the free volume of the amorphous phase of the polymer increases giving increased flexibility of the polyaniline chains, therefore allowing more solvent to escape.

The second weight loss between 220°C and 370°C is attributed to the removal of (+)-HCSA from the polyaniline chains, assisted by its melting (198°C) and its subsequent decomposition at temperatures above 230°C. The weight loss associated with the removal of (+)-HCSA is slower than for the electrochemically deposited polymer,
which explains the increased level of optically activity after treatment above 200°C for the chemically doped PAN.(+)-HCSA film.

The third weight loss stage above 370°C is attributed to the degradation of the polymer backbone. The ratio of the mass losses in stages 2 and 3 indicates doping by 2.1 (+)-HCSA moieties for every tetramer repeat unit in the polymer.

3.4 Conclusions

Uv-visible and CD spectroscopic studies show electrochemically deposited and chemically cast optically active PAN.(+)-HCSA films have different conformations for their polyaniline chains, assigned as "compact coil" and partial "extended coil", respectively.

The electrochemically deposited PAN.(+)-HCSA films in the "extended coil" conformation can be converted to the "compact coil" conformation by heating the films at 140°C for 10 min.

Heating the electrochemically deposited and chemically cast optically active PAN.(+)-HCSA films past progressively the glass transition temperature results in thermal de-doping to form racemic emeraldine base. At these elevated temperatures, the polyaniline chains apparently have sufficient mobility to undergo the inversion leading to racemization. Chemical cast PAN.(+)-HCSA films are somewhat more stable towards thermal de-doping than their electrochemically derived analogues.
CHAPTER 4

Effect of Solvent on the Conformation of Optically Active Polyanilines

4.1 Introduction

Solvatochromism has been extensively studied in substituted polythiophenes, where changing the solvent can have a dramatic effect upon the colour of the polymer solution.\textsuperscript{114} A marked blue shift of the highest wavelength absorption band on transferring from a "poor" to a "good" solvent was attributed to a twisting of the polymer backbone from an essentially planar to a less ordered non-planar conformation.

Mattoso et al\textsuperscript{118,126} recently briefly reported the solvatochromism of electrochemically deposited racemic PAn.(±)-HCSA on a platinum electrode after dissolution in chloroform, NMP and m-cresol. In each solvent, the polymer exhibited a broad, localized polaron band absorption near 800 nm, as well as a free carrier tail in the near-infrared region. The extent of electron delocalization in the polymer, as indicated by the free carrier tail, was highly dependent on the solvent. The free carrier tail was most prominent when PAn.(±)-HCSA was dissolved in m-cresol, but was also present to a much lesser extent in NMP and chloroform solvents.

In order to provide further insights into the conformations adopted by electrochemically generated emeraldine salts in various solvents, this chapter describes solvatochromic studies on similarly generated optically active PAn.(+)\textendashHCSA salts, where circular dichroism (CD) spectroscopy can be employed as a powerful, additional structural
probe. A greater range of solvents is also explored, including DMSO, DMF, NMP, CHCl₃ and benzyl alcohol.

There have also been brief reports of solvatochromism⁷⁷,¹²⁷ for optically active PAn.(+)-HCSA prepared by the chemical doping of emeraldine base with (+)-HCSA in several organic solvents. Chiroptical studies indicated that the emeraldine salt possessed a “compact coil” conformation in CHCl₃, DMSO, DMF and NMP⁷⁷, but an “extended coil” conformation in m-cresol and CHCl₃/m-cresol mixtures with ≥60% (v/v) m-cresol. Films cast from such doped solutions generally retained the conformation observed in the precursor solution.⁵⁴,⁵⁵,⁷⁷,¹²⁷

Interestingly, MacDiarmid et al.¹²⁸ have recently reported that the uv-visible spectra of chemically doped, racemic PAn.(±)-HCSA in CHCl₃ and NMP solvents slowly change over a period of days, due to what they believe is de-aggregation of the polymer chains. This chapter further explores the nature of this proposed de-aggregation by investigating the time dependence of both the uv-visible and CD spectra of chemically derived, optically active PAn.(+)-HCSA salts in a range of organic solvents (CHCl₃, NMP, DMSO and DMF).

4.2 Experimental

4.2.1 Solvatochromism in Chemically Doped PAn.(+)-HCSA

Dilute solutions of optically active PAn.(+)-HCSA were prepared via the doping of emeraldine base (EB) with 0.1 M (+)-HCSA in a range of organic solvents (NMP, DMSO, DMF or CHCl₃) using the procedure outlined in Chapter 2. The chiroptical
properties of these chemically generated emeraldine salts were then measured periodically over 48 hours, as described in Chapter 2.

### 4.2.2 Solvatochromism in Electrochemically Deposited PAN.(+)-HCSA

Electrochemically deposited films of PAN.(+)-HCSA were obtained on a 4 cm$^2$ Pt working electrode using the procedure described in Chapter 2 (applied potential of +0.8 V vs Ag/AgCl; 480 mC charge passed). The deposited polymer was then dissolved in 5 mL of the desired organic solvent (NMP, DMSO, DMF, CHCl$_3$ and benzyl alcohol). The chiroptical properties of these solutions were recorded after filtering through a 0.45 μm syringe filter.

### 4.3 Results and Discussion

#### 4.3.1 Solvatochromism in Chemically Doped PAN.(+)-HCSA

Previous solvatochromism studies on chemically doped PAN.(+)-HCSA by Majidi et al$^{77}$ showed that the $\lambda_{\text{max}}$ for the long wavelength, localized polaron band undergoes a large red shift of 85 nm along the series CHCl$_3$, DMF, DMSO, NMP. This was interpreted in terms of increasing conjugation length for the polyaniline chains along this solvent series. However, this earlier study was limited to recording the chiroptical properties of the dissolved polymer immediately upon doping.

Significantly, MacDiarmid et al$^{128}$ have recently shown that when emeraldine base is doped with racemic (±)-HCSA in chloroform solvent, the high wavelength localized polaron band of the PAN.(±)-HCSA formed gradually shifts to longer wavelengths over 72 hours. GPC studies of the freshly generated PAN.(±)-HCSA solution showed a small
"pseudo" high molecular weight peak in addition to the major polyaniline peak. This indicated the presence of a small proportion of polymer chains in an aggregated state, resulting in a larger hydrodynamic volume than for separated polymer chains in solution. The magnitude of the "pseudo" high molecular weight peak gradually decreased with time subsequent to doping, indicating the slow de-aggregation of the polyaniline chains.

The authors postulated\textsuperscript{128} that the emeraldine base powder is highly cross-linked due to inter-polymer hydrogen bonding between the amine and imine nitrogen sites. When the emeraldine base is doped with (±)-HCSA in solution, the protonation of the imine nitrogens breaks up these inter-polymer hydrogen bonds, therefore making the polymer soluble in the organic solvent.\textsuperscript{129} With stirring, the aggregated/cross-linked polymer chains gradually becomes disentangled resulting in an increased conjugation length for the polyaniline chains and the observed red shift of the polaron band initially seen at 730 nm in chloroform. This phenomenon was also observed for emeraldine base dissolved in NMP.\textsuperscript{130}

Based on these observations, it should follow that when emeraldine base is doped with (+)-HCSA in chloroform, the bisignate CD bands associated with the high wavelength polaron band of the optically active PAn.(+)-HCSA formed should undergo a similar red shift with time as polymer de-aggregation occurs. The time dependent changes in the uv-visible and CD spectra for emeraldine base doped with (+)-HCSA in chloroform in the present study are shown in Figures 4.1 and 4.2, respectively. The uv-visible spectrum for the doped polymer after 35 min had an intense, localized polaron band at 730 nm. As can be seen from Figure 4.1, this band gradually red-shifted to 795 nm after
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stirring for 48 hrs. However, the position of the two lower wavelength absorption bands at 350 and 420 nm (assigned as the benzenoid \( \pi-\pi^* \) transition and a second polaron band, respectively) did not change significantly with time. These changes in the absorption spectra are consistent with the slow de-aggregation of the polyaniline chains in solution resulting in an increase in the polymer conjugation length.

![Figure 4.1. Uv-visible spectra of EB doped with (+)-HCSA in chloroform after (a) 30 min, (b) 2 hr (c) 8 hr, (d) 24 hr and (e) 48 hr](image)

The corresponding CD spectra (Figure 4.2) are consistent with the changes in the absorption spectra. The CD spectrum for the PAn.(+)-HCSA 35 min after the initial rapid doping showed four visible CD bands at 405, 450, 700 and 755 nm. The CD bands at 405 and 450 nm, are assigned as the bisignate exciton coupled bands associated with the low wavelength polaron absorption band at 425 nm, while the CD bands at 700 and 755 nm are related to the long wavelength polaron absorption band at 730 nm. With
time, the position of the latter bisignate CD bands gradually shifted to longer wavelengths, in agreement with the red shift of their associated absorption band (Figure 4.1).

Figure 4.2. CD spectra of EB doped with (+)-HCSA in chloroform after (a) 30 min, (b) 8 hr and (c) 48 hr

Analogous uv-visible and CD spectral studies for the doping of EB with (+)-HCSA in NMP, DMSO and DMF solvents showed similar spectral changes to those observed in chloroform. The change with time of the position of the long wavelength, polaron absorption band as a function of the doping time in these solvents for the PAn. (+)-HCSA formed in each of these solvents is shown in Figure 4.3. After 48 hours stirring, its position shifted from 740 to 805 nm in DMSO, from 745 to 812 nm in DMF and 777 to 839 nm in NMP. These significant red shifts (~ 65 nm) over 48 hours indicate from
an increase in the polymer conjugation length and are consistent with the polyaniline chains undergoing slow de-aggregation in each solvent with time.

![Graph showing the time dependence of the position of $\lambda_{\text{max}}$ for the long wavelength polaron absorption band of chemically generated PAn.(+)-HCSA in various solvents.]

**Figure 4.3.** Time dependence of the position of $\lambda_{\text{max}}$ for the long wavelength polaron absorption band of chemically generated PAn.(+)-HCSA in various solvents.

Interestingly, Meijer et al\(^79\) have proposed that optical activity for polyaniline in solution can only occur for an aggregated phase in a "poor" solvent, while the polymer is optical inactive when dissolved in a "good" solvent. A poor solvent (e.g. chloroform) is defined as one in which the polymer-polymer interactions between different segments on the same chain are greater than the polymer-solvent interactions. On the other hand, a "good" solvent (e.g. $m$-cresol) is defined as one where the polymer-solvent interactions are greater than the polymer-polymer interactions.
Significantly, the observation in the present study that the intensity of the optical activity of the PAN.(+)-HCSA salt in CHCl₃ did not decrease over the 48 hours during which de-aggregation occurred (see Figure 4.2), strongly suggests that aggregation is not an essential requirement for optical activity in polyanilines.

### 4.3.2 Solvatochromism in Electrochemically Deposited PAN.(+)-HCSA

It is well known that polyaniline salts, PAN.HA, produced by electrochemical polymerization are generally almost completely insoluble in common solvents.\(^{14}\) However, Mattoso et al\(^ {118,126}\) have recently shown that electrochemically synthesized polyaniline salts, PAN. (±)-HCSA, doped with the “surfactant-like” acid, racemic (±)-HCSA, are quite soluble in m-cresol, CHCl₃ and NMP.

In the present study, optically active PAN.(+)-HCSA films deposited on Pt electrodes were found to be readily soluble in DMSO, NMP, CHCl₃ and benzyl alcohol. The polymers were slightly soluble in DMF and methanol, but insoluble in acetone and acetonitrile. However, the solubility of these electrochemically deposited PAN.(+)-HCSA films was considerably less than that of analogous emeraldine salts made by the chemical doping of emeraldine base with (+)-HCSA.

The uv-visible spectra of these electrochemically deposited PAN.(+)-HCSA films after dissolving in DMSO, DMF, NMP, CHCl₃ and benzyl alcohol solvents are shown in Figure 4.4. The most striking feature in each case was the presence of a strong free carrier tail in the near-infrared region, suggesting that the polymer has an “expanded coil” conformation. However, a localized polaron band or a shoulder was also present in each case at ca. 810 (±60) nm, indicating that some of the polyaniline chains are in a
"compact coil" conformation. The position and intensity of the localized polaron band/shoulder was highly dependent on the solvent. For example, only a broad, weak shoulder was observed at 740 and 830 nm in benzyl alcohol and NMP, respectively; while the polymer dissolved in chloroform and DMSO showed a well defined polaron band at 750 and 870 nm, respectively. The spectra in each case also showed a single broad, asymmetric absorption in the low wavelength region (330-470 nm) rather than the two peaks usually observed for the "compact coil" conformation. These results overall are consistent with a predominantly "extended coil" conformation for the PAn.(+)-HCSA salt in each solvent, i.e. retention largely of their original solid-state conformation.

The uv-visible spectra for the electrochemically deposited optically active salts in CHCl₃ and NMP are essentially identical to those reported by Mattoso et al.¹¹⁸ for racemic PAn.(+)-HCSA. However, they are very different to the spectra of optically active PAn.(+)-HCSA films generated by the acid doping of emeraldine base with (+)-HCSA in the same solvents. The latter chemically derived salts showed an intense, well-defined polaron band at 750-800 nm, characteristic of a "compact coil" conformation for the polyaniline chain, as well as two lower wavelength absorption bands at 425 nm and 350 nm, assigned as a second polaron band and a benzeniod π-π* transition, respectively.
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Figure 4.4. Uv-visible spectrum of an electrochemically deposited PAn.(+)-HCSA film on a Pt electrode dissolved in CHCl₃, NMP, DMSO and benzyl alcohol

The corresponding CD spectra (Figure 4.5) of the electrochemically deposited PAn.(+)-HCSA salts in solution also confirm that they have a different conformation from the chemically prepared PAn.(+)-HCSA salt in the same solvents. They exhibited a broad shoulder at 330 nm and a well defined peak at 450 nm, which are assigned as the bisignate exciton coupled CD bands associated with the broad absorption band at ca. 425 nm. Interestingly, their CD spectra at these lower wavelengths were very similar to those of electrochemically deposited PAn.(+)-HCSA films on ITO-coated glass (see Chapter 3, Figure 3.2). This again suggests that this emeraldine salt retains its “extended coil” conformation after dissolution in these organic solvents. In contrast, the chemically doping of EB with (+)-HCSA in the same solvents yielded CD bands for PAn.(+)-HCSA at 345, 405 and 460 nm (see Figure 4.2), characteristic of a “compact coil” conformation for the polymer chains.
4.3.3 Optical Purity in PAn.(+)-HCSA Salts

The optical purity of the PAn.(+)-HCSA salts in the above solutions is uncertain. Techniques such as $^1$H nmr studies in the presence of chiral shift reagents cannot be used, due to the very broad resonances for the polyaniline chains. However, chiral anisotropy factors ($g = \Delta \varepsilon / \varepsilon$) calculated for the PAn.(+)-HCSA salts suggest that they are only weakly optically active. For example, from Figures 4.1 and 4.2, a $g$ value (at 430 nm) of ca. 0.04% was calculated for chemically prepared PAn.(+)-HCSA dissolved in chloroform solvent. A similar $g$ value (at 430 nm) was also estimated for the electrochemically deposited PAn.(+)-HCSA film dissolved in DMSO. These values compare with the highest $g$ value observed to date for a chiral conducting polymer, namely ca. 2.0% for a substituted polthiophene.\(^{74}\)
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4.4 Conclusions

Following the doping of EB with (+)-HCSA in a range of organic solvents (NMP, DMSO, DMF and CHCl₃), the high wavelength, localized polaron band and the related bisignate CD bands gradually shift to longer wavelengths over 48 hours. This indicates an increase in the polymer conjugation length and, in keeping with GPC studies by MacDiarmid et al¹²⁸ on the related racemic PAn.(±)-HCSA, is attributed to the polyaniline chains undergoing slow de-aggregation in these solvents.

The fact that the intensity of the optical activity for the PAn.(+)-HCSA salt in CHCl₃ does not decrease over the 48 hours while de-aggregation occurs argues strongly against a recent suggestion by Meijer et al⁷⁹ that aggregation is an essential requirement in order to observe optical activity in polyanilines.

Solutions of the electrochemically prepared PAn.(+)-HCSA salt in various organic solvents (benzyl alcohol, NMP, DMSO, DMF and CHCl₃) exhibit marked solvatochromism, with uv-visible and CD spectral studies indicating that the polymer has a largely “extended coil” conformation in each solution. This contrasts with the chemical doping of EB in with (+)-HCSA in these solvents where the polymer adopts a “compact coil” conformation. These chiroptical results therefore provide further support for the earlier conclusion (Chapter 3) that the conformation of the polymer chains in polyaniline salts is sensitive not only to the solvent, but also to the mode of polymer synthesis.
CHAPTER 5

Effect of Novel Secondary Dopants on the Conformation of Optically Active Polyanilines

5.1 Introduction

There has been much recent interest\textsuperscript{52-56} in improving the conductivity and crystallinity of the polyaniline salt PAn.(±)-HCSA obtained via doping emeraldine base with racemic (±)-HCSA, by processing the polymer in \textit{m}-cresol or exposing a polymer film to \textit{m}-cresol vapour. The \textit{m}-cresol is considered to act as a "secondary dopant" which promotes the adoption of an "extended coil" conformation by the polyaniline chains and a resultant enhanced conductivity.

Theoretical studies\textsuperscript{57,58} suggest that these effects associated with \textit{m}-cresol arise from a synergistic combination of interactions between the \textit{m}-cresol, HCSA and the polyaniline chains. These involve H-bonding between the phenolic OH group of the \textit{m}-cresol and the carbonyl group of the HCSA and \textpi-stacking of phenyl rings in the secondary dopant and the polyaniline chain.

Unfortunately, the high toxicity and the corrosive nature of \textit{m}-cresol limit its suitability for the commercial processing of these polymers. This chapter explores the use of the less toxic related chemicals, thymol 1 and carvacrol 2, as alternative agents for the "secondary doping" of EB in the presence of the chiral (+)-HCSA dopant for the production of highly conducting optically active PAn.(+)-HCSA films (equation 5.1).
The effect on the conductivity and chiroptical properties of PAn.(+)-HCSA films (cast from DMSO) of exposure to thymol and carvacrol vapour is also investigated. Finally, the doping of EB with another m-cresol derivative, the dye Thymol Blue 3, to produce achiral emeraldine salt films is studied. Thymol Blue has the potential to act as both a “primary” and a “secondary” dopant for polyaniline via the SO₃H and thymol groups, respectively.

5.2 Experimental

5.2.1 Doping of EB with (+)-HCSA in Molten Thymol and Carvacrol as a Solvent

EB (10 mg) was dissolved in 1.25 g of molten thymol (temperature ca. 60°C) to give a blue solution. The EB solution was then doped to the emeraldine salt PAn.(+)-HCSA form with solid (+)- or (-)-HCSA (26.5 mg), 5% in excess of the amount required of to fully dope the EB. After 30 min a few drops of the green molten thymol solution were
cast onto a glass slide and allowed to cool to room temperature to give a film of the PAn.(+)-HCSA for chiroptical studies.

For the doping of EB in carvacrol with (+)-HCSA, 0.5 mg of the EB was dissolved in 5 mL of carvacrol at 50°C. The EB solution was then doped to the emeraldine salt form with 116 mg of (+)- or (-)-HCSA (giving 0.1 M HCSA). The chiroptical properties of the doped polymer were recorded after the solution was filtered using a 0.45 μm syringe filter.

**5.2.2 Exposure of PAn.(+)-HCSA Films to Thymol and Carvacrol Vapour**

Chemically prepared PAn.(+)-HCSA films were obtained by casting a concentrated solution of emeraldine base doped with (+)-HCSA in DMSO onto a microscope glass slide as described in Chapter 2. For the exposure of the PAn.(+)-HCSA film to thymol vapour, solid thymol (mp 50°C) was placed in a 30 mL beaker and heated to 150°C using a hot plate. The film of PAn.(+)-HCSA was suspended over the molten thymol and exposed to the vapour for 3.5 hr.

For the exposure of the PAn.(+)-HCSA film to carvacrol vapour, 5 mL of carvacrol was placed in a 30 mL beaker. The film of PAn.(+)-HCSA was suspended over the carvacrol and exposed to the vapour at room temperature for 18 hours.

The chiroptical properties and conductivity (four point probe method) of the optically active polyaniline films were measured before and after the films were exposed to thymol and carvacrol vapour.
5.2.3 Doping of EB with (+)-HCSA in Organic Solvents Containing Thymol

Emeraldine base (2 mg) was dissolved in 20 mL of DMSO, DMF, NMP or chloroform and solid thymol (0.100 g) added, i.e. \([\text{thymol}] = 0.033 \, \text{M}\). The EB was then doped to produce PAn.(+)-HCSA by the addition of 117 mg (+)-HCSA (0.1 M). In separate experiments, the doping of EB with (+)-HCSA in the above solvents was repeated in the presence of 1.0 M thymol.

5.2.4 Doping of EB with Thymol Blue

50 mg of EB was dissolved in 5 mL of the desired organic solvent (NMP, DMSO and DMF) to form a 1 wt\% solution, that was subsequently doped with the stoichiometric amount of Thymol Blue (253 mg) to fully dope the EB. The resultant emeraldine salt films were obtained by evaporative casting using the same procedure described in Chapter 2 for the PAn.(+)-HCSA films.

5.3 Results and Discussion

5.3.1 Doping of EB with (+)-HCSA in Molten Thymol and Carvacrol

5.3.1.1 Doping of EB with (+)-HCSA in Molten Thymol

Emeraldine base was readily soluble in molten thymol (60°C), resulting in the formation a blue solution. The dissolved EB was rapidly doped by (+)-HCSA, resulting in the rapid formation of a green solution. The solution cast onto a microscope glass slide solidified upon cooling to room temperature giving a green, uneven film. The unevenness in the cast film was due to small, surface thymol crystals formed during
solidification. The uv-visible spectrum of the cast PAn.(+)-HCSA film (Figure 5.1) exhibited a broad absorption band at 430 nm, but only a weak shoulder at ca. 820 nm for the localized polaron band. The presence instead of a broad, strong absorption in the near infrared (NIR) region indicated that the doping of EB with (+)-HCSA in thymol caused the polymer backbone to adopt an “extended coil” conformation. This conformation has been previously reported\textsuperscript{52,53} to be obtained when PAn.(±)-HCSA films were cast from m-cresol (except there was no evidence of a localized polaron band at ca. 800 nm). In contrast, as shown in Chapter 4, films of PAn.(+)-HCSA cast from solvents such as DMF, DMSO, NMP or CHCl\textsubscript{3} exhibited a strong localized polaron band at ca. 800 nm and no NIR absorption, indicative of a “compact coil” conformation.

Figure 5.1. Uv-visible spectrum of a PAn.(+)-HCSA film cast from molten thymol

A reproducible CD spectrum could not be obtained for this film due to its uneven nature arising from surface thymol crystals that interfered with the circularly polarized light
beam. The film was subsequently dissolved in DMF (20 mL), the uv-visible spectrum (Figure 5.2) revealing that the intense free carrier tail for the polymer in the solid state was replaced by a strong localized polaron band at ca. 900 nm. However, it still retained a free carrier tail in the near infrared region of significantly weaker intensity. The change in the absorption spectrum suggests that the polymer has undergone a partial reversion in the DMF solvent towards a "compact coil" conformation. This change in conformation is also supported by the presence of two lower wavelength absorption bands at ca. 335 and 425 nm in the DMF solution compared to the broad absorption band at 430 nm observed for the thymol cast film. The absorption peaks at 335 and 425 nm are assigned as the bezenzoid $\pi-\pi^*$ band and the low wavelength polaron band for emeraldine salt.

However, the position of the localized polaron band was red shifted by ca. 100 nm compared to EB doped with (+)-HCSA in DMF in the absence of thymol (see Chapter 4), suggesting a longer conjugation length. This indicates a substantial influence of the thymol on the PAN.(+)-HCSA conformation even upon dissolution of the film in DMF.
Figure 5.2. Uv-visible spectrum of the PAn.(+)-HCSA salt from Figure 5.1 dissolved in DMF

The CD spectrum (Figure 5.3) of the PAn.(+)-HCSA film upon dissolution in DMF supported the partial adoption of a "compact coil" conformation, since bisignate CD bands were observed at 395 and 450 nm (associated with the polaron absorption band at 425 nm).
Figure 5.3. CD spectrum of the PAn.(+)-HCSA salt from Figure 5.1 dissolved in DMF

5.3.1.2 Doping of EB with (+)-HCSA in Carvacrol as a Solvent

Emeraldine base was made soluble in carvacrol by heating the mixture at 50°C for 10 min to form a blue solution. The dissolved EB was readily doped by (+)-HCSA, resulting in the rapid formation of a green solution of PAn.(+)-HCSA. The uv-visible spectrum (Figure 5.4) showed a localized polaron band at 790 nm and significant near infra-red absorption. A broad shoulder at ca. 425 nm can be assigned as the second expected polaron band. However, the strong absorption by the carvacrol solvent below 375 nm prevented the clear identification of the benzenoid π—π* transition band expected at ca. 350 nm. Significantly, the presence of both the localized polaron band

† Dai et al. have recently shown that the doping of EB with racemic (±)-HCSA in carvacrol similarly results in the appearance of a free carrier tail with a maximum at ca. 2500 nm, characteristic of the “expanded coil” conformation.
and a NIR free carrier tail indicates that the polymer is in an intermediate conformation between pure “compact coil” and pure “extended coil” conformation.

Figure 5.4. Uv-visible spectrum of EB doped with 0.1 M (+)-HCSA in carvacrol

The corresponding CD spectrum (Figure 5.5) of EB doped with 0.1 M (+)-HCSA in carvacrol exhibited bisignate CD bands at 395 and 450 nm associated with the low wavelength polaron absorption band. This indicates that the polyaniline chains are still largely in the “compact coil” conformation. Bisignate CD bands are also apparent around 750 nm associated with the high wavelength polaron absorption band at 790 nm (although instrument limitations and high noise prevented clear definition).
5.3.2 Exposure of PAN.(+)-HCSA Films to Thymol and Carvacrol Vapour

5.3.2.1 Exposure of PAN.(+)-HCSA Films to Thymol Vapour

The exposure of a PAN.(+)-HCSA film (evaporatively cast from DMSO) to thymol vapour for 30 min caused significant changes to its UV-visible spectrum (Figure 5.6). The initial localized polaron band at 825 nm shifted to 855 nm and decreased substantially in intensity. However, the near infrared absorption at 1100 nm was little affected, indicating that the polyaniline salt had partially converted to the “expanded coil” conformation. However, the low wavelength $\pi-\pi^*$ band and the second polaron band at 350 nm and 425 nm, respectively, were unaffected by the thymol exposure. This indicates that the majority of the polyaniline film is still in the “compact coil”
Prolonged exposure to thymol vapour did not cause any further change in the uv-visible absorption spectrum.

**Figure 5.6.** Uv-visible spectra of a PAN.(+)-HCSA film cast from DMSO before and after exposure to thymol vapour

Exposure of the PAN.(+)-HCSA film to thymol also caused no significant changes to the CD spectrum at lower wavelengths, the film exhibiting bisignate CD bands at ca. 395 and 450 nm both before and after thymol treatment (Figure 5.7). This is not surprising in view of the minor changes to the polaron absorption band at 420 nm. However, the shift of the high wavelength localized polaron band from 825 to 855 nm resulted in a

\[\text{Abs.} \]

\[\text{Wavelength (nm)}\]

\[0 \text{ hr}\]

\[3.5 \text{ hr}\]

\[2.4\]

\[1.8\]

\[1.2\]

\[0.6\]

\[0\]

\[300 \text{ nm}\]

\[400 \text{ nm}\]

\[500 \text{ nm}\]

\[600 \text{ nm}\]

\[700 \text{ nm}\]

\[800 \text{ nm}\]

\[900 \text{ nm}\]

\[1000 \text{ nm}\]

\[1100 \text{ nm}\]

\[\text{In an analogous study by Dai et al}^{131} \text{ for a racemic PAN.(±)-HCSA film cast from DMF, exposure to thymol vapour resulted in the polaron band at 825 shifting to 900 nm and decreasing substantially in intensity, together with the appearance of a NIR free carrier tail, characteristic of the “expanded coil” conformation.}\]
corresponding red shift of the bisignate CD bands. The CD spectrum therefore confirms that the polyaniline film had only undergone a partial conversion to an "expanded coil" conformation but that is was still largely in a "compact coil" arrangement.

**Figure 5.7.** CD spectra of a PAN.(+)-HCSA film cast from DMSO before and after exposure to thymol vapour

A partial change in the PAN.(+)-HCSA film to an "expanded coil" conformation upon exposure to thymol vapour should result in an increase in the conductivity of the film. A 51 μm thick PAN.(+)-HCSA film cast from DMSO exhibited an electrical conductivity (measured by the four point probe) of 2 S/cm. After exposure to thymol vapour for 30 min, and washing with acetone, the film conductivity increased to 34 S/cm. (The film was washed with acetone to remove the thymol crystals that formed an insulating layer on the surface of the polymer film). Although substantially smaller than the conductivity increase reported for m-cresol vapour\textsuperscript{52}, the order of magnitude
increase in conductivity again confirms a significant conformational change caused by this less toxic substituted phenol.

5.3.2.2 Exposure of PAN\textsubscript{n}(\text{+})-HCSA to Carvacrol Vapour

The exposure of a PAN\textsubscript{n}(\text{+})-HCSA film (evaporatively cast from DMSO) to carvacrol vapour for 18 hr also resulted in significant changes to its uv-visible spectrum (Figure 5.8). The localized polaron band at 815 nm shifted to 845 nm and decreased substantially in intensity. More importantly, the near infrared absorption at 1100 nm was increased significantly, indicating that the polyaniline salt had partially converted to the "expanded coil" conformation.\textsuperscript{†} This latter NIR absorption was more intense than that caused by the thymol vapour, indicating that carvacrol is a more effective "secondary dopant", as its structure is identical to that of \textit{m}-cresol, except that it an isopropyl group is attached to the ring in the 3-position. However, the low wavelength $\pi-\pi^*$ band and the second polaron band at 345 nm and 415 nm, respectively, were relatively unaffected by the carvacrol exposure.

\begin{footnote}{ Analogous studies by Dai et al\textsuperscript{131} for the exposure of a racemic PAN\textsubscript{n}(\pm)-HCSA film (cast from DMF) to carvacrol vapour showed the localized polaron band at 825 nm decreasing substantially in intensity, accompanied by the appearance of an intense free carrier tail in the NIR, characteristic of an "expanded coil" conformation.}
The CD spectrum (Figure 5.9) after the PAn.(+)-HCSA film was exposed to carvacrol showed no significant changes at lower wavelengths, the film exhibiting identical bisignate CD bands at ca. 395 and 450 nm both before and after carvacrol exposure. This is not surprising in view of the minor changes to the polaron absorption band at 415 nm. The red shift in the position of the high wavelength polaron band from 815 nm to 835 nm caused the associated CD bands to shift to higher wavelengths. This change in the CD spectrum of the polyaniline film therefore also supports a partial conversion to an “expanded coil” conformation, although the polymer chains remain largely in a “compact coil” arrangement.
Figure 5.7. CD spectra of a PAn.(+)-HCSA film cast from DMSO before and after exposure to carvacrol vapour

The change in conductivity of the PAn.(+)-HCSA film cast from DMSO upon exposure to carvacrol vapour strongly supports this partial conversion of polymer to an “expanded coil” conformation. The conductivity of the initial PAn.(+)-HCSA film was 2 S/cm and this increased to 131 S/cm after exposure to carvacrol vapour. The latter conductivity value is much higher than the conductivity found for a similar PAn.(+)-HCSA film exposed to thymol vapour (34 S/cm) again indicating that carvacrol is a better vapour phase “secondary” dopant for polyaniline than thymol.

5.2.3 Doping of EB with (+)-HCSA in Organic Solvents Containing Thymol

The chiroptical properties of emeraldine salts generated by doping EB with 0.1 M (+)-HCSA in various organic solvents (DMF, DMSO, NMP and CHCl₃) in the presence of
added thymol were also examined. The concentrations of thymol investigated were 0.033 M and 1.0 M. The addition of 0.033 M thymol to EB dissolved in DMSO undergoing doping with (+)-HCSA had no significant effect on the chiroptical properties of the emeraldine salt formed. It should be noted, however that the position of the high wavelength localized polaron band underwent a red shift from ca. 735 to 805 nm over a period of 24 hours. These latter changes were independent of the added thymol and can be attributed to slow de-aggregation of the polyaniline chains caused by the solvent, as described in Chapter 4. The absence of significant near infrared absorption and the presence of bisignate CD bands at 400 and 455 nm were both consistent with a “compact coil” conformation for the polyaniline chain.

When the concentration of thymol was increased to 1.0 M, a more pronounced effect on the uv-visible spectrum after 5 min of doping was observed (Figure 5.8). The higher concentration of thymol caused a 60 nm red shift of the high wavelength polaron band from 735 to 785 nm. However, this spectrum again showed no change in the near infrared absorption, indicating that the polyaniline chains were still in the “compact coil” conformation. This was confirmed by the CD spectrum which showed bisignate CD bands at ca. 400 and 455 nm and only a slight red shift of the bisignate CD bands for the high wavelength polaron band, characteristic of a “compact coil” conformation for the polyaniline chains.

Similar behaviour was shown in the other solvents (DMF, NMP and CHCl3), except that the initial position of the high wavelength localized polaron band was highly dependent in the nature of the solvent, as described in Chapter 4. The addition of the thymol to these solutions resulted in a ca. 60 nm red shift in this localized polaron band.
Figure 5.8. Uv-visible spectra for emeraldine base doped with (+)-HCSA in DMSO with (a) no thymol and (b) 1.0 M thymol present.

5.2.4 Doping of EB with Thymol Blue

Thymol Blue (see structure 3) was soluble in a range of organic solvents including NMP, DMF and DMSO to form a deep red solution. Its uv-visible spectrum dissolved in DMSO (Figure 5.10) showed two peaks at 390 and 560 nm. A similar red colour and absorption bands were observed in NMP and DMF. The red colour of the dye suggests that the pH of the solutions is quite acidic, so Thymol Blue (HA) should acid dope emeraldine base via its sulfonic acid group (equation 5.2).

\[
\text{EB} + \text{HA} \rightarrow \left[ \begin{array}{c} \text{A} \\ \text{N} \\ \text{H} \\ \text{N} \end{array} \right]_n
\]  \quad (5.2)
Chapter 5: Effect of Novel Secondary Dopants

2.1 -

1.4 -

Si

<

0.7 -

300 400 500 600 700

Wavelength (nm)

Figure 5.10. Uv-visible spectrum of Thymol Blue dissolved in DMSO

To test this hypothesis, a 1 wt % solution of EB was dissolved in the desired organic solvent (NMP, DMSO and DMF) and doped with the stoichiometric amount of solid Thymol Blue to form a green solution. These doped solutions were then evaporatively cast onto a glass slide, and their uv-visible spectra are shown in Figure 5.11. These revealed a combination of the absorption bands for Thymol Blue overlapping with the absorption bands expected for the emeraldine salt PAn.HA (HA = Thymol Blue) formed. The presence of a localized polaron band at 745 nm in DMSO, 795 nm in DMF and 805 nm in NMP, together with the absence of a free carrier tail absorption in the NIR region indicates that the polymer is in the “compact coil” conformation in each of these solvents, i.e. the same conformation as formed when EB is doped with simpler sulfonic acid (+)-HCSA (see Chapter 4). Thus, although Thymol Blue readily acid dopes EB via its sulfonic acid group, it does not act as a “secondary dopant” for EB, despite the presence of the thymol-type moiety in its structure 3.
Figure 5.11. Uv-visible spectra of a cast films of the emeraldine salt formed by doping EB with Thymol Blue in DMSO, DMF and NMP

5.4 Conclusions

The doping of emeraldine base in molten thymol and liquid carvacrol with (+)-HCSA results in the PAn.(+)-HCSA salts formed partially adopting an "extended coil" conformation, as reflected by the appearance of a strong, broad free-carrier tail in the near infrared region. However, the CD spectra of these solutions indicate that the majority of the polyaniline chains are still in the "compact coil" conformation.

Changes to the chiroptical properties of PAn.(+)-HCSA films (cast from DMSO) upon exposure to thymol and carvacrol vapours also indicate partial conversion of the polymer chains from a "compact coil" to an "extended coil" conformation. The conductivity of these latter PAn.(+)-HCSA films increased from 2 S/cm to 34 S/cm and 131 S/cm after exposure to thymol and carvacrol vapour, respectively. Although smaller
than the conductivity increases reported for \textit{m}-cresol vapour, the one or two orders of magnitude increase in conductivity and the development of a free carrier tail in the near-infrared region support "secondary doping" of the polyaniline chains by both thymol and carvacrol vapours.

While the related Thymol Blue, containing both a sulfonic acid and a thymol group in its structure, readily dopes emeraldine base to give the corresponding emeraldine salt, no "secondary doping" occurs.

The overall results indicate that the strength as secondary dopants decreases along the series carvacrol > thymol > Thymol Blue. The effectiveness of thymol to modify the conformation of PAN.(+)\text{-}HCSA salts also decreases down the series: molten thymol > thymol vapour > thymol in organic solvents.
CHAPTER 6
Chiroptical Properties of Polyaniline in Various Oxidation States

6.1 Introduction

Polyaniline is unique among conducting polymers in that it exhibits three oxidation levels, varying from the fully oxidized pernigraniline state, to the intermediate emeraldine state, to that of the fully reduced leucoemeraldine. Also, the imine nitrogen atoms in the pernigraniline and emeraldine oxidation states can be reversibly protonated with the addition of acid to give the corresponding doped salt forms, which leads to complex redox and pH relationships (Scheme 6.1). The protonation of emeraldine base to emeraldine salt proceeds at pH ≤ 3-4, while the acid-base transition of pernigraniline requires a stronger acid medium (pH ≤ 0-1).

Of the five readily accessible forms of polyaniline (Scheme 6.1), the only one exhibiting electrical conductivity is the emeraldine salt form. Consequently, the emeraldine oxidation state has been the most extensively studied, with less emphasis being placed to date on the leucoemeraldine and pernigraniline oxidation states.

This chapter provides a study of the preparation, stability and chiroptical properties of optically active polyaniline in each of its five accessible redox and pH states, prepared via the oxidation/reduction or de-doping of both electrochemically and chemically derived PAn.(+)-HCSA salts. Apart from the useful fundamental insights provided into their structures, the ability to reversibly generate these novel optically active polyaniline materials is of significance for several potential applications, including their use as
enantioselective ion-exchange materials, chiral redox agents and as electroactive chiral membranes for the selective transport of enantiomeric chemicals.\textsuperscript{132}

![Scheme 6.1.](image)

6.2 Experimental

6.2.1 Film Preparation

Electrochemically deposited films of PAn.(+)-HCSA were obtained on 4 cm\(^2\) ITO-coated glass using the procedure described in Chapter 2 (applied potential of +1.1 V vs Ag/AgCl; 120 mC/cm\(^2\) charge passed).

Chemically prepared PAn.(+)-HCSA films were obtained by casting a concentrated solution of emeraldine base doped with (+)-HCSA in NMP onto a hydrophobic microscope glass slide, as described in Chapter 2. The glass slide was made
hydrophobic by dipping the slide into a 1 % (v/v) aminopropyltriethoxy silane solution for 30 min. The glass slide was then washed thoroughly with distilled water before drying with an air gun before use.

### 6.2.2 De-doping, Oxidation and Reduction of PAn.(+)-HCSA Films

The procedures to reduce, oxidize and de-dope the optically active PAn.(+)-HCSA films were identical for both the electrochemically deposited and chemically cast films. The PAn.(+)-HCSA films were de-doped to emeraldine base by immersing in 30 mL of aqueous 1.0 M NH₄OH solution for 1 hr. Reduction of the films to leucoemeraldine base was achieved by immersing for 30 min in 30 mL of aqueous 0.1 M phenylhydrazine. Oxidation to pernigraniline salt was achieved by suspending the PAn.(+)-HCSA film for 30 min in 0.1 M ammonium persulfate in aqueous 2.0 M HCl or in aqueous 0.1 M FeCl₃·6H₂O. Similar treatment of the PAn.(+)-HCSA films with aqueous eerie ammonium sulfate (0.1 M) for 1 hour gave a film of optically active pernigraniline base. The above films were then air dried for 10 min, before the uv-visible and CD spectra were recorded.

### 6.3 Results and Discussion

#### 6.3.1 Oxidation States of Electrochemically Deposited Polyanilines

##### 6.3.1.1 Optically Active Emeraldine Base

Treatment of a green film of electrochemically deposited PAn.(+)-HCSA with aqueous 1.0 M ammonium hydroxide rapidly turned it blue due to alkaline de-doping to give emeraldine base. The formation of emeraldine base was confirmed by the disappearance of the uv-visible and near infrared bands of the initial emeraldine salt film, and the
appearance of characteristic absorption bands at 360 and 640 nm (Figure 6.1). The band at 360 nm is associated with the benzenoid $\pi-\pi^*$ transition of the emeraldine base, while the absorption band at 640 nm is assigned to the molecular exciton arising from a quinoid group.\textsuperscript{133,134}

![Figure 6.1](image.png)

**Figure 6.1.** Uv-visible spectra of (a) initial electrochemically deposited \(\text{PAn.}(+)\)-HCSA film, and (b) emeraldine base film derived via alkaline de-doping

The CD spectrum (Figure 6.2) of the emeraldine base film confirmed that the polymer was optically active, with CD bands at 320, 390, 520 and $> 700\text{nm}$. The CD peaks at 320 and 390 nm may be tentatively assigned as the bisignate, exciton-coupled bands associated with the observed 360 nm absorption band, while the CD bands at 520 and $> 700\text{nm}$ are the bisignate, exciton-coupled bands related to the 640 nm absorption band.
Figure 6.2. CD spectra of (a) initial electrochemically deposited PAN.(+)-HCSA film, and (b) emeraldine base film derived via alkaline de-doping

The absence of any racemization of the polymer backbone in the emeraldine base, after the loss of the chiral (+)-CSA⁺ dopant in alkaline solution, apparently arises from steric constraints on the polyaniline chains in the solid state. It has been shown that the optically active emeraldine base film can be subsequently re-doped with HCl to form an optically active PAN.HCl salt film.¹²⁰

However dissolution of the emeraldine base film in a variety of organic solvents resulted in the loss of optical activity due to the expected facile inversion of the helical chains in the absence of stabilization by the chiral dopant.
6.3.1.2 Optically Active Leucoemeraldine Base

Upon immersion in aqueous 0.1 M phenylhydrazine solution, the green PAN.(+)-HCSA film turned immediately blue due to rapid alkaline de-doping to give emeraldine base. Over a period of 30 min the blue film then faded to the pale yellow colour anticipated for reduction to leucoemeraldine base. This was confirmed from the uv-visible spectrum (Figure 6.3) observed for the film immediately after removal from the phenylhydrazine solution. The absorption bands for the initial emeraldine salt were replaced by a single strong band at ca. 335 nm characteristic of leucoemeraldine. Recently, analogous studies by Nicolini et al.\textsuperscript{135} for the reduction of an electrochemically deposited, achiral PAN.HCl film with phenylhydrazine showed a similar absorption band at 330 nm for the leucoemeraldine base product.

![Figure 6.3. Uv-visible spectra of (a) initial emeraldine salt PAN.(+)-HCSA film and (b) leucoemeraldine base film derived by reduction with PhNHNH\textsubscript{2}](image)

The CD spectrum (Figure 6.4) of the leucoemeraldine base film confirmed that the polymer was optically active, with CD bands at 310 and 365 nm. These may be assigned as the bisignate, exciton-coupled bands associated with the $\pi-\pi^*$ absorption band at 330 nm (Figure 6.3). Importantly, the optically activity observed for the leucoemeraldine base indicates that the polyaniline chains are still retained in their preferential, one-sense helical screw arrangement despite the loss of the chiral (+)-CSA$^-$ dopant during reduction.

**Figure 6.4.** CD spectra of (a) initial emeraldine salt PAn.(+)-HCSA film and (b) leucoemeraldine base film derived by reduction with PhNHNH$_2$

The dissolution of the optically active leucoemeraldine base film in NMP gave a pale yellow solution. Its CD spectrum showed that the leucoemeraldine base dissolved in NMP is optically inactive, due to the expected facile inversion of the helical chains in the absence of stabilization by the chiral dopant.
Upon standing in air for 21 days, the yellow leucoemeraldine base film turned pale blue, indicating gradual aerial oxidation to emeraldine base. The chiroptical properties of the film after standing in air for 21 days were essentially identical to those of the emeraldine base film obtained above by the alkaline de-doping of PAn.(+)-HCSA with NH₄OH. Dipping this emeraldine base film in 1.0 M aqueous HCl for 10 min gave a green film whose CD spectrum was very similar to that of the initial optically active PAn.(+)-HCSA, except that the CD band at 290 nm for the (+)-HCSA was now absent.

### 6.3.1.3 Optically Active Pernigraniline

Treatment of a green film of PAn.(+)-HCSA with aqueous 0.1 M ceric ammonium sulfate led to the rapid generation of a blue/violet film, indicating that the film was oxidized to pernigraniline base. The uv-visible spectrum (Figure 6.5) after 30 min reaction confirmed that the oxidation product was pernigraniline base, showing an absorption band at 540 nm (and possibly a band at 330 nm which unfortunately overlaps the tail of the ITO absorption). The 540 nm absorption band has been assigned as the Peierls gap transition, while the 330 nm band has been assigned to a benzenoid $\pi-\pi^*$ transition.¹³⁶
Figure 6.5. Uv-visible spectra of (a) initial emeraldine salt PAn.(+)-HCSA film and (b) pernigraniline base film derived by oxidation with ceric ammonium sulfate

The CD spectrum of the pernigraniline base film (Figure 6.6) confirmed that the polymer was optically active, with CD bands at < 320, 370, 480 and ≥ 700 nm. The band at 470 nm may be assigned as one of the bisignate exciton-coupled bands associated with the Peierls gap absorption band at 540 nm. The CD bands at < 320 and 370 nm may be tentatively assigned as the bisignate, exciton-coupled bands associated with the benzenoid π-π* transition at 330 nm.
Figure 6.6. CD spectra of (a) initial emeraldine salt PAn.(+)
HCSA film and (b) pernigraniline base film derived by oxidation with ceric ammonium sulfate.

In contrast, upon oxidation of a PAn.(+)-HCSA film with 0.1 M ammonium persulfate in strong acid (2.0 M HCl) or an aqueous 0.1 M ferric chloride solution, the green emeraldine salt film turned immediately blue due to rapid oxidation of the polymer to pernigraniline salt. This blue colour was a different shade to that of emeraldine base. In some cases, partial degradation of the film occurred during the oxidation, which has also been observed by others\textsuperscript{137}. The uv-visible spectrum (Figure 6.7) showed the characteristic absorption band for pernigraniline salt at 720 nm, which is associated with the protonated quinone imine group.\textsuperscript{41} The low wavelength absorption band has been assigned as the benzenoid $\pi-\pi^*$ transition for pernigraniline salt.
Figure 6.7. Uv-visible spectra of (a) initial emeraldine salt PAn.(+)·HCSA film and (b) pernigraniline salt film derived by oxidation with $S_2O_8^{2-}$ in 2 M HCl.

The CD spectrum (Figure 6.8) of the pernigraniline salt film confirmed that the polymer was optically active. The CD band observed at ca. 650 nm is associated with the absorption band at 720 nm, while a further CD band at ca. 390 nm is presumably linked to the strong absorption from the benzenoid $\pi-\pi^*$ transition found in this region.
6.3.2 Oxidation States of Chemically Doped PAn.(+)-HCSA Films

Since the studies in Chapter 3 had shown that electrochemically and chemically derived PAn.(+)-HCSA films possess different structures/conformations, the oxidation/reduction and de-doping of optically active PAn.(+)-HCSA obtained by the chemical doping of emeraldine base with (+)-HCSA were also examined for comparison.

6.3.2.1 Optically Active Emeraldine Base

Immersion of a chemically derived optically active PAn.(+)-HCSA film in aqueous 1.0 M NH₂OH caused immediate de-doping to emeraldine base. It was necessary to pre-treat the glass slide with aminopropyltriethoxy silane to improve the adhesion of polyaniline film to the slide upon immersion. Formation of emeraldine base was
confirmed by its uv-visible spectrum shown in Figure 6.9, with peaks at 330 and 600 nm, typical of emeraldine base films.

![UV-visible spectra](image)

**Figure 6.9.** Uv-visible spectra of (a) initial emeraldine salt PAn.(+) -HCSA film and (b) emeraldine base film derived by alkaline de-doping

The CD spectrum of the emeraldine base film in Figure 6.10 showed that it was optically active. The CD bands at 375 nm may be tentatively assigned as the high wavelength CD band for the expected bisignate, exciton-coupled bands associated with the absorption band 360 nm, while the CD bands at 585 and > 700 nm are the bisignate, exciton-coupled bands associated with the 600 nm absorption band.
Figure 6.10. CD spectra of (a) initial emeraldine salt PAN.(+)-HCSA film and (b) emeraldine base film derived by alkaline de-doping.

The emeraldine base film could be subsequently re-doped with HCl to form an optically active PAN.HCl salt film. This had the same CD spectrum as the original PAN.(+)-HCSA salt film, except that as expected, the CD band at 295 nm for (+)-HCSA dopant was absent.

Interestingly, the CD spectra for the emeraldine base films derived by the de-doping of the electrochemically deposited and chemical cast PAN.(+)-HCSA salt films are different (compare Figure 6.2 and 6.10). This implies that these emeraldine base films have different conformations. This is not unexpected as their precursor electrochemically deposited and chemical cast PAN.(+)-HCSA films possessed “extended coil” and “compact coil” conformations, respectively. Further evidence is
that upon re-doping of these emeraldine base films, the re-formed emeraldine salt films return to their initial conformations as reflected by their chiroptical properties.

### 6.3.2.2 Optically Active Leucoemeraldine Base

Upon immersion in aqueous 0.1 M phenylhydrazine solution, the green emeraldine salt PAN.(+)-HCSA film turned immediately blue due to rapid alkaline de-doping to give emeraldine base. Within 5 min, the blue colour faded to the pale yellow colour anticipated for reduction to leucoemeraldine base. This was confirmed from the uv-visible spectrum (Figure 6.11) observed for the film immediately after removal from the phenylhydrazine solution. The absorption spectrum only exhibited a π-π* transition at 335 nm, typical of leucoemeraldine base films.

![Figure 6.11. Uv-visible spectra of (a) initial emeraldine salt PAN.(+)-HCSA film and (b) leucoemeraldine base film derived by reduction with PhNHNH2](image)

Figure 6.11. Uv-visible spectra of (a) initial emeraldine salt PAN.(+)-HCSA film and (b) leucoemeraldine base film derived by reduction with PhNHNH2
The CD spectrum of the leucoemeraldine base film (Figure 6.12) confirmed that the polymer was optically active, with CD bands at 340 and 395 nm. These CD bands may be assigned as the bisignate, exciton-coupled bands associated with the $\pi-\pi^*$ absorption band at 330 nm.

![Figure 6.12. CD spectra of (a) initial emeraldine salt PAn.(+)-HCSA film and (b) leucoemeraldine base film derived by reduction with PhNHNH$_2$](image)

Again, the leucoemeraldine film underwent aerial oxidation to emeraldine base upon standing. The chiroptical properties of the re-oxidized film after 21 days were similar to those reported above for the emeraldine base film obtained by the alkaline de-doping of the emeraldine salt (see Figures 6.9 and 6.10). However, the rate of aerial oxidation was faster than the corresponding electrochemically deposited film treated under identical conditions.
6.3.2.3 Optically Active Pernigraniline Base

Treatment of a green film of PAn.(+)-HCSA with aqueous 0.1 M ceric ammonium sulfate led to the rapid generation of a blue/violet colour, indicating that the film was oxidized to pernigraniline base. The uv-visible spectrum after 30 min reaction (Figure 6.13) showed absorption bands at 350 and 545 nm which are assigned as the benzenoid π-π* transition and the Peierls gap transition, respectively. Upon standing in air, the pernigraniline base film was reduced to emeraldine base. The instability of pernigraniline films has been previously reported by Sun, who observed that pernigraniline films upon drying reduced to the emeraldine oxidation state.

![Figure 6.13. Uv-visible spectra of (a) initial emeraldine salt PAn.(+)-HCSA film and (b) pernigraniline base film derived by oxidation with ceric ammonium sulfate](image)

The CD spectrum of the pernigraniline base film (Figure 6.14) confirmed that polymer the was optically active. The CD bands observed at < 320 and 350 nm may be assigned
as the bisignate, exciton-coupled bands associated with the $\pi-\pi^*$ absorption band at 350 nm. The other CD bands at 510 and $\geq$700 nm are assigned as the bisignate, exciton-coupled bands associated with the Peierls gap transition at 545 nm.

**Figure 6.14.** CD spectra of (a) initial emeraldine salt PAN.(+)-HCSA film and (b) pernigraniline base film derived by oxidation with ceric ammonium sulfate

Similarly, the oxidation of PAN.(+)-HCSA films with 0.1 M ammonium persulfate in 2 M HCl or with aqueous ferric chloride resulted in the formation of a blue film. The UV-visible spectrum of this film, shown in Figure 6.15, exhibited two absorption bands at 330 and 690 nm which are characteristic of pernigraniline salt. The 330 nm band is assigned as the benzenoid $\pi-\pi^*$ transition, while the 690 nm band is associated with the protonated quinone imine group. This film was highly unstable, as it reduced to emeraldine salt upon standing in air within 10 min after its removal from the oxidizing solution.
The CD spectrum of the pernigraniline salt film (Figure 6.16) confirmed that the polymer was optically active, with CD bands at 360, 415 and 620 nm. The CD bands at 360 and 415 nm may be tentatively assigned as the bisignate, exciton-coupled bands associated with the benzenoid $\pi-\pi^*$ absorption band 360 nm. The CD band at 730 nm is probably the lower wavelength component of the expected pair of bisignate exciton-coupled CD bands associated with the absorption band at 690 nm. After standing in air for 30 min, the CD spectra of such pernigraniline salt films became identical to the CD spectra of the initial emeraldine salt film, confirming their reduction to the emeraldine oxidation state.
Figure 6.16. CD spectra of (a) initial emeraldine salt PAN.(+)-HCSA film and (b) pernigraniline salt film derived by oxidation with S$_2$O$_8^{2-}$ in 2 M HCl

The CD spectra obtained for the pernigraniline base and salt were again different to those obtained by identical treatment of an electrochemically deposited PAN.(+)-HCSA film. This indicates that the different conformations of electrochemically and chemically derived emeraldine salt films are retained after the oxidation of the amine groups to imine groups along the polymer backbone.

6.4 Conclusions

The preparation and chiroptical properties of optically active polyaniline films in the following redox and pH states are reported for the first time: leucoemeraldine base, emeraldine base, pernigraniline base and pernigraniline salt. These new materials, exhibiting main chain chirality of the polymer backbone, were obtained via the
chemical reduction or oxidation of optically active PAn.(+)-HCSA films and via dedoping with NH$_4$OH.

It is significant that optical activity is still retained in these new materials despite the loss of the chiral (+)-HCSA dopant during the redox and alkaline treatments. This is presumably due to steric constraints in the solid state preventing the movement of the polyaniline chains required for racemization.

The reversible generation of these novel optically active materials in the solid state is of significance for potential applications, such as their use as chiral electrodes in electrochemical asymmetric synthesis and as chiral reagents in stereospecific oxidations and reductions.

The chiroptical properties of the new optically active polymers derived depend on the conformation of the precursor emeraldine salt employed, with different behaviour being found with electrochemically deposited ("extended coil") and chemically deposited ("compact coil") PAn.(+)-HCSA precursor films.
CHAPTER 7

In-situ Deposition of Optically Active Polyaniline Films

7.1 Introduction

MacDiarmid et al\textsuperscript{138,139} have shown that high quality thin films of emeraldine salts, PAn.HCl, can be easily deposited onto glass or plastic substrates from dilute aqueous solutions of aniline undergoing chemical oxidation. The \textit{in situ} deposition allows the reproducible production of smooth, highly conductive polyaniline films, with the thickness being controlled by the deposition time. These \textit{in situ} deposited films are similar to electrochemically deposited films, in that they have never been in contact with or exposed to any organic liquid or vapour. In contrast, the majority of chemically prepared polyaniline films require the protonation of emeraldine base films cast from an organic solvent or the casting of emeraldine base solutions doped with a functionalized acid in an organic solvent.

It was later shown that the thickness, electronic properties and conformation of \textit{in situ} PAn.HCl films are dependent on the nature of the substrate surface.\textsuperscript{140,141} For the same deposition time, the thickness of the polyaniline films deposited on a hydrophobic surface was greater than when the polymer was deposited onto a hydrophilic surface. This was rationalized\textsuperscript{141,142} as due to aniline being a covalent monomer and therefore is preferentially absorbed from the bulk solution onto the covalent hydrophobic surface rather than on the polar hydrophilic surface. This should favour polymerization and subsequent deposition at the hydrophobic surface compared to the hydrophilic surface. The films deposited have different sheet resistivity and uv-visible-near infrared spectra. These differences were attributed to the polyaniline film deposited on the hydrophilic
substrate adopting a "compact coil" conformation, while the polymer deposited on the hydrophobic substrate partially adopted an "extended coil" conformation.

This chapter investigates whether the simple expedient of replacing the dopant HCl with the chiral acids (+)- and (-)-HCSA will result in the deposition of optically active polyanilines on both ordinary and chemically modified glass slides. Also examined is the de-doping of these \textit{in situ} polyaniline films with NH$_4$OH and subsequent re-doping with HCl, in order to ascertain whether the macroasymmetry of the polyaniline backbone is altered during this de-doping/re-doping cycle. Finally, the reduction of these \textit{in situ} polyaniline films with hydrazine to leucoemeraldine base is explored to see if the main chain chirality is disrupted during the reduction (which will involve the removal of the chiral CSA$^-$ ions).

\section*{7.2 Experimental Details}

\subsection*{7.2.1 Substrate Preparation}

The microscope glass slides (Fisher Scientific) were initially made hydrophilic (water contact angle 5$^\circ$) by placing the slides in 200 mL of Piranha solution (140 mL of 98\% sulfuric acid and 60 mL of 30\% hydrogen peroxide) for 1 hour at 70$^\circ$C. The glass slide was thoroughly washed with distilled water to remove all traces of the Piranha solution before being dried under vacuum for 2 hours. The bottom half of the slide was made hydrophobic (water contact angle 110$^\circ$) by dipping the glass slide in 0.4\% octadecyltrichlorosilane dissolved in hexane for 5 min. The glass slide was then dried in air for 30 minutes before use.
7.2.2 Preparation of PAn.HCSA Films

Thin films of PAn.(+)-HCSA and PAn.(-)-HCSA were prepared by the \textit{in situ} chemical oxidation of aniline using a procedure analogous to that previously reported\textsuperscript{138,139} for the PAn.HCl salt:

The untreated and chemically modified glass slides were suspended via plastic clips in a beaker containing a stirred solution of 2 mL aniline dissolved in 200 mL of 1.0 M (+)- or (-)-HCSA at room temperature. A solution containing 1.12 g of ammonium persulfate dissolved in 10 mL of 1.0 M (+)- or (-)-HCSA was then quickly added. The reaction proceeded at room temperature with constant stirring. After 30 min, the microscope slides upon which the polyaniline films had been deposited were removed from the polymerization solution.

These polyaniline films were then rinsed with 100 mL of 0.1 M (+)- or (-)-HCSA to remove the larger particles that deposited on the films as well as unreacted \((\text{NH}_4)_2\text{S}_2\text{O}_8\). To reduce any polyaniline in the pernigraniline oxidation state to green films characteristic of the emeraldine salt, the films were then soaked in a solution of 100 mL of 1.0 M (+)- or (-)-HCSA aqueous solution containing 1 mL of aniline for 30 min at room temperature. These PAn.(+)-HCSA or PAn.(-)-HCSA films were then rinsed with 200 mL of 0.1 M (+)- or (-)-HCSA to remove excess HCSA and dried using an air gun at room temperature.

The \textit{in situ} deposited films were then characterized by uv-visible-NIR and circular dichroism spectroscopy. Solutions for subsequent spectroscopic studies were prepared
by dissolving the films in 5 mL of chloroform, DMSO, DMF or NMP, followed by filtration through a 0.45 μm syringe filter.

### 7.2.3 Preparation of PAn.HCSA Powders

During the initial formation of the PAn.HCSA films on microscope slides described above, a dark green suspension also formed in the reaction beaker. Following removal of the microscope slides, the reaction mixture was stirred for a further 1.5 hours at room temperature. After the reaction was completed, the precipitate was collected on a Buchner funnel with a No. 1 Whatman filter paper. The resulting wet precipitate was washed with 400 mL of 0.1 M (+)- or (-)-HCSA and then dried using a mechanical pump at room temperature for 48 hours in a vacuum desiccator.

The chiroptical properties of the PAn.(+)-HCSA and PAn.(-)-HCSA powders were recorded by magnetically stirring 0.5 mg (or 1.5 mg) in 5 mL of the appropriate solvent (chloroform, DMSO, DMF or NMP ) for 30 min followed by filtration through a 0.45 μm syringe filter.

### 7.2.4 De-doping, Re-doping and Reduction of In situ Deposited Films

These PAn.HCSA films were de-doped to give emeraldine base films by suspending the films in 50 mL of 0.1 M NH₄OH aqueous solution for 1 hour and drying in a vacuum for 2 hours. The EB films were re-doped with HCl to give corresponding PAn.HCl films by:

(i) exposure to the vapour above concentrated HCl for 20 min, or

(ii) suspending the film in a 1.0 M solution of HCl for 1 hour.
The PAN.HCSA films were reduced to leucoemeraldine by suspending the films in 50 mL of aqueous 1.0 M phenylhydrazine solution for 1 hour and then drying in a vacuum for 2 hours.

7.3 Results and Discussion

7.3.1 Chiroptical Properties of PAN.HCSA Films

The in situ deposition technique is similar to the electrochemical deposition of polyaniline films in that the polymer is deposited directly onto the substrate from the polymerization solution without using an organic solvent. However, this does not automatically imply that the deposited polymer has the same conformation, as the reaction mechanisms for the electrochemical and chemical oxidation of aniline are different.14,15

The in situ chemical oxidation of aniline in the presence of (+)- or (-)-HCSA resulted in the deposition of thin, uniform green films on the untreated glass slide. The uv-visible-NIR spectrum of the PAN.(+)-HCSA film after a dipping time of 30 min is shown in Figure 7.1. A dipping of 30 min was necessary to deposit a film of sufficient thickness for circular dichroism spectra to be recorded. It has been shown that the deposited polymer reaches a maximum thickness after 30 min dipping time.138
Chapter 7: In-situ Deposition of Optically Active Polyaniline Films

Figure 7.1. Uv-visible-NIR spectrum of an *in situ* deposited PAn.(+)-HCSA film after a 30 min dipping time

The uv-visible-NIR spectra of the PAn.(+)-HCSA and PAn.(-)-HCSA films (e.g. Figure 7.1) were similar to *in situ* deposited achiral PAn.HCl films, showing a localized polaron absorption band at 790 nm, indicating that the films were deposited at least partially in the “compact coil” conformation, as well as a benzenoid $\pi-\pi^*$ absorption band at 345 nm and a broad shoulder for the second polaron band at 420 nm.

The CD spectra of the *in situ* deposited PAn.(+)-HCSA and PAn.(-)-HCSA films (Figure 7.2) confirmed that the polymers were optically active, with mirror imaged bands at 295 and 440 nm for the PAn.(+)-HCSA and PAn.(-)-HCSA films. The 440 nm CD band is associated with the macroasymmetry of the polyaniline chains, rather than the presence of the chiral (+)- and (-)-HCSA dopants, which only have CD signals in the UV region at 295 nm. The optical activity associated with the polymer backbone
indicates that the *in situ* chemical oxidation of aniline in the presence of (+)- or (-)-HCSA is enantioselective. However, the relatively low $g$ ($\Delta \epsilon / \epsilon$) value of 0.02% estimated for the *in situ* deposited PAN.(+)-HCSA film from Figures 7.1 and 7.2 indicates that it is less optically active than related electrochemically deposited and chemically cast films (see Section 4.3.3).

![Figure 7.2](image)

**Figure 7.2.** CD spectra of *in situ* deposited PAN.(+)-HCSA and PAN.(-)-HCSA films (using a 30 min deposition time).

These chiroptical properties are different to those of electrochemically deposited PAN.(+)-HCSA or PAN.(-)-HCSA. As described in Chapter 3, films of the latter optically active salts showed broad absorption bands at 420 and 800 nm, together with a free-carrier tail in the near-infrared region, and have been assigned an "extended coil" conformation. The corresponding CD spectra exhibited CD bands at 295 nm (due to the incorporated HCSA), 340 and 445 nm, as well as showing significant CD ellipticity in
the region 500-700 nm. These contrasting observations indicate that the conformation of the PAn.HCSA salts formed electrochemically and by the new *in situ* chemical technique are different.

The uv-visible spectra for the *in situ* deposited PAn.HCSA films are also different to those of generated by chemically doping of EB with HCSA in various organic solvents (e.g. see Figure 3.1 in Chapter 3). The latter emeraldine salts, exhibited two distinct bands at low wavelengths (350 and 420 nm), in contrast to the peak and shoulder shown by the *in situ* generated films in this region (Figure 7.1). Also, the *in situ* generated salts showed significant near-infrared absorption, whereas the chemically doped analogues have been reported\textsuperscript{143} to have no absorption at wavelengths longer than 1250 nm. These differences explain why the CD spectra of the optically active *in situ* deposited PAn.HCSA films (Figure 7.2) are broader and less well defined in the low wavelength region.

Overall, the chiroptical properties for the *in situ* deposited PAn.(+)-HCSA films indicate that they possess neither a pure "compact coil" nor a pure "extended coil" conformation, but may possess an intermediate conformation.

### 7.3.2 Effect of Modified Substrate on the Chiroptical Properties of PAn.(+)-HCSA Films

Recent studies have shown that the *in situ* deposition of achiral PAn.HCl films on chemically modified glass slides of varying hydrophobicity for 5 minutes caused changes in the polymer subsequently produced.\textsuperscript{140} The PAn.HCl film exhibited a localized polaron band at 790 nm when deposited on a hydrophilic surface compared to a band at 830 nm for a hydrophobic surface. The differences in thickness and conformation between the hydrophobic and hydrophilic substrates were most noticeable
after 5 minutes of deposition, and the differences in deposition rate and conformation decreased with increasing dipping time.

The uv-visible spectra for PAn.(+)-HCSA optically active films deposited by the *in situ* method on hydrophobic and hydrophilic substrates for 30 min dipping time are shown in Figure 7.3. As expected, the polymerization and deposition of polyaniline occurred more rapidly on the CH$_3$-terminated, hydrophobic surface than on the OH-terminated, hydrophilic surface, as shown by the higher absorption in the former case.

![Figure 7.3](image)

**Figure 7.3.** Uv-visible spectra for PAn.(+)-HCSA films deposited by the *in situ* method on hydrophobic and hydrophilic substrates

However, the uv-visible spectra for the polymers deposited on the hydrophobic and hydrophilic substrates were similar to each other and also to the polymer deposited on the untreated glass slide (absorption bands at 350, 420 and 770 nm). This suggests that the PAn.(+)-HCSA films have the same conformation in each case.
The corresponding CD spectra for the polymer deposited on the hydrophobic and hydrophilic substrates, shown in Figure 7.4, support this conclusion. They showed the same spectra with CD bands at 295 and 445 nm, confirming the same conformation for their polymer chains. Interestingly, the identical intensity for the two films, despite the significantly higher absorption by the film deposited on the hydrophobic surface, suggests that the first several layers of polyaniline deposited on the surface are optically active, while subsequent layers (as in the hydrophobic case) are deposited in an achiral conformation.

**Figure 7.4.** CD spectra for PAn.(+)-HCSA films deposited by the *in situ* method on hydrophobic and hydrophilic substrates
7.3.3 Chiroptical Properties of PAn.HCSA Films Dissolved in Organic Solvents

The *in situ* deposited PAn.(+)-HCSA and PAn.(-)-HCSA films were soluble in a range of organic solvents (CHCl₃, DMSO, DMF or NMP). The solution uv-visible spectrum (Figure 7.5) for the PAn.(+)-HCSA film dissolved in DMSO showed two distinct absorption bands at 350 and 425 nm, corresponding to the $\pi-\pi^*$ transition and the second polaron band respectively, as well as a localized polaron band at 820 nm. The better defined low wavelength peaks and the red shift of the localized polaron from 785 nm band to 820 nm (described above for the *in situ* solid state PAn.(+)-HCSA and PAn.(−)-HCSA films) suggests a change in polymer conformation and/or a longer conjugation length for the polymer dissolved in DMSO. Similar absorption spectra were obtained in the other solvents, except the position of the high wavelength localized polaron band was dependent on the nature of the solvent. For example, the position of this polaron band was 835 nm in NMP and 810 nm in CHCl₃.

![Figure 7.5. Uv-visible spectrum of an *in situ* deposited PAn.(+)-HCSA film dissolved in DMSO](image.png)
More significantly, the solution CD spectra in DMSO (shown in Figure 7.6) were very different from those of their precursor films, in that they showed two bisignate CD bands at 405 and 450 nm. These CD bands may be assigned as the bisignate, exciton-coupled bands associated with the localized polaron absorption band observed for the salts at ca. 425 nm. However, these spectra are identical to emeraldine salts generated by the enantioselective doping of EB in DMSO with (+)- or (-)-HCSA, where the polymer has been assigned a “compact coil” conformation. The change in CD spectra for the in situ films dissolved in organic solvents provides strong evidence that a change in polymer conformation occurred upon dissolution.

Figure 7.6. CD spectra of an in situ deposited PAn.(+)-HCSA and PAn.(-)-HCSA films dissolved in DMSO
7.3.4 Chiroptical Properties of PAn.HCSA Powders Dissolved in Organic Solvents

The PAn.(+)-HCSA and PAn.(-)-HCSA powders isolated from the above in situ film preparations (see Section 7.2.3) were confirmed to be PAn.HCSA salts, as shown from elemental analysis and their infrared spectra (KBr pellet). Elemental analyses obtained using a Perkin Elmer 240 CHN analyzer showed that the sample consisted of 62.36% C, 6.88% N and 6.12% H by weight. As camphorsulfonic acid does not contain any nitrogen, the percentage of polyaniline in a given weight of the sample can be calculated from the nitrogen analysis. If it is assumed that the sample only contains polyaniline doped with camphorsulfonic acid, the molar ratio of the tetramer unit of emeraldine base (0.339 mol) and camphorsulfonic acid (0.661 mole) in the sample is 1:96, which suggests that the polyaniline is fully doped by camphorsulfonic acid. The infrared spectrum also revealed a strong $\nu$(CO) band at 1745 cm$^{-1}$ and $\nu$(SO$_3$) bands at 1080 cm$^{-1}$ and 600 cm$^{-1}$ characteristic of camphorsulfonate ion incorporated into conducting polymers.\textsuperscript{144}

Like the in situ deposited films, the PAn.(+)-HCSA and PAn.(-)-HCSA powders were soluble in a range of organic solvents, that allowed their chiroptical properties to be examined in solution. The solution spectra for the PAn.(+)-HCSA powder dissolved in NMP, CHCl$_3$ and DMSO at a concentration of 0.5 mg/5 mL solvent are shown in Figure 7.7.
Figure 7.7. UV-visible spectra of in situ generated PAN(+)-HCSA powder dissolved in CHCl₃, DMSO and NMP

The solution spectra for the dissolved polymer were highly dependent on the basicity of the solvent and on the concentration of polymer. For these dilute solutions, partial deprotonation of the PAN.HCSA salt occurred in the basic solvents (DMF and DMSO), as evidenced by the presence of both a localized polaron band ca. 840 nm due to the salt and a band or shoulder at ca. 630 nm due to emeraldine base. This deprotonation was essentially complete in NMP solvent (Figure 7.9c), the only absorption bands observed being those anticipated for EB. Similar deprotonation of dilute solutions of PAN.HClO₄ and PAN.H₂SO₄ in NMP has been previously described by Neoh et al.₁⁴⁵
The deprotonation described above in DMSO, DMF and NMP is reduced or prevented by addition of HCSA to the solvent. For example, the uv-visible spectrum of PAn.(+)-HCSA powder (0.5 mg) dissolved in 5 mL DMSO containing 0.1 M (+)-HCSA showed an intense localized polaron band attributable to PAn.(+)-HCSA at ca. 830 nm. No band at 630 nm due to EB was present. Dissolving the polymer at higher concentrations can also eliminate the deprotonation of the PAn.HCSA salts. For example, solutions prepared by dissolving the PAn.(+)-HCSA and PAn.(-)-HCSA at a concentration of 1.5 mg/5 mL solvent in DMSO or DMF gave uv-visible spectra characteristic of PAn.HCSA salts, with no evidence for the presence of EB. The lack of deprotonation in the solutions containing higher polymer concentrations arises from the higher HCSA concentration of the solution.

The optical activity of these PAn.HCSA powders formed during the \textit{in situ} deposition was confirmed from their solution CD spectra. For example, the CD spectrum of PAn.(+)-HCSA in DMSO (at a concentration of 1.5 mg/5 mL solvent) revealed characteristic bisignate CD bands at 400 and 450 nm, while the enantiomeric PAn.(-)-HCSA exhibited mirror imaged signals at the same wavelengths (Figure 7.8). The bisignate CD peaks may be assigned as the exciton-coupled bands associated with the polaron absorption band at 420 nm. These spectra are identical to those obtained by the dissolution of the \textit{in situ} deposited films in DMSO.
Figure 7.8. CD spectra of PAn.(+)-HCSA and PAn.(-)-HCSA powders formed during the \textit{in situ} synthesis, after dissolving in DMSO (1.5 mg/5 mL solvent)

In contrast, no measurable CD bands were observed for dilute solutions of the PAn.(+)-HCSA powder in NMP or DMF (0.5 mg in 5 mL solvent). This undoubtedly arises from the spontaneous deprotonation of the polymer to give EB, as shown above from the uv-visible spectra of such dilute solutions. In the absence of the CSA\(^-\) anion to maintain a preferred helical configuration for the polymer chains, rapid rearrangement to an achiral configuration occurs for the emeraldine base in solution. Majidi et al\textsuperscript{120} recently noticed that the dissolution of an electrochemically produced PAn.(+)-HCSA film with the strong base pyrrolidine resulted in similar deprotonation to give achiral EB. However, by using higher concentrations of PAn.(+)-HCSA (or by adding (+)-HCSA to the solution), measurable CD spectra could be obtained for solutions in NMP or DMF.
7.3.3 De-doping, Re-doping and Reduction of *In situ* Deposited Films

It has been shown in Chapter 6 that electrochemically deposited and chemically cast PAn.(+)-HCSA films retain their optical activity when undergoing redox and de-doping reactions. As the *in situ* deposited polyaniline films have a different conformation to the emeraldine salt films produced by these latter techniques, a study was therefore undertaken to determine whether the optical activity of an *in situ* deposited PAn.(+)-HCSA film was retained upon de-doping to emeraldine base (EB) or reduction to leucoemeraldine base (LB) (Scheme 7.1).

![Scheme 7.1](image)

### 7.3.3.1 De-doping/Re-doping

The uv-visible and CD spectra of the initial PAn.(+)-HCSA emeraldine salt film are shown in Figures 7.9a and 7.10a respectively. The treatment of this *in situ* deposited PAn.(+)-HCSA film with 1.0 M NH₄OH resulted in rapid deprotonation to produce a blue film of emeraldine base. The uv-visible spectrum of the latter film (Figure 7.9b) exhibited the characteristic emeraldine base peak at 620 nm. Significantly, its CD spectrum showed that the film was optically active, with strong CD bands at ca. 290, 365, 505 and ca. 690 nm (Figure 7.10b). The CD bands at 290 and 365 nm can be assigned as bisignate exciton-coupled bands associated with the absorption band at 330 nm, while the 505 and 690 bands are the bisignate exciton-coupled bands associated with the absorption band at 620 nm. The retention of optical activity in the emeraldine
base film, despite the removal of the (+)-HCSA group, again demonstrates that the observed optical activity arises from the macroasymmetry of the polymer backbone.

Re-doping of the above optically active emeraldine base film with HCl via exposure to conc. HCl vapour for 20 min regenerated a visible spectrum (Figure 7.9c) essentially identical to that of the initial PAn.(+)-HCSA, except that the position of the localized polaron band underwent a red shift to 830 nm. Also, as expected, the CD spectrum of this regenerated PAn.HCl film (Figure 7.10c) did not possess the ultraviolet region CD band associated with the incorporated (+)-HCSA.

These studies therefore confirm that *in situ* deposited polyaniline films retain their optical activity during reversible de-doping/re-doping processes.

![Uv-visible spectra of (a) in situ deposited PAn.(+)-HCSA film, (b) after de-doping to EB with NH₄OH and (c) re-doping with HCl vapour](image)

**Figure 7.9.** Uv-visible spectra of (a) *in situ* deposited PAn.(+)-HCSA film, (b) after de-doping to EB with NH₄OH and (c) re-doping with HCl vapour
2.5 -a

\[ \text{PAn.}(+)\text{-HCSA} \]

\[ \text{PAn.HCl} \]

\[ \text{EB} \]

\[ \text{Wavelength (nm)} \]

\[ \text{Ellipticity (mdeg)} \]

270 330 390 450 510 570 630 690

Figure 7.10. CD spectra of (a) in situ deposited PAn.(+)HCSA film, (b) after dedoping to EB with NH4OH and (c) re-doping with HCl vapour

7.3.3.2 Reduction

The treatment of an in situ deposited PAn.(+)HCSA film with aqueous 1.0 M phenylhydrazine resulted in the rapid reduction of the film to produce a pale yellow leucoemeraldine base film. This was confirmed by the UV-visible spectrum (Figure 7.11), which showed the generation of the characteristic leucoemeraldine base peak at 335 nm.
Figure 7.11. Uv-visible spectrum of an in situ deposited PAn.(+)-HCSA film reduced to leucoemeraldine base with aqueous phenylhydrazine

The corresponding CD spectrum (Figure 7.12) displayed bands at 315 and 375 nm, which confirmed that the reduced leucoemeraldine base was optically active. The CD bands at 315 and 375 nm can be assigned as bisignate exciton-coupled bands associated with the absorption band at 335 nm. Upon standing in air, the pale yellow leucoemeraldine base film gradually turned blue, indicating aerial oxidation to the emeraldine base oxidation state. After standing in air for 2 weeks, the chiroptical properties of this film were identical to a film obtained by the de-doping of the PAn.(+)-HCSA film with NH₄OH, indicating that all of the leucoemeraldine base film had been oxidized to emeraldine base.
These results, as in the previous de-doping experiments, confirm that the \textit{in situ} generated polyaniline films retain their optical activity during reversible redox processes. The absence of any observable racemization during the reversible redox and pH switching processes in Scheme 7.1, despite the removal of the chiral CSA$^-$ dopant during de-doping and reduction, apparently arises from steric constraints on the polyaniline chains in the solid state.

\subsection*{7.3.4 Conclusions}

A simple, new method for the \textit{in situ} deposition of films of optically active emeraldine salts from aqueous solution of aniline undergoing oxidative polymerization in the presence of (+)- and (-)-camphorsulfonic acid has been developed. The chiroptical properties for the \textit{in situ} deposited PAn.(+)-HCSA and PAn.(-)-HCSA films indicate
that they possess neither a pure "compact coil" nor a pure "extended coil" conformation, but may possess an intermediate conformation.

The polymerization and deposition of polyaniline occurs more rapidly on CH₃-terminated, hydrophobic surfaces than on OH-terminated, hydrophilic surfaces, as shown by the higher visible region absorption in the former case. However, the chiroptical properties of the PAN.(+)-HCSA films suggests that they have the same conformation in each case.

Deprotonation of an \textit{in situ} deposited PAN.(+)-HCSA film using NH₄OH results in the formation of an optically active emeraldine base (EB) film. The main chain chirality of the polymer backbone is still retained when this EB film is then converted to the corresponding PAN.HCl salt by treatment with HCl. Reduction of an \textit{in situ} deposited PAN.(+)-HCSA film also results in the formation of optically active leucoemeraldine. Slow aerial oxidation then results in the generation of optically active emeraldine base.
CHAPTER 8

Synthesis of Optically Active Polyaniline Colloids

8.1 Introduction

An important factor that has to date limited some of the potential commercial applications of polyanilines in the emeraldine salt oxidation state has been their intractability, being insoluble in common solvents and infusible (making thermal processing also impossible). However, solubility of polyaniline salts in organic solvents can be enhanced by using functionalized acids including 10-camphorsulfonic acid and dodecylbenzenesulfonic acid as the dopant acid. A major drawback of this processing route is that a number of organic solvents employed, such as m-cresol and 1-methyl-2-pyrrolidinone, are highly toxic and expensive, making them industrially undesirable.

Recently, research has focussed on achieving water “solubility” of polyaniline by synthesizing the polymer as a colloidal dispersion. This alternate approach, pioneered by Armes at al, initially involved the chemical oxidation of aniline with ammonium persulphate in the presence of a steric stabilizer. The steric stabilizers that aided the formation of polyaniline colloids included poly(ethylene oxide), poly(vinyl alcohol) and poly(styrenesulfonate).

It has been recently shown in the IPRI laboratories that conducting polymer colloids can also be synthesized electrochemically using a flow-through cell. This electrohydrodynamic technique for conducting polymer synthesis is based on removing
the polymer as it is formed above the electrode surface and stabilizing the colloidal particles with a steric stabilizer. In the initial stages of electropolymerization, the processes of monomer oxidation and oligomerization occur in the diffusion layer above the electrode surface.\textsuperscript{154,155} Once the oligomer grows to a sufficient chain length, it exceeds its solubility limit and subsequently deposits on the electrode surface. To prevent such deposition, the colloidal particle is “wrapped up” in a steric stabilizer and is removed from the diffusion layer before deposition occurs by flowing the electrolyte across the electrode surface.\textsuperscript{156}

The aims of this chapter are to:

(i) synthesize chiral conducting polyaniline PAn.(+)-HCSA and PAn.(-)-HCSA salts in the form of water soluble colloidal dispersions, via the electrohydrodynamic polymerization technique using polyethylene oxide and poly(styrenesulfonic acid) as steric stabilizers;

(ii) characterize the colloidal dispersions in terms of yield, chiroptical properties, particle size and stability;

(iii) examine the effect of polymer oxidation state on the stability and chiroptical properties of the polyaniline salt colloids.

8.2 Experimental

8.2.1 Cell Design

For this study, two divided electrochemical flow-through cells were investigated for the electropolymerization of aniline: a linear flow-through cell and a cylindrical flat flow-through cell. The linear flow-through cell (LFC) shown in Figure 8.1 was developed by Barisci et al\textsuperscript{152} for the electrohydrodynamic synthesis of polypyrrole colloids. The LFC
was a two compartment electrochemical cell, with an anion exchange membrane (Neosepta AMH A-2119, Tokuyama Corp.) to prevent mixing of the anode and cathode compartment solutions. Each cell compartment had a diameter of 2.8 cm and a volume of 30 mL without the electrode present. The anode consisted of a porous 1.1 cm thick, 2.8 cm diameter disk of 100 PPI reticulated vitreous carbon (RVC) with an approximate surface area of 530 cm$^2$. The cathode consisted of a 3.8 cm thick, 2.8 cm diameter RVC disk with an approximate surface area of 1825 cm$^2$.

![Figure 8.1. Linear Flow-Through Cell (LFC)](image)

The second cell design investigated was the cylindrical flat flow-through cell (CFFC) that was developed by Innis et al$^{153}$ to overcome the limitations of the LFC. The modifications in the cell design were increasing the anode surface area to increase colloid yield, reducing the cell resistance (the $iR$ drop between the anode and cathode) by sandwiching the anode between two cathodes, and improving cell hydrodynamics.
The CFFC, shown in Figure 8.2, consisted of a RVC disk anode that was separated from the two RVC cathodes by a Neosepta anion exchange membrane to prevent mixing of the anolyte and catholyte solutions. Two cathode disks (20 x Φ50 mm, 2576 cm²) were employed on the opposite faces of the anode (15 x Φ50 mm, 1932 cm²) to give uniform electric field distribution.

**Figure 8.2.** Cylindrical Flat Flow-Through Cell (CFFC)

### 8.2.2 Electrochemical Polymerization

#### 8.2.2.1 Synthesis of PAn.HCSA colloids using the LFC

For the synthesis of polyaniline colloids using the LFC, the electrolyte (500 mL) for the anode compartment in the divided cell contained 1 M HCl, 0.2M (+)- or (-)-HCSA (23.231 g), 0.1 M aniline (4.647 g), and 3 g/L PEO (1.500 g). For the cathode compartment, a 250 mL solution containing 1 M HCl and 0.2 M (±)-HCSA was prepared. The electrolyte solutions were pumped through the RVC electrodes, within their respective cell compartments, at 160 mL/min using a peristaltic pump. The
electropolymerization of aniline was carried out by applying a potential of +0.90 V (vs Ag/AgCl) to the RVC anode using a PAR 363. The synthesis was carried out for a total of 90 min with aliquots (ca. 20 mL) withdrawn at 30 min intervals to measure their chiroptical properties.

The colloidal dispersion formed after 90 min was than ultracentrifuged (Beckman Optima™ L80) at 49,000 rpm for 90 min. The supernatant was decanted, while the sediment was re-suspended in Milli Q water.

8.2.2.2 Synthesis of PAn.HCSA colloids using the CFFC

For the synthesis of optically active polyaniline colloids using the CFFC, an anode synthesis solution (500 mL) was prepared containing 0.25 M H₂SO₄, 0.25 M aniline, 0.2 M (+)- or (-)-HCSA and 3 g/L PSS or PEO (1.50 g). For the cathode compartment, a separate 500 mL solution containing 0.5 M NaN₃ was prepared. These electrolyte solutions were passed through their respective compartments at a flow rate of 165 mL/min by a peristaltic pump. The electropolymerization of aniline was carried out at +0.90 V (vs Ag/AgCl) for a total of 90 min. Aliquots (ca. 20 mL) were withdrawn at 30 min intervals for the chiroptical properties to be recorded.

UV-visible spectra of the aliquots sampled after various electropolymerization times were measured after diluting 250 μL of colloidal dispersion in 1.25 mL of Milli-Q water. Circular dichroism spectra were measured after diluting 1.0 mL of sample in 1.50 mL of Milli Q water. The chiroptical properties were also recorded for these samples and then at 1, 2, 4 and 24 hrs intervals upon standing in sealed containers.
The colloidal dispersions formed after 90 min were then dialyzed for 24 hours using cellulose membrane dialysis tubing with a molecular weight cut-off greater than 12,000 Daltons (Sigma) to remove excess aniline, HCSA and H$_2$SO$_4$. Separate studies with aqueous PSS solutions indicated that dialysis under these conditions would also remove 17 ± 1% of the polyelectrolyte steric stabilizer.

Thin films of PAn.(+)-HCSA/PSS were prepared by concentrating ca. 400 mL of the dialyzed colloidal dispersions to ca. 20 mL by rotary evaporation at 45°C. Approximately 0.5 mL portions of this solution were then cast onto glass slides and dried at 60°C in an oven overnight to produce thin, green films of the PAn.(+)-HCSA/PSS salt suitable for chiroptical studies.

**8.2.3 Particle Size and Zeta Potential Analysis**

The particle size and zeta potential of the colloidal dispersions were measured using a Malvern Zetamaster PCS. This technique is based upon laser light scattering, which assumes that the colloidal particles are spherical.

**8.2.4 Microscopy Studies**

Transmission electron microscopy (TEM) measurements were performed on the PA.(+)-HCSA/PSS colloidal dispersion using a JOEL 2000 TEM (80 kV), by evaporating a drop of the solution onto a 300 mesh Lacey Carbon (Type A) Copper TEM grid (Pelco Int.). *In-situ* electron diffraction studies were also performed on individual colloid particles to investigate the occurrence of crystallinity, as well as to confirm the identities of the TEM image features.
8.2.5 Electrochemical Characterization

Cyclic voltammetry studies on the dialyzed concentrate of the PAn.(+)HCSA/PSS colloid were performed using a PAR 273A potentiostat. The potential was cycled between -0.2 and +1.0 V (vs Ag/AgCl) at a scan rate of 50 mV/sec. The electrochemical cell employed a 1.8 mm² Pt disk working electrode, a Ag/AgCl reference electrode and a Pt gauze auxiliary electrode.

8.2.6 Redox Studies on the PAn.(+)-HCSA/PSS Colloids

A dialyzed and concentrated PAn.(+)-HCSA/PSS colloidal dispersion was diluted by a factor of 80 in Milli Q water and its uv-visible and circular dichroism recorded. The diluted dispersion was then divided into four 5 mL portions for reduction, oxidation and de-doping studies.

The PAn.(+)-HCSA/PSS colloid was reduced to leucoemeraldine by adding hydrazine dihydrate (sufficient to give \([N_2H_4] = 1.0 \text{ M}\) to a 5 mL portion of the colloidal dispersion. Oxidation of the PAn.(+)-HCSA/PSS colloid to pernigraniline base was achieved by adding solid ammonium persulfate (sufficient to give \([S_2O_8^{2-}] = 0.1 \text{ M}\) to a 5 mL portion of the colloidal dispersion. De-doping of the diluted colloidal dispersion to emeraldine base was similarly carried out by adding conc. \(\text{NH}_4\text{OH}\) to the dispersion to give \([\text{NH}_4\text{OH}] = 1.0 \text{ M}\), or a solid KOH pellet to give \([\text{KOH}] = 0.35 \text{ M}\).

The chiroptical properties of the polyaniline colloids after reduction, oxidation and de-doping were recorded after 10 min and then measured periodically over 24 hr.
8.3 Results and Discussion

8.3.1 Synthesis of PAn. (+)-HCSA/PEO and PAn.(-)-HCSA/PEO Colloids using the LFC

The electropolymerization of aniline was carried out for 90 min at + 0.9V (vs Ag/AgCl) in the presence of 1.0 M HCl, 0.2 M (+)- or (-)- HCSA and 3 g/L PEO as the steric stabilizer using the LFC generated a deep green anolyte “solution”. Following ultracentrifugation to remove any unreacted aniline, HCl and (+)-HCSA and re-suspension of the PAn.(+)-HCSA/PSS colloid, the mass of colloid recovered was 0.24 ± 0.02 g.

8.3.1.1 Chiroptical Studies

The uv-visible spectra of the aliquots taken from the electrochemical cell at 30 min intervals during the electrosynthesis are shown in Figure 8.3. These reveal absorption bands at ca. 375 and 730nm, characteristic of emeraldine salts. The broad absorption band at 375 nm is a combination of the benzenoid \( \pi-\pi^* \) band and the high energy polaron band, while the peak at 735 nm is attributed to the lower energy localized polaron band. The intensity of the 375 and 730 nm absorption bands increased with increasing electropolymerization time from 5-60 min, indicating an increase in the concentration of the emeraldine salt dispersion with time. However at longer polymerization times (60-90 min) a significant shoulder also began to appear at ca. 540 nm, suggesting some over-oxidation to pernigraniline. There was also a small decrease in intensity of the 735 nm peak characterization of the emeraldine salt. However, the UV-visible spectra of the individual aliquots and the re-suspended colloid changed slightly when subsequently allowed to stand only over a 24 hr period.
Figure 8.3. Uv-visible spectra of PAn.(+)-HCSA/PEO colloidal dispersion sampled at various electropolymerization times in the LFC.

The corresponding CD spectra (Figure 8.4) extracted after 30 and 60 min of electropolymerization showed no significant optical activity, despite the formation of emeraldine salt. However, a sample taken after 90 min polymerization displayed optical activity, with the CD spectra exhibiting broad CD bands ca. 400 and 500 nm. These visible CD bands are clearly associated with the macroasymmetry of the polyaniline chains, rather than the presence of the chiral (+)- and (-)-HCSA dopants, which only have CD signals in the UV region (ca. 290 nm). The CD band at 400 nm may be assigned as one of the expected pair of exciton coupled bisignate signals associated with the 375 nm absorption band. The other negative (lower wavelength) member of this expected pair of CD bands is presumably hidden under the CD signal of the incorporated (-)-HCSA dopant (Figure 8.4). The origin of the broad CD band observed at ca. 505 nm is uncertain, but may be associated with the over-oxidation products.
Mirror imaged CD spectra were obtained for the PAn.(+)-HCSA/PEO and (-)-HCSA/PEO colloids, indicating that the electrohydrodynamic polymerization of aniline was enantioselective.

Interestingly, the CD spectra of all the PAn.HCSA/PEO colloid samples increased markedly in intensity after standing for 24 hrs (Figure 8.5), although their UV-visible spectra remained essentially constant. This indicates that the asymmetric rearrangement of the polyaniline chains which gives rise to the optical activity in the colloids is much slower than the initial doping process itself. A similar phenomena has been previously observed in chiroptical studies of the doping of the emeraldine base form of poly(o-toluidine)\textsuperscript{78} and poly(o-methoxyaniline) (refer to Chapter 9) with (+)-HCSA in DMSO.
Figure 8.5. CD spectral changes for the 60 min reaction sample of the PAn.(-)-HCSA/PEO colloid after standing for 0, 1 and 2 hrs after sampling.

After 24 hrs, both the PAn(+)-HCSA/PEO and PAn.(-)-HCSA/PEO, were ultracentrifuged to remove the excess (+)- or (-)-HCSA, HCl and monomer, re-suspended in water and their CD spectra recorded (Figure 8.6). These spectra show that the colloidal particles retain their chirality in the absence of excess HCSA and are approximate mirror images for the two enantiomers. Small deviations are due to slightly different colloid concentrations on re-suspension.
8.3.1.2 Particle Size and Zeta Potential Analysis

Particle size analysis of the PAN.(+)-HCSA/PEO colloidal dispersion after ultracentrifugation and re-dispersion in water was performed using laser light scattering. This indicated that this dispersion experienced particle aggregation, since the particle size measured for the aggregate was approximately 4 μm with a mean zeta potential of -8 mV. The aggregation of the colloidal dispersion indicated that the re-suspended, colloidal PAN.(+)-HCSA/PEO dispersion was unstable with time.

8.3.2 Synthesis of PAN.(+)-HCSA/PEO and PAN.(-)-HCSA/PEO colloids using the CFFC

Using the flat cylindrical flow-through cell (CFFC), the electropolymerization of aniline at + 0.9 V (vs Ag/AgCl) in the presence of 0.25 M H2SO4, 0.2 M (+)- or (-)- HCSA and
3 g/L PEO as the steric stabilizer initially generated a green coloured anolyte. However, as the synthesis time increased the anolyte changed from green to purple, indicating considerable over-oxidation of the colloidal polyaniline.

The over-oxidation of the colloidal dispersion was confirmed by monitoring the UV-visible spectrum during polymerization. The UV-visible spectra of the aliquots diluted by a factor of 6 using Milli Q water (Figure 8.7) displayed three peaks at 386, 535 and 712 nm. The absorption bands at 386 and 712 nm are associated with the emeraldine salt oxidation state, while the absorption at 535 nm is typical of the fully oxidized pernigraniline form of polyaniline, confirming the over-oxidation of the polymer. The ratio of this 535 nm over-oxidation absorption band and the localized polaron absorption band at 712 nm increased with increasing electropolymerization time, implying that the colloidal dispersion became increasingly over-oxidized as the synthesis proceeded.

![Figure 8.7. UV-visible spectra of PAn.(+)-HCSA/PEO colloidal dispersions sampled after various electropolymerization times in the CFFC](image-url)
8.3.3 Synthesis of PAn.(+)-HCSA/PSS and PAn.(-)-HCSA/PSS colloids using the CFFC

The limited stability observed for the PAn.HCSA/PEO colloids prompted the study of optically active polyaniline colloids using polystyrene sulfonate (PSS) as an alternative steric stabilizer. The electropolymerization of aniline at + 0.9 V (vs Ag/AgCl) in the presence 0.25 M H₂SO₄, 0.2 M (+)- or (-)- HCSA and 3 g/L PSS as the steric stabilizer using the CFFC again resulted in the formation of a deep green coloured anolyte. Following dialysis of a 90 min reaction sample, 1.53 ± 0.03 g of PAn.(+)-HCSA/PSS colloid was recovered. After correction for the PSS estimated to be lost during dialysis (17%), this reduced to a mass of 0.29 ± 0.01 g of PAn.(+)-HCSA produced in the total synthesis volume (500 mL). This was substantially higher than that found above for PAn.HCSA/PEO colloids produced using the less efficient linear flow-through cell (LFC).

8.3.3.1 Chiroptical Studies

The uv-visible spectra of aliquots taken from the electrochemical cell at 30 min intervals is shown in Figure 8.8. Due to the increased rate of colloid production using this cell, it was necessary to dilute the aliquots by a factor of 6 with Milli Q water.
Figure 8.8. Uv-visible spectra of PAn.(+)-HCSA/PSS colloidal dispersion sampled at various electropolymerization times

The uv-visible spectra of the PAn.(+)-HCSA/PSS and PAn.(-)-HCSA/PSS colloids show two absorption peak at 385 and 775 nm, characteristic of an emeraldine salt dispersion. The broad absorption band at 385 nm is a combination of the benzenoid $\pi-\pi^*$ band and the higher energy polaron band, while the peak at 775 nm is assigned to the lower energy, localized polaron band. A free-carrier tail was also present in the near infrared region, which suggests that polyaniline colloid is partially synthesized in the “extended coil” conformation. The intensity of these peaks increased with synthesis time, indicating a progressive increase in concentration of the emeraldine salt formed.

The colloidal dispersion was synthesized without any over-oxidation of the polymer, as the uv-visible spectra showed no absorption band at 535 nm, in contrast to the PAn.(+)-HCSA/PEO colloid produced above under identical conditions. This implies that PSS is
superior to PEO as a steric stabilizer for electrochemically produced PAn.HCSA colloids using the CFFC.

As was the case for the PAn.(+)-HCSA/PEO and PAn.(-)-HCSA/PEO colloids synthesized using the LFC, the CD spectra for the above PAn.(+)- and (-)-HCSA/PSS colloids withdrawn after 30 and 60 min electropolymerization revealed no significant optical activity (Figure 8.9). However, the aliquot withdrawn after 90 min exhibited broad CD bands 390 and 465 nm. These visible region bands are clearly associated with the macroasymmetry of the polyaniline chains. The 390 and 465 nm CD peaks may be assigned as the bisignate, exciton-coupled bands associated with the polyaniline absorption band at 385 nm (Figure 8.8). The CD band(s) associated with the localized polaron absorption band at 775 nm could not be recorded, due to instrumentation limitations at these longer wavelengths. The CD spectra of the PAn.(+)-HCSA/PSS and PAn.(-)-HCSA/PSS colloids were mirror imaged, again indicating enantioselective induction of chirality in the polyaniline chains caused by the chiral HCSA dopants.
Chapter 8: Synthesis of Optically Active Polyaniline Colloids

Figure 8.9. CD spectra of PAn.(+)-HCSA/PSS colloidal dispersions sampled after various electropolymerization times

The CD spectra for the electrochemically synthesized PAn.(+)-HCSA/PSS and PAn.(−)-HCSA/PSS colloids are markedly different to those found for optically active PAn.(+)-HCSA and PAn.(−)-HCSA films potentiostatically deposited on ITO-coated glass electrodes in a static electrochemical cell (see Chapter 3, Figure 3.2). The latter films were assigned an “extended coil” conformation. However, the CD spectra of the colloids in Figure 8.9 are similar in band position and sign to those observed when PAn.HCSA salts are generated by doping emeraldine base (EB) with (+)- or (−)-HCSA in organic solvents (e.g. bands at 400 and 450 nm in DMSO, as shown in Figure 3.2). This suggests that the polyaniline chains in the PAn.HCSA/PSS colloids are largely in a “compact coil” conformation. This is supported by the corresponding absorption spectra (Figure 8.8), which exhibited a localized polaron band at 775 nm despite the presence also of a partial free-carrier tail absorbance in the near infra-red region.
The CD spectra of the PAn.HCSA/PSS colloid aliquots removed from the cell at different synthesis times again increased considerably in intensity after standing for 24 hrs (Figure 8.10), although their UV-visible spectra remained constant. This phenomenon is not just specific to steric-stabilized polyaniline colloids, as Aboutanos et al\textsuperscript{157} recently observed similar changes in the chiroptical properties of electrochemically synthesized optically active PAn.HCSA/silica colloidal dispersions. This confirms that the optical activity in the colloids arises from an asymmetric rearrangement of the polyaniline chains subsequent to the initial doping process. The bisignate CD bands associated with the absorption band at ca. 420 nm give a small $\Delta \varepsilon/e$ value of 0.011%. This suggests that only a relatively small proportion of the emeraldine salt present in the PAn.HCSA/PSS colloid is in the optically active form, with the remainder of the polyaniline chains being in an achiral conformation or arrangement. However, this is not unexpected since the anolyte contains both $\text{PSS}^-$ and $\text{SO}_4^{2-}/\text{HSO}_4^-$ ions, that can act in competition with (+)-CSA$^-$ or (-)-CSA$^-$ as achiral dopants for the formation of the emeraldine salt colloid.
Figure 8.10. CD spectra of PAn.(-)-HCSA/PSS colloidal dispersions after ageing for 24 hours.

The uv-visible and CD spectra of the dialyzed PAn.(+)-HCSA/PSS colloid were essentially unchanged after standing for 6 months, indicating the excellent stability of this colloid.

8.3.3.2 TEM, Electron Diffraction Analysis, and Particle Size Analysis

The PAn.(+)-HCSA/PSS and PAn.(-)-HCSA/PSS colloid particles were imaged by TEM to determine their morphology. In Figure 8.11a, colloid particles of PAn.(+)-HCSA/PSS were observed as dark spherical features that stuck to the surfaces of the TEM lacey grid. The larger particles (100 nm), also shown at a higher magnification in Figure 8.11b, were clearly aggregate structures of the smaller colloid particles ca. 10 to 20 nm in size. The void spaces between the TEM grid were bridged by the excess PSS (Figure 8.11a).
Figure 8.11. TEM of PAn.(+)-HCSA/PSS colloid at (a) 80,000 magnification, and (b) 200,000 magnification.

Further identification of these image features was derived from electron diffraction measurements on the PSS and PAn.(+)-HCSA/PSS components. The broad ill-defined
diffraction pattern for the bridging PSS material indicated an amorphous character. In contrast, a PAn.(+)-HCSA/PSS colloid particle (Figure 8.12) exhibited a distinct crystalline diffraction pattern similar to those reported for aligned fibres of PAn.HCSA cast from m-cresol\textsuperscript{158,159}.

![Electron diffraction pattern of a PAn.(-)-HCSA/PSS colloid particle](image)

**Figure 8.12.** Electron diffraction pattern of a PAn.(-)-HCSA/PSS colloid particle

Particle size and mobility analysis of colloidal dispersions of PAn.(+)-HCSA/PSS (90 min synthesis time) revealed a mean particle size of 180 ± 10 nm, in a skewed distribution with a broad particle size tail at up to 1000 nm. The presence of the larger particles above 1000 nm indicated the presence of some macroscopic colloid aggregation. The zeta potential of the colloids was – 45 ± 4 mV, consistent with the presence of the negatively charged PSS\textsuperscript{−} anion as a stabilizer.
8.3.3.3 Electrochemical Characterization

The conductivity and electroactivity of the optically active colloid was confirmed from cyclic voltammetry on the dialyzed concentrate of the PAn.(-)-HCSA/PSS colloid. The cyclic voltammogram for the colloid, shown in Figure 8.13, displayed two reversible redox responses similar to those reported for optically active PAn.HCSA films.\textsuperscript{76} The oxidation peak at 0.155 V (vs Ag/AgCl) corresponds to the conversion of leucoemeraldine to emeraldine salt, while the peak at 0.515 V corresponds to the subsequent oxidation to the pernigraniline form.

![Cyclic voltammogram of PAn.(-)-HCSA/PSS colloidal dispersion on a Pt disc electrode (scan rate 50 mV/s).](image)

**Figure 8.13.** Cyclic voltammogram of PAn.(-)-HCSA/PSS colloidal dispersion on a Pt disc electrode (scan rate 50 mV/s).

8.3.3.4 Redox Studies of the PAn.(-)-HCSA/PSS Colloids

As the cyclic voltammogram of the PAn.(-)-HCSA/PSS colloid showed that the polymer could be reduced to leucoemeraldine and oxidized to pernigraniline, it was decided to examine the chiroptical properties of the optically active colloid after its
chemical reduction and oxidation with \((N_2H_4\) and \((NH_4)_2S_2O_8\), respectively) as well as its de-doping with \(NH_4OH\) or \(KOH\). Similar studies by Stejskal et al\(^{41}\) have demonstrated that achiral colloidal dispersions of \(PAn.HCl\) stabilized with poly(vinyl alcohol) can be readily reduced, oxidized and de-doped.

The addition of hydrazine dihydrate to the green \(PAn.(+)-HCSA/PSS\) colloidal dispersion resulted in rapid reduction to give the pale yellow colour characteristic of leucoemeraldine base. The formation of the leucoemeraldine base was confirmed by the disappearance of the localized polaron band of the emeraldine salt at 775 nm and the appearance of a characteristic \(\lambda_{\text{max}}\) at 335 nm (Figure 8.14).

\[\text{Figure 8.14.} \text{Uv-visible spectrum for a PAn.(+)-HCSA/PSS colloidal dispersion reduced to leucoemeraldine base with 1.0 M hydrazine dihydrate}\]

Similarly, oxidation of the \(PAn.(+)-HCSA/PSS\) colloidal dispersion resulted in the rapid formation of a stable pernigraniline base dispersion. This was evidenced by the
disappearance within 10 min of the localized polaron band for the initial emeraldine salt at 775 nm and the appearance of the expected pernigraniline base absorption band at 515 nm, as shown in Figure 8.15.

![Uv-visible spectrum for a PAN.(+)-HCSA/PSS colloidal dispersion to pernigraniline base oxidized with 0.1 M ammonium persulfate](image)

**Figure 8.15.** Uv-visible spectrum for a PAN.(+)-HCSA/PSS colloidal dispersion to pernigraniline base oxidized with 0.1 M ammonium persulfate

Similarly, treating a PAN.(+)-HCSA/PSS colloid dispersion with either 1.0 M NH₄OH or 0.35 M KOH led to its rapid de-doping to produce a blue emeraldine base dispersion. The uv-visible spectrum revealed that the large majority of the initial emeraldine salt had been converted to emeraldine base (characteristic $\lambda_{\text{max}}$ at 330 and 590 nm) within 10 min (Figure 8.16).
The CD spectra for the polyaniline colloidal dispersions generated above in the different oxidation states are shown in Figure 8.17. Remarkably, the CD spectrum for the reduced, oxidized and de-doped colloids were identical to the CD spectrum for the initial emeraldine salt colloidal dispersion. There were no further changes to the absorption and CD spectra observed over the next 24 hr.

**Figure 8.16.** Uv-visible spectrum after de-doping a PAn.(+)-HCSA/PSS colloidal dispersion to emeraldine base with 1.0 M ammonium hydroxide.
This redox and pH behaviour of the PAn.(+)-HCSA/PSS dispersion indicates that only optically inactive emeraldine salt component of the colloids undergoes the facile reduction, oxidation and de-doping observed, while the optically active fraction is essentially inert to such treatment. This phenomenon has also been recently observed in the more optically pure electrochemically synthesized PAn.(+)-HCSA/silica colloidal dispersions.\textsuperscript{157} Although the cause of this chemical inertness is not fully understood, it possibly arises from steric constraints associated with the inter- and intra-strand arrangements of the polyaniline chains in the optically active component of the colloid. Alternatively, the high degree of crystallinity observed in the colloid by electron diffraction are associated with the optically active portions of the colloid, while the optically inactive emeraldine salt fractions have a lower degree of crystallinity and therefore undergo facile oxidation, reduction and alkaline de-doping. In this respect,
Minto and Vaughan\textsuperscript{125} have observed that an optically active film of PAN.(+)-HCSA cast from \textit{m}-cresol is more crystalline and has greater stereoregularity than the corresponding racemic PAN.(\textpm)-HCSA salt.

Using the chemical inertness of the optically active portions of the PAN.(+)-HCSA/PSS colloid, it is possible to calculate the optical purity of the colloid. For example, by analyzing the uv-visible spectrum of the colloid treated with 1.0 M ammonium hydroxide, to calculate the ratio of \(\text{ES}_{\text{remaining}}/\text{EB}_{\text{formed}}\), an optical purity of ca. 2\% is estimated for the PAN.HCSA/PSS colloid.

8.4 Conclusions

Optically active polyaniline colloids can be readily prepared via the electrohydrodynamic polymerization of aniline in acidic aqueous solutions containing one enantiomer of the chiral dopant HCSA in the presence of a steric stabilizer. Either a linear flow-through cell (LFC) or a flat cylindrical flow-through cell (CFFC) can be employed. While the PAN.HCSA/PEO dispersions synthesized aggregate upon standing, the PAN.HCSA/PSS dispersions synthesized in the CFFC remain stable for 6 months, indicating that PSS is superior to PEO as a steric stabilizer for these colloidal emeraldine salts.

The chiroptical properties of these colloidal polyaniline dispersions indicate that the polymer is synthesized largely in the “compact coil” conformation. The optical activity of the colloidal dispersions increase markedly upon standing for 24 hr, indicating that the asymmetric rearrangement of the polyaniline chains induced by the chiral HCSA dopant occurs much more slowly than the initial doping process itself.
The optically active fractions of polyaniline colloids PAn. (+)-HCSA/PSS are remarkable inert to oxidation, reduction and alkaline de-doping. This contrasts with the optically inactive polyaniline components of these colloids, which like previously studied PAn.HA salts, undergo facile redox and pH switching.
CHAPTER 9

Synthesis and Chiroptical Properties of Optically Active Poly(o-methoxyaniline)

9.1 Introduction

An increasing amount of recent research into conducting polymers has targeted improving the solubility, and hence processability, of these polymers by the polymerization of substituted aniline derivatives. These include alkyl\(^ {160,161} \), alkoxy\(^ {162,163} \) and sulfonate\(^ {164,165} \) substituents placed on the aniline ring in the ortho position. The alkyl and alkoxy substituents enhance organic solubility, while the sulfonate group results in water soluble polyanilines. The improved solubility of substituted polyanilines results from the incorporation of flexible groups into the polymer chains that decrease the rigidity of the polymer backbone and/or the presence of polar substituents increasing the overall polarity of the polymer chain. However, the steric effect of such substituents, resulting in a twisting of the polyaniline chain from planarity, may have a detrimental effect on the electrical properties of the polymer.

An emeraldine salt film of poly(o-methoxyaniline) was first prepared\(^ {166} \) in 1988 via the oxidation of o-methoxyaniline with \((\text{NH}_4)_2\text{S}_2\text{O}_8\) in aqueous HCl. The POMA.HCl obtained, unlike the analogous polyaniline PAN.HCl salt, was soluble in a range of organic solvents. The successful electrochemical preparation of poly(o-methoxyaniline) films doped with HCl has also been recently reported by Mattoso et al\(^ {162} \), the POMA.HCl salts formed again showing higher solubility than the similarly prepared polyaniline salt in common organic solvents.
This chapter investigates the first synthesis of optically active poly(o-methoxyaniline) salts, namely POMA.(+)-HCSA and POMA.(-)-HCSA, via:

(i) The electropolymerization of o-methoxyaniline on platinum or ITO-coated glass electrodes in the presence of (+)- or (-)-HCSA, and

(ii) the chemical doping of the emeraldine base form of o-methoxyaniline with (+)- or (-)-HCSA in organic solvents.

It was anticipated that, if successful, this would lead to more organic solvent-soluble chiral polyanilines. Also of particular interest was to establish the influence of the methoxy substituent on the conformation and chiroptical properties of the polymers. In the case of the chemical doping route (ii), the influence of polymer molecular weight on the induction of chirality into the poly(o-methoxyaniline) backbone has also been examined.

Finally, the de-doping of the electrochemically deposited POMA.(+)-HCSA salt with aqueous NH₄OH has also been explored (Scheme 9.1), in order to ascertain whether the macroasymmetry of the poly(o-methoxyaniline) chains is altered by the removal of the chiral (+)-HCSA dopant.

Scheme 9.1
9.2 Experimental

9.2.1 Electrochemical Polymerization

The electropolymerization studies were performed in a three electrode cell (described in Chapter 2) at room temperature using a 20 mL aqueous solution containing 0.2 M $o$-methoxyaniline and 1.0 M (+)- or (-)-HCSA as the supporting electrolyte. Nitrogen was flushed through the electrochemical cell and the polymerization solution prior to all experiments in order to minimize the influence from oxidation products. The working electrode was either platinum or indium-tin-oxide (ITO) coated glass. Both potentiostatic and potentiodynamic polymerization techniques were employed.

(i) potentiostatic polymerization

The majority of electropolymerizations were carried out potentiostatically. The POMA.HCSA films were deposited by applying a potential of +0.8 V ($vs$ Ag/AgCl) for the Pt working electrode and +1.1 V ($vs$ Ag/AgCl) for the ITO-coated glass electrode, using a charge density of 120 mC/cm$^2$.

(ii) potentiodynamic polymerization

For the potentiodynamic polymerizations, a Pt (1.8 mm$^2$) working electrode was employed and the potential was cycled between −0.2 and +1.0 V ($vs$ Ag/AgCl) at a scan rate of 20 mV/s. Cyclic voltammograms were recorded during polymer growth. The final scan was stopped with the potential at the extreme positive value.

9.2.2 Cyclic Voltammetry

The electrochemical characterization of a POMA.(+)-HCSA film deposited potentiostatically on Pt as described above was performed using cyclic voltammetry.
The potential was cycled between −0.2 and +0.9 V (vs Ag/AgCl) at a scan rate of 50 mV/s in aqueous 1.0 M (+)-HCSA as the supporting electrolyte.

9.2.3 Spectroscopic Characterization
The chiroptical properties of the novel, chiral POMA.(+)−HCSA and POMA.(−)-HCSA salts were recorded in the solid state directly for the films deposited on the ITO-coated glass electrodes. In addition, solution spectra were recorded by dissolving the films grown on both platinum and ITO-coated glass electrodes (for 480 mC) in 5.0 mL of the desired organic solvent (chloroform, DMSO, DMF, NMP and methanol). These solutions were filtered through a 0.45 µm syringe filter before measuring their uv-visible and CD spectra within 5 min after dissolution.

9.2.4 Chemical De-doping/Re-doping of Electrochemically Deposited POMA.(+)−HCSA Films
These POMA.(+)−HCSA films were de-doped to give emeraldine base films by suspending them in 30 mL of aqueous 1.0 M NH₄OH for 30 min and drying in air. The EB films were then re-doped with HCl to give the corresponding PAn.HCl films by suspending the films in 30 mL of 1.0 M HCl for 30 min.

9.2.5 Chemical Doping of Poly(o-methoxyaniline) Emeraldine Base with (+)− and (−)-HCSA in Organic Solvents
Poly(o-methoxyaniline) emeraldine base powders with molecular weights of 30,000 and 180,000 Daltons used in this study were kindly donated by Professor Mattoso, Institute de Fiscia de Sao Carlos, Brazil, their synthesis being described elsewhere.¹⁶ For doping
experiments, solutions were prepared by dissolving $0.5 \text{ mg}$ of the substituted EB in 5 mL of DMSO, and then doped to the POMA.HCSA emeraldine salt by the addition of $116 \text{ mg}$ of (+)- or (-)-HCSA (giving $0.1 \text{ M}$ HCSA). The chiroptical properties of these POMA.HCSA solutions, after they were filtered through a $0.45 \mu \text{m}$ syringe filter, were recorded periodically over 48 hrs.

9.3 Results and Discussion

9.3.1 Electrochemical Synthesis of Optically Active Poly(o-methoxyaniline)

9.3.1.1 Electrochemical Polymerization of o-methoxyaniline

The electropolymerization of o-methoxyaniline in the presence of various acids (e.g. HCl, HClO$_4$, H$_2$SO$_4$) to produce conducting poly(o-methoxyaniline) films has been extensively studied. These electrochemically deposited POMA.HA films were found to have similar electroactivity and electrochromism, but generally an order of magnitude lower conductivity, compared to the parent polyaniline PAN.HA films. This reduced conductivity is related to the steric hindrance of the methoxy group causing adjacent phenyl rings to twist from a co-planar arrangement. Also, Jackowska et al have shown that the type of dopant acid influences the rate of o-methoxyaniline polymerization, with the oxidation rate increasing in the order HClO$_4 < \text{HCl} < \text{H}_2\text{SO}_4$. They also found that the mechanisms for nucleation and growth were dependent on the dopant acid, as has been observed for the electrochemical polymerization of the parent aniline with these acids.

In the present study, the optimal potential for the potentiostatic polymerization of o-methoxyaniline in the presence of (+)-HCSA on different substrates was determined
using cyclic voltammetry. The cyclic voltammogram for the potentiodynamic deposition of a POMA.(+)-HCSA film on a Pt electrode from an aqueous solution containing 0.2 M o-methoxyaniline and 1.0 M (+)-HCSA is shown in Figure 9.1. The current passed during the deposition of the POMA.(+)-HCSA film was considerably less than for the parent PAn.(+)-HCSA film grown under identical conditions. This indicates that the POMA.(+)-HCSA salt is less conducting than the parent polyaniline film or that less polymer was deposited on the electrode.

During the first anodic sweep, the maximum current at +0.76 V (vs Ag/AgCl) is associated with the formation of the radical cation species generated on oxidation of o-methoxyaniline. After reversing the scan direction in the first cycle, a loop in the voltammogram appeared that is probably related to a nucleation process and an increase in the electrode surface area. In subsequent cycles, new peaks appeared in the voltammogram attributed to the electrochemical response of the deposited polymer and any intermediate species formed during the oxidation process.\textsuperscript{162} The increasing current for these peaks with the number of cycles suggests an increase in film thickness. In similar experiments using an ITO-coated glass electrode, the oxidation potential for the monomer was +1.05 V (vs Ag/AgCl). The higher potential required to oxidize the monomer was due to the need to overcome the resistance of the ITO-coated glass electrode.
Figure 9.1. Cyclic voltammogram for the potentiodynamic growth of POMA.(+)-HCSA at a scan rate of 20 mV/s

The potentiostatic polymerization of o-methoxyaniline in aqueous 1.0 M (+)-HCSA on an ITO-coated glass electrode at +1.1 V (vs Ag/AgCl) resulted in the deposition of dark green, conducting emeraldine salt POMA.(+)-HCSA films. Figure 9.2 shows a typical chronoamperogram for the deposition, revealing that polymer growth occurred in two stages. The rate of deposition was initially slow, but increased as the effective surface area of the electrode increased. The slow initial stage is related to the nucleation of the polymer on the bare sections of the electrode surface, while the second stage for the rapid deposition of the polymer is related to the autocatalytic growth of polyaniline. The growth currents for POMA.(+)-HCSA were approx. 50% lower than for the potentiostatic growth of the parent polyaniline PAN.(+)-HCSA film under identical conditions.
Figure 9.2. Chronoamperogram during the deposition of POMA.(+)-HCSA on an ITO-coated glass electrode grown at +1.1 V (vs Ag/AgCl)

9.3.1.2 Chiroptical Properties of POMA.(+)-HCSA and POMA.(-)-HCSA Films

The uv-visible spectrum of the POMA.(+)-HCSA film potentiostatically grown on ITO-coated glass at +1.1 V (charge passed 480 mC) is shown in Figure 9.3. This exhibited an intense, well-defined polaron band at 785 nm, as well as two lower wavelength absorption bands at 425 nm and 350 nm, assigned as a second polaron band and a benzeniod π-π* transition, respectively. This absorption spectrum is nearly identical to that of electrochemically deposited POMA.HCl films, and is consistent with a “compact coil” conformation for the polymer chains.
Figure 9.3. Uv-visible spectrum of a POMA.(+)-HCSA film potentiostatically grown on an ITO-coated glass electrode at +1.1 V (vs Ag/AgCl)

The circular dichroism spectra of this POMA.(+)-HCSA film and the analogously deposited POMA.(-)-HCSA film (Figure 9.4) confirmed that they were optically active, with CD bands at 330, 400, 450 and 730 nm. The mirror imaged CD spectra observed for POMA.(+)-HCSA and POMA.(-)-HCSA indicate that the electrochemical polymerization of o-methoxyaniline in the presence of (+)- or (-)- HCSA is enantioselective. The CD peaks at 330 and 400 nm may be tentatively assigned as the bisignate, exciton-coupled bands associated with the benzenoid $\pi-\pi^*$ absorption band seen at ca. 350 nm. Partly overlapping with these is another probable pair of bisignate exciton-coupled CD bands (of which only the 450 nm band is observed) that correspond to the 425 nm polaron absorption band. The CD peak observed at 730 nm is probably the lower wavelength component of the expected pair of bisignate exciton-coupled CD bands associated with the localized polaron absorption band at 785 nm. The CD signal
below 330 nm arises from the (+)-HCSA or (-)-HCSA dopant incorporated into the polymer.

The optical purity of the above POMA.HCSA films is uncertain. However, from Figures 9.3 and 9.4, a chiral anisotropy factor \( g = \Delta\varepsilon/\varepsilon \) of ca. 0.06% may be calculated at 425 nm for POMA.(+)-HCSA. This compares with the highest g value of 2.0% observed to date for a chiral conducting polymer (a substituted polythiophene\(^74\)). This suggests that either the intrinsic ability of these chiral POMA salts to discriminate between left and right hand circularly polarized light is small, or that their optical purity is relatively small.

The uv-visible and CD spectra for the POMA.(+)-HCSA film are markedly different to those of the parent PAn.(+)-HCSA film. In contrast to POMA.(+)-HCSA, the uv-visible
spectrum for the latter parent complex showed only a shoulder for the high wavelength polaron band at ca. 790 nm, but exhibited a strong free carrier tail in the near infrared (see Figure 9.5 for comparison). As discussed earlier, this suggests at least a partial "extended coil" conformation for the parent PAN.(+)-HCSA salt. Also consistent with this conformation is the presence of only a single broad absorption in the low wavelength region for the parent polyaniline salt.

![Graph showing UV-visible spectra comparison](image)

**Figure 9.5.** Comparison of the UV-visible spectra of electrochemically deposited POMA.(+)-HCSA and PAN.(+)-HCSA films

Similarly, the relatively complex CD spectrum for the POMA.(+)-HCSA film at low visible wavelengths contrasts with that for PAN.(+)-HCSA, which showed only two bisignate bands in the 320-500 nm region (at 340 and 445 nm, see Figure 9.6 for comparison). Also in contrast to POMA.(+)-HCSA, the latter parent salt exhibited no well defined CD peak between 500 and 780 nm.
The different uv-visible and CD spectra for electrochemically deposited POMA.(+)-HCSA and PAn.(+)-HCSA films confirm that the poly(o-methoxyaniline) has a different conformation to the parent polyaniline salt. This change in conformation of the polymer backbone is presumably due to the methoxy substituent increasing the flexibility of the polymer chains thereby causing the polymer backbone to deviate from a co-planar arrangement.

9.3.1.3 Electrochemical Characterization of Polymers after Electrosynthesis

Cyclic voltammetry was used to characterize the electrochemical behaviour of the above optically active POMA.(+)-HCSA films. The cyclic voltammogram (Figure 9.7)
of POMA.(+)-HCSA potentiostatically deposited on a Pt electrode (at +0.8 V with a charge density of 120 mC/cm²) confirmed that the polymer was electroactive, with three redox couples at +0.15, +0.40 and +0.65 V (vs Ag/AgCl). The positions of these redox couples were nearly identical to those reported by Zotti et al\textsuperscript{172} for electrochemically deposited POMA.H\textsubscript{2}SO\textsubscript{4} films on a Pt electrode.

![Cyclic voltammogram for an optically active POMA.(+)-HCSA film in aqueous 1.0 M (+)-HCSA at a scan rate of 50 mV/s](image)

**Figure 9.7.** Cyclic voltammogram for an optically active POMA.(+)-HCSA film in aqueous 1.0 M (+)-HCSA at a scan rate of 50 mV/s

The redox couples at +0.15 V and +0.65 V observed in the cyclic voltammogram are attributed to the redox responses of POMA.(+)-HCSA. The first anodic process is related to the oxidation of the leucoemeraldine form to emeraldine salt, while the third anodic process corresponds to the oxidation of the emeraldine salt form to the pernigraniline state. The second reversible redox couple at +0.41 V is similar to that reported by Jackowska et al\textsuperscript{173} for electrochemically deposited POMA.HCl. They
assigned this reversible redox couple to a cyclic or linear o-methoxyaniline dimer incorporated into the polymer film. However, others\textsuperscript{174} have suggested that this redox peak is associated with degradation products arising from the over-oxidation of the poly(o-methoxyaniline).

9.3.1.4 Chiroptical Properties of POMA.(+)\textendash HCSA Films Dissolved in Organic Solvents

The electrochemically deposited POMA.HCSA films were found to be more soluble than the corresponding PAn.HCSA films in a range of organic solvents (NMP, DMSO, DMF, methanol and chloroform), generating deep green solutions. However, the polymers were not soluble in acetone or acetonitrile. The improved solubility of these poly(o-methoxyaniline) films, which is a benefit for processing, is believed to be due to the methoxy group decreasing the stiffness of the polyaniline chains and the polar substituent increasing the overall polarity of the polymer chains.

Uv-visible spectra recorded within 5 min of dissolution of the POMA.(+)\textendash HCSA films in NMP, DMF, chloroform, DMSO and methanol are summarized in Figures 9.8a and 9.8b. In each solvent, the emeraldine salt exhibited three characteristic absorption bands at ca. 340, 430 and 780 (± 35) nm, which are very similar to those observed for their precursor POMA.(+)\textendash HCSA film (see Figure 9.3). In particular, the presence of a strong localized polaron band at ca. 780 (± 35) nm and the absence of strong near infrared absorption supports a “compact coil” conformation for the POMA.(+)\textendash HCSA in each solvent.
It is interesting that similar conformations are maintained in each of these solvents which encompass both aprotic and protic solvents. However, changing the nature of the solvent had a significant influence on the position of the low energy polaron band.† As summarized in Table 9.1, λ_{max} for this band is red shifted (72 nm) along the series NMP < CHCl₃ < DMF, DMSO < MeOH, which is consistent with an increase in the conjugation length of the poly(o-methoxyaniline) chain along the series of solvents.

Figure 9.8a. Uv-visible spectra of electrochemically deposited POMA.(+)HCSA films dissolved in NMP, DMF and chloroform

† In contrast, the positions of the benzenoid π-π* transition (ca. 340 nm) and the high energy polaron band (ca. 430 nm) are relatively unaffected by the nature of the solvent.
Figure 9.8b. Uv-visible spectra of electrochemically deposited POMA.(+)-HCSA films dissolved in methanol and DMSO.

Table 9.1. Solvent dependence of the uv-visible spectrum of electrochemically deposited POMA.(+)-HCSA

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ for low energy polaron band (nm)</th>
<th>Shift ($\Delta$ nm) in $\lambda_{\text{max}}$ compared to film</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>745</td>
<td>-40</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>782</td>
<td>-3</td>
</tr>
<tr>
<td>DMF</td>
<td>808</td>
<td>23</td>
</tr>
<tr>
<td>DMSO</td>
<td>808</td>
<td>23</td>
</tr>
<tr>
<td>MeOH</td>
<td>817</td>
<td>32</td>
</tr>
</tbody>
</table>

The corresponding CD spectra of the electrochemically deposited POMA.(+)-HCSA films after dissolution in each of these solvents are shown in Figures 9.9a and 9.9b. All of these solutions exhibited similar CD peaks at 345 and 400 nm which are the bisignate
exciton coupled bands associated with the benzeniod $\pi-\pi^*$ absorption band at ca. 340 nm. They also exhibited a broad shoulder at 440 nm and a well defined peak at ca. 465 nm, which may be assigned as the bisignate exciton coupled bands associated with the low wavelength polaron absorption band. These spectra are very similar (apart from the 440 nm shoulder) to those attributed in earlier studies (see Chapter 3) to the parent PAN.(+)-HCSA when in the “compact coil” conformation.

**Figure 9.9a.** CD spectra of electrochemically deposited POMA.(+)-HCSA films dissolved in NMP, DMF and chloroform
However, the CD spectra for the electrochemically deposited POMA.(+)-HCSA in the above solvents are significantly different to the solid state spectra (see Figure 9.4) indicating that the dissolution results in some change, as yet undefined, to the polymer chain conformation.

9.3.15 De-doping/Re-doping of POMA.(+)-HCSA Films

It has been shown in Chapter 6 that electrochemically deposited PAn.(+)-HCSA films retain their optical activity when de-doped to emeraldine base and subsequently re-doped with HCl. Based on this observation, it was expected that the optically active POMA.(+)-HCSA films would behave in a similar manner.
The uv-visible and CD spectra of the initial POMA.(+)-HCSA emeraldine salt film are shown in Figures 9.10a and 9.11a, respectively. Treatment of this electrochemically deposited film with 1.0 M NH₄OH resulted in rapid deprotonation to produce a methoxy-substituted blue emeraldine base film. The uv-visible spectrum of the emeraldine base film (Figure 9.10b) exhibited two absorption bands at 330 nm and 590 nm, characteristic of emeraldine base. These adsorption bands are the benzenoid π-π* transition and the molecular exciton associated with the quinoid group, respectively.

Significantly, the CD spectrum of this emeraldine base film showed that it was optically active, with strong bands at < 300, 375, 515 and ca. 640 nm (Figure 9.11b). The CD peaks at < 300 and 375 nm may be assigned as the bisignate exciton-coupled bands associated with the benzenoid π-π* absorption band at 330 nm, while the 515 and 640 peaks are the bisignate exciton-coupled bands arising from the absorption band at 590 nm. The retention of optical activity in the POMA emeraldine base film, despite the removal of the (+)-HCSA group, again demonstrates that the observed optical activity arises from the macroasymmetry of the polymer backbone.

Re-doping of the above optically active emeraldine base film with aqueous 1.0 M HCl solution for 20 min regenerated a uv-visible spectrum (Figure 9.10c) essentially identical to that of the initial POMA.(+)-HCSA, except that the position of the localized polaron band underwent a small red shift to 800 nm. The CD spectrum of the POMA.HCl film (Figure 9.11c) was also identical to the initial spectrum of the POMA.(+)-HCSA film, except that the band for the incorporated (+)-HCSA was absent, and there was a slight red shift in the CD band associated with the localized polaron band from 730 to 740 nm.
In summary, these chiroptical studies confirm that the electrochemically deposited poly(o-methoxyaniline) films retain their optical activity during reversible de-doping/re-doping processes.

![Graph showing UV-visible spectra](image)

**Figure 9.10.** UV-visible spectra of (a) initial POMA.(+)-HCSA film, (b) after de-doping with NH₄OH and (c) re-doping with aqueous 1.0 M HCl
9.3.2 Chemical Doping of Poly(o-methoxyaniline) Emeraldine Base with (+)-HCSA in Organic Solvents

9.3.2.1 Doping of High Molecular Weight Poly(o-methoxyaniline) Emeraldine Base

The high molecular weight poly(o-methoxyaniline) emeraldine base (Mₗ = 180,000) was readily soluble in DMSO, resulting in the formation of a deep blue solution whose uv-visible spectrum showed characteristic emeraldine base peaks at 330 and 620 nm. The addition of 0.1 M (+)-HCSA to the solution caused rapid protonation of the emeraldine base to form POMA.(+)-HCSA, as confirmed by the generation within a minute of a deep green solution with a uv-visible spectrum characteristic of an emeraldine salt (Figure 9.12).
The time dependence of the uv-visible spectrum of this doped solution is also shown in Figure 9.12. The position of the high wavelength polaron band gradually shifted from 680 to 810 nm after stirring for 48 hours. Also a distinct low wavelength polaron band began to appear at ca. 430 nm after standing for 7-48 hours.

As discussed in Chapter 4, this large red shift (140 nm) in the position of the high wavelength polaron band with time can be attributed to slow de-aggregation of the poly(o-methoxyaniline) chains caused by the solvent. This suggests that the poly(o-methoxyaniline) emeraldine base, like the parent emeraldine base, is initially aggregated due to hydrogen bonding between the amine and imine nitrogen sites on adjacent chains, and these chains become slowly disentangled with time.

Figure 9.12. Uv-visible spectra after the doping of high molecular weight poly(o-methoxyaniline) emeraldine base with 0.1 M (+)-HCSA in DMSO after (a) 30 min, (b) 2.5 hr, (c) 7 hr, (d) 24 hr and (e) 48 hr
The corresponding CD spectra (Figure 9.13) revealed that the POMA.(+)-HCSA formed became increasingly optically active with time, as indicated by the evolution of CD bands in the visible region. The more complex low wavelength CD spectrum for POMA.(+)-HCSA compared to PAn.(+)-HCSA (see Chapter 3, Figure 3.2) is consistent with the presence of two absorption bands in this region for the substituted polyaniline rather than a single peak. The CD bands at 345 and 400 nm may be tentatively assigned as the bisignate exciton-coupled bands associated with the benzenoid $\pi-\pi^*$ absorption band at ca. 335 nm. The broad CD shoulder at 435 nm and the well defined CD band at 465 nm may be tentatively assigned as the bisignate exciton-coupled bands associated with the low wavelength polaron absorption band that grows with time at ca. 430 nm.

Interestingly, the increase in intensity of the optical activity of the POMA.(+)-HCSA solution with time while de-aggregation is believed to occur (see above) argues against the recent suggestion by Meijer et al.\textsuperscript{79} that aggregation is necessary in order to observe optical activity in polyanilines.
Figure 9.13. CD spectra after the doping of high molecular weight poly(o-methoxyaniline) emeraldine base with 0.1 M (+)-HCSA in DMSO after (a) 30 min, (b) 2.5 hr, (c) 4.5 hr, (d) 7 hr, (e) 24 hr, (f) 31 hr and (g) 48 hr

9.3.2.2 Doping of Low Molecular Weight Poly(o-methoxyaniline) Emeraldine Base

The low molecular weight poly(o-methoxyaniline) emeraldine base (M_w = 30,000) was also highly soluble in DMSO, giving a deep blue solution with uv-visible peaks at 330 and 615 nm, characteristic of emeraldine base. The addition of 0.1 M (+)-HCSA to the DMSO solution resulted in the rapid protonation of the emeraldine base to form a deep green solution of POMA.(+)-HCSA, as confirmed by the appearance of uv-visible absorption bands at 345, 425 and 808 nm, characteristic of emeraldine salts (Figure 9.14).
Unlike the high molecular weight POMA.(+)-HCSA, the position of the low energy polaron band only underwent a moderate red shift with time ($\lambda_{\text{max}}$ increasing from 810 nm at 1 hr to 840 nm after 4 days). In contrast, $\lambda_{\text{max}}$ for the polaron band shifted from 680 to 820 nm for the high molecular weight salt. These observations are consistent with the low molecular weight poly(o-methoxyaniline) being largely de-aggregated as soon as it is formed in solution.

![Graph showing UV-visible spectrum](image)

**Figure 9.14.** UV-visible spectrum after the doping of low molecular weight poly(o-methoxyaniline) emeraldine base with 0.1 M (+)-HCSA in DMSO after 24 hr

The corresponding CD spectrum (Figure 9.15) recorded 30 min after the doping of low weight poly(o-methoxyaniline) emeraldine base with 0.1 M (+)-HCSA in DMSO revealed that the POMA.(+)-HCSA formed was only weakly optically active, the only strong CD signal observed being associated with the optically active (+)-HCSA dopant.
However, with time the polymer became gradually more optically active, with the
growth of CD bands at ca. 350, 415 and 465 nm. These signals may be assigned as the
overlapping bisignate exciton coupled bands associated with the benzenoid and π-π∗
and the polaron absorption observed for the salts at 345 and 425 nm. However, it is
clear that the generation of optical activity in poly(o-methoxyaniline) is substantially
slower than for the parent polyaniline, which forms an optically active PAn.(+)–HCSA
within 5 min. Since the doping process itself to form POMA.(+)–HCSA is rapid (as
evidenced by the uv-visible spectra changes in Figure 9.12, the induction of
macroasymmetry in the polymer chains must involve a slower subsequent re-
arrangement.

Figure 9.15. CD spectra after the doping of low molecular weight poly(o-
methoxyaniline) emeraldine base with 0.1 M (+)-HCSA in DMSO after (a) 30 min, (b)
2.5 hr, (c) 5.5 hr, (d) 8.5 hr, (e) 24 hr, (f) 33 hr and (g) 72 hr
9.4 Conclusions

(i) Electrochemically Synthesized Optically Active POMA.HCSA Salts

The first reported synthesis of optically active poly(o-methoxyaniline)s has been achieved via the electropolymerization of o-methoxyaniline from aqueous solutions containing (+)- or (-)-camphorsulfonic acid. The green films of emeraldine salt exhibit strong visible region CD bands, confirming the macroasymmetry of the polymer chains. Mirror imaged CD spectra are observed for POMA.(+)-HCSA and POMA.(-)-HCSA films, indicating enantioselection in the electrochemical deposition.

The chiroptical properties of these novel POMA.(+)-HCSA salts indicate a “compact coil” conformation for the polymer chains, in contrast to the analogous parent PAn.(+)-HCSA films which are largely in the “extended coil” conformation. These differences are attributed to the steric influence of the methoxy substituent on the aniline rings.

These electrochemically prepared salts are highly soluble in a range of organic solvents, such as DMF, NMP, CHCl₃, DMSO and methanol. Uv-visible and CD studies show that the POMA.(+)-HCSA adopts a similar “compact coil” type conformation in each solvent. However, dissolution causes some change in the polymer conformation compared to the precursor POMA.(+)-HCSA film. The nature of the solvent has a strong influence on the position of the low energy, localized polaron band of the emeraldine salt, which is strongly red shifted (Δ = 72 nm) along the solvent series NMP < CHCl₃ < DMF ~ DMSO < MeOH. This solvatochromism indicates an increase in the conjugation length of the polymer chain along this solvent series. However, the CD spectra for the POMA.(+)-HCSA films dissolved in the above solvents are significantly
different to their solid state CD spectra. This indicates that dissolution of the poly(o-methoxyaniline) salts results in some change in polymer conformation.

Deprotonation of the electrochemically deposited POMA.(+)-HCSA film using aqueous 1 M NH₄OH results in the formation of an optically active methoxy-substituted emeraldine base film. The main chain chirality of the polymer backbone is still retained when this emeraldine base film is subsequently converted to the corresponding emeraldine salt, POMA.HCl, by treatment with HCl.

(ii) Chemical Doping Route to Optically Active POMA.(+)-HCSA

The optically active poly(o-methoxyaniline) emeraldine salt, POMA.(+)-HCSA, can also be synthesized in solution via the acid doping of the methoxy-substituted emeraldine base with (+)-HCSA in DMSO solvent. However, the generation of optical activity in the polymer is substantially slower than for the corresponding parent polyaniline, taking several days to fully develop.

Following the rapid doping of the high molecular weight POMA emeraldine base with (+)-HCSA, the localized polaron band of the POMA.(+)-HCSA formed undergoes a large (140 nm) red shift over 48 hours. This indicates an increase in the polymer conjugation length which is attributed to the poly(o-methoxyaniline) chains undergoing slow de-aggregation in solution. However, after doping the low molecular weight POMA emeraldine base with (+)-HCSA, only a small subsequent red shift (30 nm) occurs for the high wavelength polaron band over 48 hours, consistent with a lower degree of initial polymer aggregation than for the high molecular weight poly(o-methoxyaniline).
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