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Synthesis and characterisation of chiral substituted polyanilines

Ekaterina V. Strounina

University of Wollongong

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SYNTHESIS AND CHARACTERISATION OF
CHIRAL SUBSTITUTED POLYANILINES

A thesis submitted in fulfilment of the requirements
for the award of the degree
DOCTOR OF PHILOSOPHY

from
UNIVERSITY OF WOLLONGONG

by
EKATERINA V. STROUNINA, M.Sc.

Intelligent Polymer Research Institute
Department of Chemistry
2001
CERTIFICATION

I, Ekaterina V. Strounina, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Department of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Ekaterina V. Strounina
8 October 2001
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF FIGURES</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xix</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xxi</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>xxv</td>
</tr>
</tbody>
</table>

## CHAPTER 1

**General Introduction** | 1
--- | ---
1.1 General Properties of Conducting Polymers | 1
1.2 Polyanilines | 2
1.3 Doping in Conducting Polymers | 9
1.4 Substituted Polyanilines | 10
1.4.1 N-Substituted Polyanilines | 11
1.4.1.1 N-Alkylanilines | 12
1.4.1.2 Poly(diphenylamine) | 13
1.4.2 Ring-Substituted Polyanilines | 15
1.4.2.1 Alkyl- and Alkoxy-Substituted Polyanilines | 15
1.4.2.2 Sulfonated Polyanilines | 17
1.4.2.3 Co-polymers | 21
1.5 Applications of Sulfonated Polyanilines | 22
1.6 Optical Activity in Conducting Polymers | 23
1.7 Polymer Conformation and Properties | 27
1.8 Aims of the Project | 28
CHAPTER 2

General Experimental ................................................. 30

2.1 Materials ....................................................... 30

2.1.1 Monomers .................................................. 30

2.1.2 Polymers ..................................................... 30

2.1.3 Reagents ..................................................... 30

2.1.4 Solvents ..................................................... 31

2.1.5 Electrodes ................................................... 31

2.2 pH Measurements ............................................... 31

2.3 Synthesis of Optically Active Polyanilines .................. 31

2.3.1 Electrochemical Synthesis ................................ 32

2.3.2 Chemical synthesis ........................................ 33

2.4 Polymer Characterisation .................................... 34

2.4.1 UV-visible-NIR Spectroscopy ............................ 34

2.4.2 Circular Dichroism Spectroscopy ......................... 35

2.4.3 Electrical conductivity .................................... 37

2.4.4 Electrochemical Characterisation - Cyclic Voltammetry 38

2.4.5 Gel Permeation Chromatography (GPC) ................. 39

2.4.6 Atomic Force Microscopy ................................ 39

2.4.7 Atomic Absorption Spectroscopy ......................... 40

CHAPTER 3

Electrochemical Synthesis of Chiral PMAS in the Presence of (+)- and (-)-1-Phenylethylamine ................................................. 41

3.1 Introduction .................................................... 41
3.2 Experimental ................................................................. 45

3.2.1 Cyclic Voltammetry of Aqueous MAS Solutions ............ 46

3.2.2 Potentiodynamic Polymerisation of MAS in the Presence of (+)- or (-)-PhEA ........................................... 46

3.2.3 Potentiostatic Polymerisation of MAS in the Presence of (+)-PhEA ............................................................... 46

3.2.4 Immobilisation of PMAS.(+)-PhEA with Poly(4-vinylpyridine) .... 47

3.2.5 UV-vis-NIR and Circular Dichroism Spectroscopy ............ 47

3.2.6 Interaction of PMAS.(+)-PhEA with HCl and Ammonia .... 47

3.3 Results and Discussion ..................................................... 48

3.3.1 Cyclic Voltammetry of Aqueous MAS Solutions .......... 48

3.3.2 Potentiodynamic Polymerisation of MAS in the Presence of (+)-PhEA ........................................................ 48

3.3.3 Polymerisation Mechanism for PMAS ......................... 50

3.3.4 Chiroptical Properties of PMAS.(+)-PhEA ................. 52

3.3.5 Influence of Various Parameters on Polymer Deposition and Chirality .................................................... 57

3.3.6 Deposition of PMAS-(+)-PhEA Films using the Square-Wave Potential Pulse Method ..................................... 61

3.3.7 Potentiostatic Polymerisation of MAS in the Presence of (+)-PhEA ............................................................. 64

3.3.8 Surface Morphology of a Potentiodynamically Deposited PMAS.(+)-PhEA Film ......................................... 66

3.3.9 Molecular Weight of PMAS-(+)-PhEA ....................... 66

3.3.10 DC Conductivity of PMAS.(+)-PhEA ....................... 68
3.3.11 Interaction of PMAS.(+)-PhEA Films with Gaseous HCl and Ammonia

3.3.11.1 Exposure to Hydrochloric Acid Vapour

3.3.11.2 Exposure to NH3 Vapour

3.3.12 Immobilisation of PMAS.(+)-PhEA on Poly(4-vinylpyridine)

3.4 Conclusions

CHAPTER 4

Chirality Induction in pre-formed PMAS via Acid-Base Interaction with Chiral Amines

4.1 Introduction

4.2 Experimental

4.2.1 Materials

4.2.2 Preparation of PMAS.(RNH2) Films

4.2.2.1 Evaporatively Cast Films

4.2.2.2 Spin-Cast Films

4.2.2.3 Preparation of PMAS.(+)-NEA Films via Dipping Method

4.2.3 Crosslinking of PMAS.(+)-PhEA Films

4.2.4 UV-vis-NIR and CD Spectroscopic Studies

4.3 Results and Discussion

4.3.1 Chiroptical Properties of PMAS.(+)-PhEA in Solution

4.3.2 Chiroptical Properties of PMAS.(+)-PhEA Films Cast on Glass

4.3.3 Chiroptical Properties of Other Spin-Cast PMAS.(RNH2) Films

4.3.3.1 Chiral Amines as Inducing Agents

4.3.3.2 Chiral Aminoalcohols as Inducing Agents
4.3.4 Influence of the Amine : PMAS Ratio .............................................. 100
4.3.5 Crosslinking of PMAS.(+)-PhEA with PVA ..................................... 101
4.4 Conclusions ................................................................. 104

CHAPTER 5
Ionochromic Effects with Aqueous PMAS ........................................ 106
5.1 Introduction ................................................................. 106
5.2 Experimental .............................................................. 109
  5.2.1 Materials ................................................................. 109
  5.2.2 Ionochromism Studies with PMAS .................................... 109
  5.2.3 Preparation of Alkaline Earth Metal Salts of PMAS ...................... 110
  5.2.4 Electrical Conductivity Measurements ................................ 110
  5.2.5 Metal Ion Analysis ..................................................... 110
5.3 Results and Discussion ..................................................... 111
  5.3.1 UV-vis-NIR Spectroscopy of Aqueous PMAS ........................... 111
  5.3.2 Spectral and Associated Structural Changes for PMAS
     in the Presence of Metal Salts ........................................... 112
    5.3.2.1 Influence of the Nature of the Metal Cation ..................... 117
    5.3.2.2 Influence of the Nature of Anion ................................ 125
    5.3.2.3 Influence of the Metal Salt (Electrolyte) Concentration ........ 129
    5.3.2.4 Influence of the Polymer Concentration ........................... 130
  5.3.3 Isolation and Characterisation of Metal Salts of PMAS .................. 130
  5.3.4 Reversal of Spectral Changes with Acid ................................ 132
5.4 Conclusions ............................................................. 133
CHAPTER 6
Redox and pH Switching of PMAS

6.1 Introduction

6.2 Experimental

6.2.1 Materials

6.2.2 Spectroscopic Studies of Aqueous PMAS in NaOH Solutions

6.2.3 Electrical Conductivity Measurements

6.2.4 Chemical Oxidation and Reduction of the Aqueous PMAS

6.3 Results and Discussion

6.3.1 PMAS Behaviour in Basic Solutions

6.3.2 Redox Switching of PMAS in Aqueous Solution

6.3.2.1 Oxidation in Weakly Acidic Media

6.3.2.2 Oxidation of PMAS in Strongly Acidic Media (pH 1)

6.3.2.3 Reduction of PMAS at pH 9

6.3.2.4 Reduction of PMAS at pH 13

6.3.2.5 Reduction of PMAS in 0.5 M KCl at pH 9

6.3.2.6 Reoxidation of the Leucoemeraldine Form of PMAS

6.4 Conclusions

CHAPTER 7
Synthesis and Characterisation of Other Substituted Polyanilines

7.1 Introduction

7.2 Experimental

7.2.1 Electrochemical Synthesis of PNMA.(+)-HCSA and PDPA.(+)-HCSA Films
7.2.2 Spectroscopic Characterisation of PNMA.(+)-HCSA and PDPA.(+)-HCSA Films and Study of their Redox Reactions

7.2.3 Chiral Discrimination Studies

7.2.4 Synthesis of Poly{(S)-anilinomethyl)pyrrolidine} (PAMP)

7.3 Results and Discussion

7.3.1 Electrochemical Preparation and Properties of PNMA.(+)-HCSA

7.3.2 Electrochemical Preparation and Properties of PDPA.(+)-HCSA

7.3.3 Synthesis and Properties of Poly{(S)-(+)-(anilinomethyl)pyrrolidine} (PAMP)
LIST OF FIGURES

1. Figures

Figure 2.1 Electrochemical cell for polymerizations.

Figure 2.2 Position of contacts on a symmetrical sample for determination of conductivity by the Van der Pauw method.

Figure 3.1 Absorption spectra of the cast films of a partially ring-sulfonated PAN in a self-doped form (solid line) and of the unsubstituted PAN.HCl (dashed line) [140].

Figure 3.2 Cyclic voltammetry of aqueous 0.10 M MAS / 0.10 M (+)-PhEA on an ITO-coated glass electrode (2.5 cm²); 1st, 3rd and 5th scans only shown. Scan rate 50 mV/s.

Figure 3.3 UV-vis-NIR spectrum of a PMAS.(+)-PhEA film deposited on ITO-coated glass electrode by CV from -0.20 to 1.00 V (scan rate 50 mV/s).

Figure 3.4 CD spectra of the PMAS.(+)-PhEA and PMAS.(-)-PhEA films deposited potentiodynamically on ITO-coated glass from aqueous 0.10 M MAS / 0.10 M (+)- or (-)-PhEA.

Figure 3.5 Dependence of the chiral anisotropy factor ($\Delta \varepsilon / \varepsilon$) on the MAS concentration for PMAS.(+)-PhEA polymers deposited by CV from -0.20 V to 1.00 V, scan rate 50 mV/s, using 0.10 M (+)-PhEA.

Figure 3.6 Dependence of the chiral anisotropy factor ($\Delta \varepsilon / \varepsilon$) on the (-)-PhEA concentration for the PMAS.(-)-PhEA polymers deposited by CV from -0.20 V to 1.00 V, scan rate 50 mV/s, using 0.10 M MAS.

Figure 3.7 Dependence of the chiral anisotropy factor on the scan rate for PMAS.(+)-PhEA polymer films deposited by CV.
Figure 3.8 UV-vis spectrum of a PMAS.(+)-PhEA film deposited by the square-wave potential pulse method from aqueous 0.10 M MAS / 0.10 M (+)-PhEA (potential applied: 1.0 V for 10 s, -0.2 V for 5 s).

Figure 3.9 CD spectrum of the PMAS.(+)-PhEA film from Figure 3.8.

Figure 3.10 UV-vis spectrum of a polymeric film potentiostatically deposited on ITO-coated glass with an applied potential of 0.90 V during 2 hrs (from aqueous 0.10 M MAS / 0.10 M (+)-PhEA).

Figure 3.11 AFM image of the PMAS.(+)-PhEA surface.

Figure 3.12 The GPC molecular weight profile for PMAS deposited potentiodynamically in the presence of (+)-PhEA.

Figure 3.13 UV-vis spectra recorded during the GPC analysis in Figure 3.12.

Figure 3.14 UV-vis-NIR spectra of a PMAS.(+)-PhEA film exposed to HCl vapour: (1) original film; (2) after 5 min exposure to HCl vapour (over conc. HCl).

Figure 3.15 CD spectra of a PMAS.(+)-PhEA film exposed to HCl vapour: (1) original film; (2) after 5 min exposure to HCl vapour (over conc. HCl).

Figure 3.16 UV-vis-NIR spectra of a PMAS.(+)-PhEA film: (1) original film; (2) after 30 min exposure to NH₃ (over conc. NH₃).

Figure 3.17 CD spectra of a PMAS.(+)-PhEA film: (1) original film; (2) after 30 min exposure to NH₃.

Figure 3.18 UV-vis spectra of a potentiodynamically deposited PMAS.(+)-PhEA film: (1) original film; (2) after crosslinking with protonated PVA.

Figure 3.19 CD spectra of the potentiodynamically deposited PMAS.(+)-PhEA film from Figure 3.18: (1) original film; (2) after crosslinking with protonated PVP.

Figure 3.20 Cyclic voltammogram of an immobilised PMAS.(+)-PhEA.PVP film in 0.1 M NaNO₃ (scan rate 100 mV/s).
Figure 4.1 UV-vis-NIR spectra of an aqueous PMAS.(+)-PhEA solution: (1) unfiltered and (2) filtered.

Figure 4.2 CD spectra of the PMAS.(+)-PhEA solution from Figure 4.1 recorded ca. 1 hr after mixing: (1) unfiltered and (2) filtered.

Figure 4.3 UV-vis-NIR spectrum of a PMAS.(+)-PhEA film evaporatively cast onto a glass slide.

Figure 4.4 CD spectra of the PMAS.(+)-PhEA films evaporatively cast onto glass slides. Times shown are the periods between mixing and casting.

Figure 4.5 UV-vis-NIR spectra of the PMAS.PhEA films spin-cast from aqueous 5 % (w/v) PMAS / (+)-PhEA (1) and PMAS / (-)-PhEA (2) (amine : PMAS ratio 1:2). The films were spin-cast 1 hr after mixing.

Figure 4.6 CD spectra of the PMAS.(+)-PhEA and PMAS.(-)-PhEA films from Figure 4.5.

Figure 4.7 UV-vis-NIR spectra of PMAS.(RNH$_2$) films spin-cast from mixtures of PMAS with (+)-CHEA (1) and (-)-DMBA (2) (amine : PMAS ratio 1:2).

Figure 4.8 CD spectrum of the PMAS.(+)-CHEA film from Figure 4.7.

Figure 4.9 CD spectrum of the PMAS.(-)-DMBA film from Figure 4.7.

Figure 4.10 UV-vis-NIR spectrum of a spin-cast PMAS.(-)-BNDA film.

Figure 4.11 CD spectrum of the PMAS.(-)-BNDA film from Figure 4.10.

Figure 4.12 UV-vis-NIR spectrum of a PMAS.NEA film prepared via adsorption of PMAS onto a (+)-NEA film.

Figure 4.13 CD spectrum of the PMAS.(+)-NEA film from Figure 4.12.

Figure 4.14 UV-vis-NIR spectra obtained for PMAS.(amino alcohol) films formed from mixtures of PMAS with (-)-AP (1) and (+)-ADPE (2) (with an amino alcohol : PMAS ratio of 1:2).
Figure 4.15 CD spectrum of the PMAS(-)-AP film from Figure 4.14.

Figure 4.16 CD spectrum of the PMAS(+)-ADPE film from Figure 4.14.

Figure 4.17 UV-vis-NIR spectra of crosslinked PMAS(+)-PhEA.PVA films (with PhEA:PMAS ratio of 1:8), spin-cast from aqueous: (1) 5% PMAS / 1 % PVA; (2) 5% PMAS / 2% PVA.

Figure 4.18 CD spectra of the PMAS(+)-PhEA.PVA films (with PhEA:PMAS ratio 1:8): (1) 5% PMAS / 1 % PVA, before crosslinking; (2) same film, crosslinked; (3) 5% PMAS / 2% PVA, before crosslinking; (4) same film, crosslinked.

Figure 5.1 UV-Vis-NIR spectra of PMAS in solution: (1) acid form, (2) ammonium salt; (3) dialysed form; [PMAS] = 6 x 10^{-5} M.

Figure 5.2 UV-vis-NIR spectra of PMAS (dialysed): (1) in water; (2) after 22 hrs in 1.0 M NaCl at room temperature; [PMAS] = 6 x 10^{-5} M.

Figure 5.3 UV-vis spectra of PMAS (NH_{4}^{+}): (1) in water and (2) immediately after added to 1.0 M NaCl; [PMAS] = 4.0 x 10^{-5} M.

Figure 5.4 UV-vis-NIR spectral changes for PMAS (NH_{4}^{+}) in 1.0 M NaCl (slow second step); [PMAS] = 4 x 10^{-5} M.

Figure 5.5 UV-vis-NIR spectra of PMAS (dialysed) added to 1.0 M NaCl.

Figure 5.6 UV-vis-NIR spectra of PMAS (H^{+}) added to 1.0 M NaCl.

Figure 5.7 UV-vis-NIR spectra of PMAS (dialysed) immediately after adding to 1.0 M MCl; [PMAS] = 4.0 x 10^{-5} M.

Figure 5.8 UV-vis-NIR spectra of PMAS (dialysed) added to 1.0 M KCl.

Figure 5.9 UV-vis-NIR spectra of PMAS (dialysed) added to 1.0 M MCl. Spectra obtained 24 hrs after mixing.

Figure 5.10 UV-vis-NIR spectra of PMAS (dialysed) added to 1.0 M LiCl.

Figure 5.11 UV-vis-NIR spectra of PMAS (dialysed) added to 1.0 M CsCl.
Figure 5.12 UV-vis-NIR spectra of PMAS recorded 9 days after adding to 1.0 M LiCl.

Figure 5.13 UV-vis-NIR spectra of PMAS (NH₄⁺) added to 1.0 M CaCl₂.

Figure 5.14 UV-vis-NIR spectra of PMAS (dialysed) added to 1.0 M BaCl₂.

Figure 5.15 UV-vis-NIR spectra of PMAS (dialysed) added to 1.0 M MgCl₂.

Figure 5.16 UV-vis-NIR spectra of PMAS (dialysed) recorded 24 hrs after adding to 1.0 M MCl₂.

Figure 5.17 UV-vis-NIR spectra of the PMAS (dialysed) added to 1.0 M NaX. Spectra obtained immediately after mixing.

Figure 5.18 UV-vis-NIR spectra of the PMAS (dialysed) added to 1.0 M NaX. Spectra obtained 24 hrs after mixing.

Figure 5.19 UV-vis-NIR spectra of PMAS (dialysed) recorded 24 hr after adding to 1.0 M NaCl and 100 hr after adding to 1.0 M NaSCN.

Figure 5.20 UV-vis-NIR spectra of PMAS (NH₄⁺) in “compact coil” conformation in 1.0 M NaCl (pH 3.7) and than after pH was lowered to 1.0.

Figure 6.1 UV-vis-NIR spectrum of PMAS in 1.0 M NaOH, pH 14.

Figure 6.2 UV-vis-NIR spectra of PMAS: (1) in 1.0 M NaCl; (2) 1.0 M NaOH (after the completion of the spectral changes).

Figure 6.3 UV-vis-NIR spectra of an aqueous 3 x 10⁻⁴ M PMAS solution with increasing pH, Stage I.

Figure 6.4 UV-vis-NIR spectra of a 3 x 10⁻³ M PMAS solution with increasing pH, Stage II.

Figure 6.5 Changes in absorbance at 473 nm and 750 nm from Figures 6.3 and 6.4 with increasing pH.

Figure 6.6 UV-vis-NIR spectrum of PMAS in aqueous 5.0 M NaOH.
Figure 6.7 UV-vis-NIR spectrum of PMAS (2.8 x 10^{-4} M) during oxidation with (NH₄)₂S₂O₈, pH 3.7. Times stated in minutes.

Figure 6.8 UV-vis-NIR spectra of PMAS (2.8 x 10^{-4} M) during oxidation in 0.1 M (NH₄)₂S₂O₈, pH 1.

Figure 6.9 UV-vis-NIR of spectral changes for PMAS (2.8 x 10^{-4} M) during reduction in 0.08 M hydrazine, pH 9.

Figure 6.10 UV-vis-NIR spectra of PMAS during reduction with hydrazine, pH 13.

Figure 6.11 Reduction of PMAS with hydrazine in 0.5 M KCl, pH 9, during 30 min.

Figure 6.12 UV-vis-NIR spectral changes during the reoxidation of the Species I form of PMAS in air at pH 1 to regenerate PMAS.

Figure 7.1 CV of a 0.2 M NMA solution in aqueous 1.0 M (+)-HCSA on a Pt disc electrode (1 mm diameter), scan rate 100 mV/s.

Figure 7.1(a) Enlarged section of the CV chart from Figure 7.1.

Figure 7.2 CV of a 1.0 M NMA / 1.0 M (+)-HCSA solution on a Pt disc electrode (1 mm diameter), scan rate 100 mV/s.

Figure 7.3 UV-vis spectra of the PNMA. (+)-HCSA films deposited potentiostatically from 1.0 M NMA, 1.0M (+)-HCSA solution at applied potential of: (1) 0.6 V; (2) 0.8 V.

Figure 7.4 UV-vis-NIR spectra of PNMA. (+)-HCSA deposited potentiostatically from 1.0 M NMA / 1.0 M (+)-HCSA at an applied potential of 1.2 V.

Figure 7.5 CD spectrum of the PNMA. (+)-HCSA film from Figure 7.4 deposited potentiostatically at 1.2 V.

Figure 7.6 Cyclic voltammogramm of a PNMA. (+)-HCSA film in aqueous 0.1 M (+)-HCSA on a Pt disc working electrode (1 mm diameter), scan rate 100 mV/s.

Figure 7.7 UV-vis-NIR spectra of a PNMA. (+)-HCSA film: (1) as grown; (2) after oxidation in 0.1 M (NH₄)₂S₂O₈ / 1.0 M HCl for 10 min.
Figure 7.8 UV-vis-NIR spectra of the PNMA.(+)-HCSA film: (1) as grown and (2) after reduction in aqueous 0.1 M N₂H₄ for 10 min.

Figure 7.9 Cyclic voltammogram of a 0.2 M DPA, 0.7 M (+)-HCSA solution in acetonitrile (vs Ag/Ag⁺). Pt disk working electrode (1 mm diameter), scan rate 100 mV/s.

Figure 7.10 UV-vis-NIR spectrum of a PDPA.(+)-HCSA film deposited potentiostatically at 1.2 V from 0.2 M DPA / 0.5 M (+)-HCSA in 42 % water / 58 % acetonitrile solution.

Figure 7.11 CD spectrum of the PDPA.(+)-HCSA film from Figure 7.10.

Figure 7.12 Cyclic voltammograms of a PDPA.(+)-HCSA film in aqueous 0.10 M (+)-HCSA on a Pt disc working electrode (1 mm diameter), scan rate 100 mV/s.

Figure 7.13 UV-vis-NIR spectra of a PDHA.(+)-HCSA film: (1) as grown and (2) after 10 min oxidation in 0.1 M (NH₄)₂S₂O₈ / 0.1 M HCl.

Figure 7.14 UV-vis-NIR spectra of a PDHA.(+)-HCSA film: (1) as grown and (2) after reduction in aqueous 0.1 M N₂H₄ for 5 min.

Figure 7.15 Cyclic voltammograms of a PDPA.(+)-HCSA film in aqueous 0.02 M (a) L-valine and (b) D-valine; 0.1 M NaNO₃ supporting electrolyte.

Figure 7.16 Cyclic voltammetry of a 0.35 M AMP / 1.0 M HCl aqueous solution on ITO-coated glass electrode. Scan rate 100 mV/s.

Figure 7.17 UV-vis-NIR spectrum of the product of potentiostatic oxidation of (+)-AMP at an applied potential of 0.9 V in 1.0 M aqueous HCl.

Figure 7.18 UV-vis spectrum of the product of chemical oxidation of (+)-AMP in aqueous 1.0 M HCl.

Figure 7.19 CD spectrum of the product of chemical oxidation of (+)-AMP in aqueous 1.0 M HCl.
2. Schemes

Scheme 3.1 Proposed mechanism for electrochemical polymerisation of MAS in the presence of (+)-PhEA.

Scheme 3.2 Formation of a one-handed helix by PMAS in presence of (+)- or (-)-PhEA.

Scheme 3.3 Stereospecific acid-base interaction between chiral PhEA and PMAS.

Scheme 6.1 Interconversions between different forms of polyaniline.

Scheme 6.2 Redox and pH switching of PMAS (ES = emeraldine salt, PB = pernigraniline base, LB = leucoemeraldine base).

Scheme 7.1 Redox switching in PNMA.

Scheme 7.2 Redox switching in PDPA.

3. Tables

Table 3.1 Chiral anisotropy factors (\(\Delta\varepsilon/\varepsilon\)) for PMAS.(+)-PhEA films deposited by the square-wave potential pulse method (calculated at 480 nm).

Table 4.1 Chiral anisotropy factor (\(\Delta\varepsilon/\varepsilon\)) for PMAS.(+)-PhEA films evaporatively cast after various lengths of time.

Table 4.2 Chiral anisotropy factors (\(\Delta\varepsilon/\varepsilon\)) obtained for chiral PMAS.(RNH\(_2\)) films with amine(amine alcohol) : PMAS ratio of 1:2.

Table 4.3 Chiral anisotropy factors (\(\Delta\varepsilon/\varepsilon\)) obtained for PMAS.(RNH\(_2\)) films for different amine : PMAS ratios.

Table 5.1 Positions of the absorption peaks for the PMAS conformer formed in 1.0 M aqueous metal chlorides.
Table 5.2 Dependence of spectral changes for PMAS (NH₄⁺) in 1.0 M KCl on the PMAS concentration.

Table 5.3 GPC and DC conductivity results for the as-received PMAS (NH₄⁺) and fractions precipitated by MCl₂.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADPE</td>
<td>(1S,2R)-(+)2-amino-1,2-diphenylethanol</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AP</td>
<td>(R)-(−)-2-amino-1-propanol</td>
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<td>AMP</td>
<td>(S)-(+)-(anilinomethyl)pyrrolidine</td>
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<td>BNDA</td>
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<td>Poly(N-methylaniline)</td>
</tr>
<tr>
<td>PMAS</td>
<td>Poly(2-methoxylaniline-5-sulfonic acid)</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinylalcohol</td>
</tr>
<tr>
<td>PVP</td>
<td>Poly(4-vinylpyridine)</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(styrene-4-sulfonate)</td>
</tr>
<tr>
<td>PS</td>
<td>Pernigraniline salt</td>
</tr>
<tr>
<td>SPAN</td>
<td>Sulfonated polyaniline</td>
</tr>
<tr>
<td>UV-vis-NIR</td>
<td>Ultraviolet - visible - near infra red</td>
</tr>
</tbody>
</table>
This thesis describes the synthesis and characterisation of a range of novel, chiral conducting polymers formed from substituted anilines, which may have potential in future applications such as chirality assessment, asymmetric synthesis and chiral separations. Their redox and pH switching and ionochromic properties are also explored. A particular focus is the water-soluble sulfonated polyaniline, poly(2-methoxyaniline-5-sulfonic acid) (PMAS), where two ways of inducing main chain chirality in PMAS have been successfully developed.

In Chapter 3 it is shown that PMAS can be deposited in a highly optically active form via the potentiodynamic polymerisation of the monomer 2-methoxyaniline-5-sulfonic acid (MAS) in the presence of chiral amines (R)-(+) or (L)-(−)1-phenylethylamine (PhEA). The enantiomeric amines induced intense, mirror-imaged CD spectra for the respective PMAS.(+)-PhEA and PMAS.(-)-PhEA films, suggesting the adoption of preferred one-handed helical structures by the polyaniline chains arising from enantioselective acid-base interactions between the amines and ionised sulfonate substituents on the polymer. The polymers were also characterised by cyclic voltammetry, molecular weight and electrical conductivity measurements. It was also found that chiral PMAS.(+)-PhEA could be immobilised on protonated poly(4-vinylpyridine) while retaining its optical activity and electroactivity.

Chapter 4 describes the alternative preparation of optically active PMAS films via mixing aqueous PMAS with a wide range of chiral amines and amino alcohols, followed by evaporative- or spin-casting. Chiral induction in the PMAS was believed to
occur via a similar acid/base interaction to that proposed in Chapter 3. However, the CD spectra of the spin-cast PMAS (RNH₂) films did not exhibit bisignate Cotton effects. This indicated that spin-casting causes the loss of exciton coupling between the responsible chromophores, suggesting that they are well separated either on the same or adjacent PMAS chains. The influence of the steric bulk and other structural features of the amines and amino alcohols on the extent of chiral induction in the PMAS was also explored. Although losing their optical activity when dissolved in water, it was found that the chiral PMAS.(+)-PhEA films could be crosslinked with poly(vinylalcohol), making them insoluble in water.

Dilute aqueous solutions of PMAS have been shown in Chapter 5 to exhibit remarkable and unprecedented ionochromism when 1.0 M alkali and alkaline earth metal salts were added, the colour changing from yellow/brown to blue over hours or days. A first rapid stage (few min) was attributed to replacement of protons from the “free” SO₃H groups on the PMAS chains, leading to changes in conformation/structure. The slow (hours/days) second step was believed to involve conversion of the PMAS from an “extended coil” to a “compact coil” conformation. The ionochromic effects were found to be strongly dependent on the nature of the metal ion in the added metal salts. The speed/extent of the rapid first step increased along the metal ion series:

\[ \text{Li}^+ < \text{K}^+ < \text{Na}^+ < \text{Ba}^{2+} < \text{Cs}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} \]; while the slower second step revealed a differing order: \( \text{Cs}^+, \text{Li}^+ < \text{K}^+ < \text{Ca}^{2+} < \text{Ba}^{2+} < \text{Na}^+ \). The second step also showed marked anion dependence, the speed of the conformational/colour change increasing along the series \( \text{SCN}^-, \text{SO}_4^{2-} < \text{Br}^- < \text{Cl}^- < \text{I}^- \).
Calcium, magnesium and barium salts of PMAS have been precipitated when 1.0 M MX₂ salts were added to more concentrated (1 %) aqueous PMAS. The PMAS (Ba²⁺) salt had a higher electrical conductivity and molecular weight than the as-received PMAS (NH₄⁺), and atomic absorption analysis showed that ca. 75 % of the “free” sulfonate groups have Ba²⁺ ions attached. These ionochromic/conformational effects were reversed by the addition of 0.1 M HCl, regenerating PMAS in the original “extended coil” conformation.

PMAS was found in Chapter 6 to be remarkably resistant to alkaline dedoping, with no emeraldine base being formed even in 2.0 M NaOH. Instead, PMAS in alkaline solutions underwent very similar, but much more rapid, spectroscopic changes to those caused by adding metal salts. Its polymer backbone was therefore believed to undergo a conformational change from an “extended coil” to a “compact coil” conformation. During the titration of a PMAS (NH₄⁺) solution with aqueous NaOH, spectroscopic changes in the first stage between pH 3.7 and 8.0 were attributed to deprotonation of “free” SO₃H groups on the PMAS chains. A second stage between pH 9 and 14 was believed to involve rearrangement from an “extended coil” to a “compact coil” conformation.

Like unsubstituted polyaniline, PMAS was found to be readily oxidised by ammonium persulfate at pH 3.7 to give the corresponding pernigraniline base form. However, chemical reduction of PMAS by hydrazine displayed distinctively different behaviour to that previously reported for unsubstituted polyaniline. At pH 9, the rapid formation of a novel polymer (Species I) was observed, characterised by an intense, sharp absorption band at 408 nm, which was attributed to a conformer or isomer of leucoemeraldine
This species then slowly converted to the leucoemeraldine base form of PMAS. In contrast, hydrazine reduction of PMAS at pH 13 or in 1.0 M KCl produced only Species I. Acidification of this reduced solution resulted in aerial oxidation, leading to reformation of the initial PMAS.

The synthesis and chiroptical properties of a number of other substituted polyanilines are described in Chapter 7, employing aniline monomers bearing methyl, phenyl or a chiral substituent on the nitrogen atom. N-Methylaniline (NMA) was shown to form a chiral polymer PNMA.\( (+)\)-HCSA when potentiostatically oxidised in the presence of the chiral dopant acid \(+\)-camphorsulfonic acid. An electroactive poly(diphenylamine) (PDPA) polymer doped with \(+\)-HCSA was also electrodeposited from a water / acetonitrile mixed solvent. However, in this case the PDPA backbone was not found to form a one-handed helix in the presence of \(+\)-HCSA.

As an alternative approach, the chiral monomer, \((S)-(+)\)-(anilinomethyl)pyrrolidine, bearing a chiral substituent on the nitrogen atom of aniline, was polymerised chemically and electrochemically in 1.0 M HCl. The product was optically active, as evidenced by its CD spectrum. However, this presumably oligomeric product was found to be soluble.
ACKNOWLEDGEMENTS

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CHAPTER 1
GENERAL INTRODUCTION

1.1 General Properties of Conducting Polymers

Conducting polymers have been attracting attention since superconducting properties in poly(sulfur nitride) at low temperatures were discovered in 1975 [1] and metallic properties in polyacetylene in 1977 [2,3]. Later polyaniline, polypyrrole, polythiophene and a number of other conjugated polymers established themselves as remarkably interesting conducting materials, arising from the prospect of their use in areas of charge storage, electrochromic devices, smart membranes and a wide range of other applications.

A general feature of conducting polymers is conjugation of $\pi$-electrons extending over all the length of the polymer backbone. When electrons are removed from the $\pi$-system, this causes delocalisation of radical-cations and an increase in the electrical conductivity by several orders of magnitude. Polyaniline is a special case among conjugated polymers, as it can be transformed from an insulating to a conducting state in the presence of protonic acids.

While polyacetylene and poly(p-phenylenevinylene) are prepared chemically, polyaniline, polypyrrole and polythiophene may be synthesised via either chemical or electrochemical oxidation of the appropriate monomer. The electrochemical route is
practically useful because it gives wider opportunities for the choice of the doping anion and fine tuning of synthesis conditions.

Incorporation of substituents into the polymer chain allows the achievement of a number of goals. Apart from changing intramolecular interactions within the polymer, the interaction with media or solvent may be altered. This approach allows the synthesis of water-soluble polymers such as sulfonated polyanilines, polypyrroles and polythiophenes. However, the electrical conductivity of the polymers is usually adversely affected by such substitution.

The family of conjugated conducting polymers, being a handful 20 years ago, now includes a vast number and variety of polymers with great variations in conductivity, functionality and stability.

1.2 Polyanilines

The family of polyanilines includes the unsubstituted “parent” polyaniline (PAn) and a variety of substituted polymers with substituents either on the aniline rings or on the nitrogen atoms. Unsubstituted PAn exists in various forms depending on the degree of oxidation and protonation. The general formula of PAn may be presented as 1:
When $x = 1$, the polymer is in the fully reduced leucoemeraldine base (LB) form; when $x = 0.5$, it is in the intermediate emeraldine oxidation state, while when $x = 0$, PAn is in the fully oxidised pernigraniline state. Colour changes during transition from one PAn form to another have attracted much attention; it is a facile way to indicate the oxidation or protonation state of the polymer. Scheme 1.1 shows the reversible interconversions between the different PAn forms and their colours.

Scheme 1.1 Interconversions between different forms of polyaniline

Only one form of PAn, namely emeraldine salt (ES), possesses electrical conductivity. The conducting state may be reached either via acid doping of the emeraldine base (EB) or via reduction of the pernigraniline salt (PS) form. Introduction of a protonic acid into EB causes delocalisation of the semiquinone radical cation and an increase in
conductivity by 6 to 10 orders of magnitude. The doping converts PAn from an insulator to an ES material with a conductivity typically between 1 and \(10 \text{ S cm}^{-1}\).

PAn may be easily synthesised chemically or electrochemically. The chemical route of synthesis has been explored since 1834, with the first study undertaken by Runge; the product was analysed by Fritzsche in 1840-1843 [4, 5]. The electrochemical route has been known since the work of Letherby in 1862 [6]. Variations of the chemical method, such as emulsion and plasma polymerisation have been studied over recent years [7, 8].

**Chemical polymerisation** [9-16] is usually carried out in an acidic aqueous solution of aniline and oxidant with a slight excess of aniline, since an equivalent or excess amount of oxidant results in fast hydrolysis of the product [9, 10]. Low temperature (eg. 0°C) yields polyaniline with higher molecular weight [16]. Oxidising agents include potassium dichromate [9-11], ammonium persulfate or peroxidisulfate [9, 11-13], hydrogen peroxide, ceric nitrate and ceric sulfate [14, 15]. Acids involved in the synthesis have been varied from hydrochloric or sulfuric acids to large-anion acids such as camphorsulfonic acid and \(p\)-toluenesulphonic acid.

The mechanism of chemical oxidation was proposed by Genies *et al.* [17] and later confirmed by other researchers [18-21]. The reaction is believed to proceed in four steps (Scheme 1.2). The first step involves formation of the radical cation of aniline which exists in three resonance forms (\(N^{-}\), \(para^{-}\) and \(ortho^{-}\)). In the second step, coupling of \(N^{-}\) and \(para^{-}\)-radical cations occurs with subsequent rearomatization of the dication of \(p\)-aminodiphenylamine (PADPA). It is then oxidised to the diradical dication. Although “head-to-tail” (i.e. \(N\)-\(para\) ) coupling is predominant, some coupling
in the ortho-position also occurs, leading to defects in conjugation in the resultant polymer [22, 23]. In the third step the diradical dication couples with the monomeric radical cation of aniline, forming a trimer, and the chain propagates further via coupling of shorter polymer fragment-radicals with the aniline radical cation. The resultant polymer is a pernigraniline salt. When all oxidant is consumed, the remaining aniline reduces the pernigraniline to form the final product, the green emeraldine salt (Step 4). Colour changes during the reaction reflect the described steps: during the second step the solution is pink due to PADPA; during the third step the solution becomes deep-blue due to formation of the protonated pernigraniline, and in the final fourth step green emeraldine salt precipitates. Prolonged reaction times lead to degradation of the polymer [18], especially with an excess of oxidant, as the pernigraniline form undergoes hydrolysis more readily than the emeraldine form at the imine double bond.

**Step 1. Oxidation of monomer**
Step 2. Radical coupling and oxidation to the diradical dication

\[
\begin{align*}
&\text{PADPA} \\
&\text{Step 3. Propagation of chain} \\
&\text{Step 4. Reduction of Pernigraniline Salt to Emeraldine Salt}
\end{align*}
\]

Scheme 1.2 Mechanism for chemical polymerisation of aniline in solution [18].

Electrochemical polymerisation is routinely carried out in an acidic aqueous solution of aniline under an applied potential between 0.8 and 1.1 V (vs Ag/AgCl). A variety of working electrodes may be used including platinum or gold plates [24], glassy carbon, reticulated vitreous carbon [14], as well as indium-tin oxide (ITO)-coated glass [25].
Cyclic voltammetry of an aniline solution in acidic media shows [26] an oxidation peak for the monomer at 0.8 V (vs Ag/AgCl). Peaks relating to subsequent redox switching between different oxidation states in the formed polymer appear at potentials between -0.1 and 0.7 V. The use of potentials above 1.1 V results in overoxidation of the polymer with loss of conductivity. Polyaniline may be grown galvanostatically, potentiostatically or potentiodynamically, though the galvanostatic method may result in overoxidation of the initial layer of the polymer. A short-term increase of initial potential to 0.9 - 1.1 V during potentiostatic deposition has been reported to give more adherent films [27]. A low pH is necessary for dissolution of the aniline monomer and formation of the emeraldine salt as the only conducting form of polyaniline.

The mechanism of electrochemical oxidation has been studied by a variety of methods: Vis-NIR spectroscopy, ESR and FTIR spectroscopy, and electrochemical electrospray mass-spectrometry. The generally accepted mechanism is described [9, 28-31] as an E(CE)_n process, and is presented in Scheme 1.3. Formation of the radical cation of aniline by oxidation on the electrode surface is considered to be the rate-determining step. This is followed by coupling of radicals, mainly N- and para-forms, and elimination of two protons. The dimer (oligomer) formed then undergoes oxidation on the electrode surface along with aniline. The radical cation of the oligomer couples with an aniline radical cation, resulting in propagation of the chain. The formed polymer is doped by the acid (HA) present in solution.
Step 1. Oxidation of monomer

\[ \text{Ph-NH}_2 + e^- + A^- \rightarrow \text{Ph-N}^+ + \text{H}^- + A^- \]

Step 2. Radical coupling and rearomatization

\[ \text{Ph-N}^+ + \text{Ph-N}^- \rightarrow \text{Ph-} + \text{Ph-N}^+ + \text{NH}_2^- + A^- \]

Step 3. Chain propagation

\[ \text{Ph-NH} + \text{Ph-N}^- \rightarrow \text{Ph-N}^+ + \text{NH}_2^- + A^- \]

Step 4. Doping of the polymer

\[ \text{Ph-NH}_2^- \rightarrow \text{Ph-N}^- + \text{H}^- + A^- \]

Scheme 1.3 Mechanism of the electrochemical polymerisation of aniline on an electrode surface [28].
The dopant anion employed affects the rate of polymer deposition and film morphology [32]. For example, sulfate anion promotes polymer deposition better than do chloride, nitrate or perchlorate ions. In turn, polymer films deposited slowly are more dense and less porous than rapidly deposited ones.

The conformation of PAN has also recently been found to depend on the polymerisation method [17, 33, 34]. Depending on conditions, the polymer backbone may form a “compact coil” or an “extended coil” conformation, and this variation is reflected by conductivity and UV-Vis-NIR spectral changes.

1.3 Doping in Conducting Polymers

Doping of conducting polymers is a unique feature distinguishing them from other polymers [35-37]. The term describes the transition from an insulating to a semiconducting or metal-type conducting state, caused by the delocalisation of the π-electrons along the polymer backbone. After doping the conductivity values may increase by up to 10 orders of magnitude, approaching that of copper [38]. Doping is a reversible process, and dedoping/redoping can usually be performed a number of times without significant change in the polymer structure or properties.

There are two types of doping in polyaniline, oxidative p-type doping and protonic acid doping. Electrochemical oxidative p-type doping results in the formation of a radical cation and anions are required for charge compensation. The leucoemeraldine form of polyaniline when oxidised chemically or electrochemically in acidic media forms a nitrogen based salt. Acidic doping is unique to polyaniline among conducting polymers
and involves protonation of the emeraldine base form. Attachment of protons to the imine N atoms of the polymer leads to delocalised semiquinone radicals (Scheme 1.4).

\[
\text{Protonic acid doping} \quad +2H^+ +2A^- \quad \text{Oxidative doping} \quad -2e^- +2A^- \\
\text{Scheme 1.4} \quad \text{Doping of polyaniline.}
\]

1.4 Substituted Polyanilines

Substitution of a hydrogen atom in aniline (either at a $N$- or ring position) by an alkyl or phenyl group leads to a significant change in the properties of the polymerised product. One of the most unwelcome features of polyaniline is its insolubility in common solvents arising from stiffness of the backbone. For example, polyaniline doped with small inorganic acids is only partially soluble even in concentrated acidic solutions [39]. Doping with some organic acids, such as camphorsulfonic acid, leads to solubility in a wider variety of solvents, such as $m$-cresol, trifluoroethanol or formic acid [40, 41]. Dedoped polymer may only be efficiently dissolved in $N$-methyl-2-
pyrrolidinone, while some degree of dissolution is observed in DMF, DMSO, acetic and formic acids [42].

Solubility in common organic solvents may be achieved with an appropriate alkyl or alkoxy substituents on the PAN [43], while inclusion of polar substituents (usually sulfonic acid groups) results in solubility in water. Increased solubility leads, however, to polymers with lower molecular weight ($10^3$ - $10^4$ Da compared with $10^5$ Da for aniline [44]).

A drawback following from the facile pH switching of polyaniline is the fact that this polymer is electroactive only in a narrow pH range between 0 and 4. Broadening of the electroactivity limits may be achieved via doping PAN with an acid-bearing polymer [45-47] or incorporation of acidic groups into the polyaniline backbone.

The presence of bulky substituents on PAN decreases the electrical conductivity to $10^{-2}$ - $10^{-7}$ S cm$^{-1}$. This effect is ascribed to increased chain separation in substituted PAN and to the lower degree of conjugation due to steric hindrance by the substituents increasing the torsion angles between the aniline rings.

1.4.1 N-Substituted Polyanilines

1.4.1.1 N-Alkylanilines

Chemical synthesis of poly(N-alkylanilines) was effected by a number of authors via alkylation of polyaniline [48]. Electrochemical polymerisation of alkyl-substituted polyanilines has been carried out in a few studies [49-53]. Kilmartin et al. [49] reported difficulty in depositing of poly(N-methylaniline) (PNMA, 2); the polymer required specific dopants for successful deposition on the working electrode surface. A blue
soluble polymer formed when 0.5 M sulfuric acid or 1.0 M hydrochloric acid solutions were used. The potential for N-methylaniline oxidation was found to be 1.0 to 1.2 V (vs Ag/AgCl) which is higher than usually used for polyaniline deposition. Athawale et al. [51] also reported that the use of lower monomer concentrations led to undesirable benzidine formation.

Redox processes in PNMA are reported to be controlled by diffusion of dopant anions, as the peak currents in cyclic voltammograms of PNMA films are proportional to the square root of the sweep rate [53]. The pH does not alter the peak currents, indicating that the polymer redox processes do not involve protonation; while electrochemical quartz crystal microbalance studies show that only dopant anions are involved in anodic processes. These findings allowed Kilmartin et al. [49] to suggest a scheme for redox switching of PNMA (Scheme 1.5).

Unlike unsubstituted polyaniline, partially oxidised PNMA does not form polarons, but only dications, as indicated from magnetic studies [54].
Scheme 1.5 Redox switching in PNMA.

### 1.4.1.2 Poly(diphenylamine)

Electrochemical polymerisation of the N-phenyl substituted aniline monomer, diphenylamine, has been effected by Hayat et al. [51], Comisso et al. [55], Guay et al. [56] and other authors [57-59], to give poly(diphenylamine) (PDPA, 3). The polymerisation mechanism has been described as 4,4'-C-C phenyl-phenyl coupling [55, 57]. The resultant polymer has an interesting structure, intermediate between polyaniline and poly(p-phenylene).

\[
\begin{align*}
\text{Scheme 1.5 Redox switching in PNMA.}
\end{align*}
\]

Guay et al. [59] deposited films of PDPA potentiostatically from 0.1 M monomer solution in acetonitrile with lithium perchlorate as supporting electrolyte, incorporating
the \( \text{ClO}_4^- \) anion as dopant. Based on UV-visible spectroscopy, XPS and ESR spectroscopic studies, they proposed the following scheme for PDPA oxidation which proceeds via formation of polarons and bipolarons (Scheme 1.6).

![Scheme 1.6 Redox Switching of PDPA [59].](image)

PDPA is more readily soluble in organic solvents than polyaniline. However, despite being resistant to long-term exposure to anodic potentials in the absence of water, it is unstable when residual water is present in the organic solvent [60, 61].

### 1.4.2 Ring-Substituted Polyanilines

Substitution of a hydrogen atom on the arene rings of polyaniline causes a number of effects on the polymer properties. \textit{Para}-substituted anilines cannot be polymerised, as
polymerisation normally proceeds via \textit{N-para} coupling. Substituents in \textit{meta}- or \textit{ortho}-positions may impose steric restrictions on ring flipping and doping with large anions, decreasing the conductivity of the polymer as a result [62, 63]. However, the solubility of polyaniline in organic solvents may be dramatically increased by suitable substituents.

1.4.2.1 AlkyI- and Alkoxy-Substituted Polyanilines

Alkyl-substituted aniline derivatives may be polymerised chemically or electrochemically in the presence of a protonic acid. The conductivity of these polymers decreases with increased substituent length from 1 S cm$^{-1}$ (polyaniline) to 3x10$^{-4}$ S cm$^{-1}$ for poly (2-butylaniline) to 1x10$^{-6}$ S cm$^{-1}$ for poly (dodecylaniline), as a consequence of steric hindrance caused by the large substituents.

Electropolymerisation of alkylanilines [64-66] can be achieved with organic as well as inorganic acid dopants, and the nature of the dopant influences the structure, morphology and spectroelectrochemical response of the polymer [64]. A number of alkyl-substituted polyanilines have demonstrated a selective reaction (change in conductivity) upon exposure to aliphatic alcohols [65, 66]. For example, a negative change in resistance was observed upon exposure of poly(o-toluidine), poly(o-anisidine), poly(2,3-dimethylaniline) and poly(2,5-dimethylaniline) to methanol, ethanol or propanol vapours, whereas a reverse trend was found for butanol and heptanol vapours. Such sensitivity has been explained on the basis of vapour-induced change in the crystallinity of the polymer, with the extent of change being governed by the chain length of the alcohol and its chemical nature.
Electrodeposition of poly(2,5-dimethoxyaniline) and poly(2-methoxyaniline) [67-69] proceeds, as for polyaniline, in acidic solution. The mechanism of polymerisation studied by in situ UV-visible and ESR spectroscopic measurements appears as a C-N coupling. Interestingly, the structure and properties of poly(2-methoxyaniline) depend on the monomer concentration employed [67, 68]. At relatively high monomer concentrations (> 20 mM), the polymer obtained is similar to arylamine-conducting polymers, but shows an intermediate peak in the voltammograms obtained. The peak becomes larger as the monomer concentration decreases. For monomer concentrations below 20 mM, the polymer becomes more resistive, behaving similarly to arylamine redox polymers.

The shapes of poly(2,5-dimethoxyaniline) cyclic voltammograms strongly depend on the kind of anion incorporated, while in the case of polyaniline and poly(2-methoxyaniline) the anion does not affect redox peak positions as significantly. An unusual feature of poly(2,5-dimethoxyaniline) is the significant concentration of polarons at potentials where the reduced polymer is expected. An ESR study suggests the presence of two kinds of polaron species since the ESR signal is split. Similar to polyaniline, the nature of the anion influences the poly(2,5-dimethoxyaniline) degradation; however, this process starts at much lower (less positive) potentials in comparison to polyaniline.

Poly(2-methoxyaniline), as has been shown by Norris et al. [70], may be produced in an optically active form via electropolymerisation of the monomer in aqueous (+)-(1S)- or (-)-(1R)-camphorsulfonic acid. The chiroptical properties of the polymeric films suggest that these POMA.HCSA salts adopt a "compact coil" conformation for their polymer
chains. The films are readily soluble in a range of organic solvents, retaining their optical activity and "compact coil" conformations. A strong red shift in the position of the low energy polaron band of poly(2-methoxyaniline) along the solvent series

\[ \text{NMP} < \text{CHCl}_3 < \text{DMSO}, \text{DMF} < \text{MeOH} \]

indicates a concomitant increase in the effective conjugation length of the polymer chains, dependant on the polymer conformation. The films may also be dedoped in \( \text{NH}_4\text{OH} \) to give optically active poly(2-methoxyaniline) in the emeraldine base form. Redoping of the latter films with aqueous HCl regenerates the circular dichroism spectra of the original emeraldine salt films, confirming retention of configuration during reversible dedoping/redoping cycles in the solid state.

1.4.2.2 Sulfonated Polyanilines

Sulfonated polyanilines (SPANs) present a distinctively different class of polyanilines. The presence of the sulfonic acid groups on the aniline rings results in self-doping of the polymers and ready solubility in water. Sulfonated polyaniline may be obtained via either sulfonation of pre-formed EB or LB, or via oxidative polymerisation of the sulfonated monomer.

**Sulfonation of Polyaniline**

There is a number of synthetic routes for sulfonation of a pre-formed polyaniline. The precursor polymer is usually in the EB or LB forms, one study has described sulfonation via heating of the emeraldine salt doped with sulfuric acid [71]. Sulfonation of EB is most easily achieved via treatment of EB with ca 30% fuming sulfuric acid [45, 71]. This method gives a SPAN polymer with a sulfonation degree (S / N ratio) of ca. 0.5 and conductivity between 0.5 and 0.01 S cm\(^{-1}\). When
chlorosulfonic acid is used instead of sulfuric, the resultant polymer has a higher degree of sulfonation (ca. 0.8), but this is achieved due to some benzene rings being substituted with chlorosulfonic groups. The polymer produced via this latter method is insoluble in water, but may be solubilised by treatment with ammonia hydroxide, which presumably converts chlorosulfonic into sulfonic groups.

In a study of the sulfonation of ES by chlorosulfonic acid in dichloroethane, Ito et al. [72] proposed that HCl dopant from hydrolysis of the chlorosulfonic acid group exchanged with the original dopant. A water-soluble externally (HCl)-doped conducting polyaniline was produced from emeraldine salt (counter anion Cl\(^-\), \(\text{SO}_4^{2-}\), and \(\text{BF}_4^-\)). The sulfonation degree reached was 1.3.

Another method involves sulfonation with sulfur trioxide triethylphosphate [71]. It gives a low degree of sulfonation (ca. 0.2) which is insufficient for solubility in water, as well as for self-doping. When pernigraniline base (PB) was used as the precursor polymer in sulfonation with fuming sulfuric acid, the polymer produced had a degree of sulfonation of ca. 0.5, but this level was achieved after a longer time than when EB was used. The conductivity of the polymer reached from \(10^{-1}\) to \(10^{-3}\) S cm\(^{-1}\). The reasons for the lower efficiency of PB in the synthesis were believed to be an easy hydrolysis of the quinoid structures in PB and deactivation of the sulfonation process (as an electrophilic reaction) by the presence of the quinoid units.

When LB, which does not contain quinoid units, was used instead of EB [73, 74], the sulfonation degree could be raised to ca. 0.75 - 0.80. The solubility in water was doubled compared to the EB route. Conductivity of the polymer was reported to reach
0.1 S cm\(^{-1}\) and did not depend on pH in the 1 to 14 range. This is obviously a consequence of the presence of sulfonic acid groups not participating in self-doping. Change in pH only affects “free” sulfonic groups, without causing dedoping of the polymer.

The stability of SPAN towards dedoping has been studied by Wang et al. [75]. They showed that sulfonation of the benzene ring in PAn leads to formation of an extremely stable six-membered ring, self-doping structure. It does not appear to dedope in the pH range 1 to 14.

Facilitating the Synthesis of Sulfonated Polyaniline

Introduction of the electron-withdrawing sulfonic acid group into the aniline rings in SPAN hinders oxidative polymerisation. This drawback may be overcome by employing specific synthesis conditions, such as high pressure, or by the introduction of an electron-donating substituent, a methoxy group for example.

Use of high pressure (19 kbar) allows one to polymerise \(o\)- or \(m\)-aminobenzenesulfonic acid in aqueous LiCl via chemical oxidation with ammonia persulfate or iron (III) sulfate [76]. However, despite considered facile, this synthesis only gave a 10 % yield.

The strong electron-withdrawing properties of two sulfonic groups present on each aniline ring are confirmed by a large blue shift of the \(\pi-\pi^*\) transition band in the electronic spectrum of poly(aniline-2,5-disulfonic acid) [77, 78]. This self-doped polymer may be synthesised electrochemically and remains self-doped in the pH range 1 to 9, with a conductivity between 0.01 and 0.1 S cm\(^{-1}\). Enzymatic synthesis under
mild conditions has also been performed by Alva et al. [79], using horseradish peroxidase as the catalyst for oxidative coupling. The polymerisation reaction was rapid and the average molecular weight of the resulting polymer was ca. 18,000 Da.

Introduction of an electron-donating methoxy group in 2-methoxyaniline-5-sulfonic acid (MAS) gives a sulfonated aniline with an excellent reactivity towards oxidation. Poly(2-methoxyaniline-5-sulfonic acid) (PMAS, 4) has been synthesised via chemical oxidation of the monomer by Shimizu et al. [80]. To overcome the low solubility of the monomer in water the polymerisation was carried out under basic conditions. This process gave a polymer with an average molecular weight of 10,000 Da and a conductivity of 0.01 S cm\(^{-1}\). This polymer has also more recently been synthesised electrochemically [81] to give a higher yield (> 70 %) and purity, and similar conductivity.

Para-substituted anilines can be polymerised also, \(p\)-phenylsulfonyl-aniline being an example. In this case polymerisation does not proceed via \(para-N\) coupling, unlike aniline polymerisation, and the polymer produced has very poor conjugation as seen from its conductivity, which is in the semiconductor range [82].
1.4.2.3 Co-polymers

Sulfonated aniline monomers may be co-polymerised with aniline to give polymers with varied solubility and degree of self-doping. The co-polymers require further acid doping depending on the aniline content. The reduction in the extent of conjugation of the co-polymers due to the electron-withdrawing and steric effects of the sulfonic acid groups causes SPAN bulk conductivity to be inversely proportional to the content of sulfonated aniline units. This trend is true for co-polymers of aniline with aminobenzenesulfonic acid [76, 83-88], (2,5-disulfonic acid)aniline [89] and o-alkoxy sulfonated anilines [90, 91]. It has been suggested that the low conductivity of SPAN in comparison with polyaniline may be related also to the low quinoid content of the SPAN molecules.

During co-polymerisation, aniline and alkoxy sulfonated-derivatives exhibit two opposite effects on the initial mechanism of dimerisation and the subsequent growth process. Mechanistic studies [90, 91] have shown that, because of the steric hindrance of the bulky alkoxy and sulfonate groups, the dimerisation process involves at least one molecule of aniline. On the contrary, in the course of the propagation step, due to the electron-donating effect of the methoxy substituent, both alkoxy sulfonated anilines exhibited greater ease of oxidation than aniline and hence were easily incorporated into the growing polymer chains. This idea was supported by a solution-state NMR investigation of the structure of a water-soluble polyaniline formed by chemical co-polymerisation of 2-methoxyaniline and 3-aminobenzenesulfonic acid in hydrochloric acid medium. Mav et al. [107] showed that the content of 2-methoxyaniline in the co-polymers was much higher than in the reaction mixture. It was also shown that the incorporation of 2-methoxyaniline units in the co-polymer chains favours the formation
of a less oxidised material. The absorption spectra of co-polymers of aniline and sulfonated anilines prepared by electrochemical polymerisation show pH-dependence similar to that for polyaniline [92].

The existence of a two-stage neutralisation of polyaniline containing two kinds of sulfonic acid groups (participating in a self-doping and protonation, respectively) has been demonstrated by Chen et al. [93] on the co-polymer of aniline with (N-propanesulfonic acid)aniline. Titration of an aqueous solution of this polymer with NaOH revealed 2 stages of neutralisation: the first, reflected by constant absorbance, and the second with a decrease of the 856 nm and 410 nm bands (assigned to polaron band transitions) and growth of the 590 nm band (assigned to quinoid rings). This led the authors to propose that during the first stage of neutralisation free protons are removed from the ring SO$_3$H groups, while the second stage involves protons bonded to the imine nitrogens in self-doping.

1.5 Applications of Sulfonated Polyanilines

To date the applications of sulfonated polyanilines have been largely concentrated on photoconductivity and their use in lithium polymer batteries.

Sulfonated polyanilines have been successfully employed in composite films possessing photoconductivity [94], in blue emitting diodes [95] and in Schottky diodes [96]. Field-effect transistors were also fabricated on SPAN films deposited on an n-doped silicon substrate acting as the gate electrode with a thermally grown oxide layer. The high
value of carrier mobility in these films can be attributed to the spherulitic (partially ordered) structures observed in the SPAN thin films.

Use of a reduced, highly sulfonated form of sulfonated polyaniline for fabrication of a composite cathode for a new rechargeable lithium battery results in an improved stability and higher discharge capacity for the battery [97]. Barbero et al. [98] also found that the ion exchange properties of SPAN are favourable for applications such as cation transfer batteries. The ion exchange mechanism of chemically sulfonated polyaniline (SPAN) is different in aqueous and non-aqueous electrolytes. Protons have been found to be predominantly expelled during the first and second oxidation steps in acidic aqueous solution, this expulsion being accompanied by a counterflux of solvent. There is no exchange of alkaline metal cations in acidic (pH 1) solutions of salts. In non-aqueous electrolytes, expulsion of cations is dominant during SPAN oxidation, while solvent counterflux also plays a significant role.

1.6 Optical Activity in Conducting Polymers

Chiral polymers are being used extensively in chiral recognition studies and as materials for the separation of enantiomeric chemicals [99]. Producing chiral conducting polymers would add a new dimension and capabilities to the sensing, synthesis and separation of chiral molecules.

Optically active conducting polymers have been prepared via either polymerisation of monomers bearing a chiral substituent (eg. polypyrroles and polythiophenes) or, in the case of PAN, by doping with a chiral acid. The influence of the chiral group induces
main chain chirality, where the polymer backbone is believed to adopt a one-handed helical conformation. This preferred conformation may, in its turn, be preserved in the solid state after removing of the chiral group with base.

The first examples of chiral conducting polymers were films of polypyrroles with a chiral substituent covalently attached at each nitrogen atom, synthesised electrochemically by Baughman et al. [100] and Salmon et al. [101, 102]. Polymerisation of pyrrole monomers with chiral substituents in the 3-position on the pyrrole ring has been reported by Garnier et al. [103] and other authors [104, 105] to produce helical polymers, as evidenced by the circular dichroism spectra (CD) of the films. Chiral polythiophenes have also been similarly synthesised via polymerisation of monomers bearing chiral substituents at the 3-position on the thiophene ring [106].

Doping of polypyrrole with chiral anion has been explored by Kato et al. [107], Zhou et al. [108] and Aboutanos et al. [109] for polypyrrole. Chiral polymers were electrodeposited via doping of pyrrole with (+)- and (-)-tartaric acids and (-)-mandelic acid. However, the polymers were only weakly optically active, weakly adherent to the electrode surface and required co-polymerisation with pyrrole for better mechanical properties.

Conducting polymers have recently proven to be useful in applications based on enantioselective interactions. Chiral polypyrrole-coated electrodes have been employed as enantioselective electrochemical sensors [104, 110]. Chirality induction in the achiral polymer as a result of the polymer-chiral guest interaction suggests their use for a chirality assessment of chiral guest molecules [111-114]. Spectroscopic recognition of
enantiomeric aminoacids has been reported due to their interaction with a chiral polyaniline on a transparent substrate [115]. Chiral polypyrrole-coated electrodes have also been used for partial asymmetric synthesis [116, 117].

Helical polymers are of special value as chiral stationary phases in HPLC due to their high performance in separation of enantiomers. Polypyrrole was the first conducting polymer to receive attention as a chiral stationary phase for electrochromatographic separations [118-120], and a chiral polypyrrole membrane has been used for the separation of L- and D-isomers of tryptophan [121].

Chiral polyanilines have also recently been produced by Majidi et al. [122] via doping of PAN with the chiral anions of (+)- or (-)-camphorsulfonic acid (HCSA), and later further explored by Norris et al. [123-129]. These authors have shown that polyaniline may be easily produced in an optically-active form either chemically or electrochemically. The electrochemical route involves the oxidation of aniline in an aqueous solution of (+)- or (-)-HCSA. Doping of the chiral anion into the polymer structure during polymerisation is believed to cause the polyaniline chains to adopt a one-handed helical conformation. The CD spectra of PAN.(+)-HCSA and PAN.(-)-HCSA films grown on ITO-coated glass working electrodes exhibited strong mirror imaged CD bands in the visible region associated with the polymer absorption bands. Similarly, chemical oxidation of aniline with \((\text{NH}_4)_2\text{S}_2\text{O}_8\) in aqueous (+)-HCSA or (-)-HCSA solutions produces chiral polyaniline salts [125]. Glass slides immersed in the reaction solution became coated with PAN.HCSA polymer, allowing by this in situ method to prepare films for chiroptical studies.
Optically active polyaniline may also be prepared via post-polymerisation doping of pre-formed emeraldine base (EB). When polyaniline in the EB form was dissolved in DMSO, DMF or NMP containing chiral acids (HA = (+)- and (-)-HCSA, (+)- and (-)-tartaric, (+)-3-bromocamphor-10-sulfonic, and (+)-O,O′-dibenzoyl-D-tartaric acids), the PAn.HA emeraldine salts produced exhibited CD spectra which can be assigned to chirality in the polymer backbone, since in the measured region (330 - 700 nm) the above dopant acids do not have CD bands.

Another approach to one-handed helical polymers is acid-base interactions between an achiral polymer and a chiral guest (acid or base). This kind of chiral induction has been recently described by Okamoto et al. [111-114] for polyacetylene derivatives. They found that poly{(4-carboxyphenyl)acetylene} exhibited an induced circular dichroism in the UV-visible region upon complexation with chiral amines and amino alcohols in solution as well as in films. The CD spectra recorded for poly{(4-carboxyphenyl)acetylene} in the presence of chiral amines or aminoalcohols showed characteristic, exciton-type coupled Cotton effects in the UV-visible region, associated with the absorption bands of the polymer. Chiral guests studied included primary amines, cyclic primary amines, secondary and tertiary amines, and amino alcohols. Enantiomeric amines induced mirror-imaged, split-type Cotton effects. The intensity of the Cotton effects increased with an increase in the concentration of the chiral amine and plateaued at a 50-fold excess of amine over the concentration of monomer repeat units in the polymer. The authors proposed using the Cotton effect signs corresponding to the polymer helical sense as a novel probe for chirality assignments of amines and aminoalcohols.
1.7 Polymer Conformation and Properties

The conformation of the main chain is an important factor in determining a number of conducting polymer properties. For conducting polymers, two main aspects of the main chain conformation may be outlined, namely chirality and the degree of the extension of the main chain. It has been demonstrated by a number of authors [130-134] that the main chain arrangement has a strong influence on the polymer conductivity.

From experiments with polyaniline dissolved in m-cresol MacDiarmid et al. [135-137] concluded that PAn may exist in either the “compact coil” or “extended coil” conformations. For example, it has been shown that the effects of secondary doping of polyaniline in m-cresol are based primarily on a change in molecular conformation of the polyaniline from the “compact coil” to “expanded coil”. In the “compact coil” form the dihedral angles between arene rings are larger than in the “extended coil” conformation, resulting in poorer conjugation and, consequently, conductivity. The conformation of polyaniline also affects its optical absorption spectrum in the Vis-NIR region. Straightening of the polymer backbone in the “extended coil” conformation allows a higher degree of polaron delocalisation along the chain. As delocalised polarons absorb at higher wavelengths, the lowest-energy peak in the Vis-NIR spectrum of the polymer shifts from ca. 800 to ca. 1300 nm.

The presence of a chiral substituent or a chiral guest molecule in a conducting polymer may cause the preferential formation of a one-handed helix by the polymer backbone, otherwise randomly twisted. Understanding chirality induction in conducting polymers has importance in relation to biomedical synthesis. A large number of chiral drugs
exhibit different pharmacodynamics and pharmacokinetics for the different enantiomers [138], not to mention cases when a particular enantiomer has harmful side effects. It is becoming increasingly important to efficiently separate enantiomers in drugs production, and better still, to produce only the specific desired stereoisomer. Chiral substituted polyanilines should have potential in applications such as chirality assessment, asymmetric synthesis and chiral separations. Ease of synthesis, low cost and electrical conductivity mean these polymers may become competitors for conventional materials.

1.8 Aims of the Project

Due to their low cost, high conductivity and environmental stability, one of the most potentially useful types of chiral conducting polymers are polyanilines. To date, studies have largely concentrated on unsubstituted polyaniline.

The major aim of this thesis was to explore routes to the synthesis of new chiral conducting polymers formed from substituted anilines. A particular goal was the possibility of developing optically active forms of the water-soluble sulfonated polyaniline, poly(2-methoxyaniline-5-sulfonic acid) (PMAS). Two ways of inducing main chain chirality in PMAS were considered, namely (i) electrochemical polymerisation of the monomer 2-methoxyaniline-5-sulfonic acid in the presence of a chiral amine, or (ii) treating pre-formed PMAS with chiral amines and amino alcohols and casting films.
Another goal was the synthesis of chiral polymers from \(N\)-substituted aniline monomers, such as \(N\)-methylaniline and diphenylamine, following the route previously established for aniline and 2-methoxyaniline, where the presence of a chiral acid as dopant (e.g. (+)-camphorsulfonic acid) induced optical activity in the polymer. An alternative approach to a chiral polyaniline was also to be explored, namely the polymerisation of the monomer, \((S)-(+)-(anilinomethyl)pyrrolidine\), where the source of the chiral induction in the polyaniline product was expected to be the chiral substituent on the monomer \(N\) atom rather than a chiral acid dopant. A related goal was to explore the redox and pH switching of these novel polyanilines.

Finally, further insights into the factors affecting the conformation of polyanilines were sought by exploring the possibility of inducing conformational change in the water-soluble PMAS polymer by the addition of alkali and alkaline earth metal salts. If successful, this would provide the first example of ionochromism in polyanilines.
CHAPTER 2
GENERAL EXPERIMENTAL

2.1 Materials

2.1.1 Monomers

The monomer for PMAS synthesis, 2-methoxyaniline-5-sulfonic acid (MAS) was obtained from Mitsubishi Rayon Ltd., Japan and used as supplied. Diphenylamine and (S)-(++)-anilinomethyl)-pyrrolidine ((++)-AMP) were purchased from Aldrich Chemical Co. and used without further purification. N-Methylaniline was purchased from Aldrich Chemical Co. and doubly distilled prior to use in the polymer synthesis.

2.1.2 Polymers

Poly(2-methoxyaniline-5-sulfonic acid) (PMAS) was purchased from Mitsubishi Rayon Ltd., Japan (as its ammonium salt) and used without further purification. Poly(vinylalcohol) (PVA) (MW 70,000 – 100,000 Da) and poly(4-vinylpyridine) (PVP) (MW 60,000 Da) were purchased from Aldrich Chemical Co. and used as supplied.

2.1.3 Reagents

The sources and purities of various reagents used in this Thesis, such as chiral amines and aminoalcohols, ammonium persulfate oxidising agent, hydrazine hydrate reducing agent, acids and bases, and various alkali and alkaline earth metal salts, are detailed in the Chapters where they were employed.
2.1.4 Solvents

Spectroscopic grade dimethylsulfoxide (DMSO), 1-methyl-2-pyrrolidinone (NMP), dimethylformamide (DMF), acetonitrile and acetone were purchased from Ajax Ltd and used as supplied. Aqueous solutions were prepared using Milli-Q water.

2.1.5 Electrodes

Ag/AgCl reference electrodes were purchased from Bioanalytical Systems Ltd. Auxiliary electrodes were manufactured in-house from Pt mesh (obtained from Goodfellow Ltd). Working electrodes included in-house made Pt disc electrodes (diameter 0.5 mm) in teflon housing, in-house made Pt disc microelectrodes (diameter 20, 50, or 100 μm), Pt plate electrode (5 x 5 cm) obtained from Goodfellow Ltd, and indium-tin-oxide (ITO) - coated glass (surface resistivity 10 or 20 Ω cm$^{-2}$) purchased from Delta Technology Ltd. ITO-coated glass electrodes underwent the following cleaning prior to use: washed with detergent, rinsed with water, rinsed with isopropanol, dried and then treated in a UVO Cleaner (Jelight Co., Inc.) for 5 min.

2.2 pH Measurements

The pH of aqueous solutions was determined with a Denver Instruments Model 20 pH/conductivity meter, calibrated using standard buffer solutions (pH = 4.0 and 7.0).
2.3 Synthesis of Optically Active Polyanilines

2.3.1 Electrochemical Synthesis

Electrochemical polymerisations of appropriate monomers were carried out in a three-electrode cell presented in Figure 2.1. A rectangular or cylindrical glass beaker served as the reaction vessel. A Pt plate or a slide of ITO-coated glass served as the working electrodes. The reference electrode was connected with the polymerisation solution via a salt bridge filled with 0.50 M NaNO₃. Potential was applied to the working electrode using a PAR 363 Potentiostat, while current data were acquired using a MacLab 4e (AD Instruments) interfaced with a Macintosh computer equipped with Echem 2.2 software. Potentiostatic depositions were monitored as well with a BAS CV-27 potentiostat. For electrochemical experiments with microelectrodes, a PAR 263A Potentiostat and Electrochem software were used.

For the synthesis of the optically active PMAS.(+)-PhEA and PMAS.(-)-PhEA, 30 mL of an aqueous solution of the MAS monomer and chiral amine were used. The particular concentrations of MAS and chiral amine employed are detailed in Chapter 3.

Two methods were employed for the deposition of PMAS, namely potentiostatic and potentiodynamic. The galvanostatic method was found undesirable for PMAS growth due to a high initial potential, capable of overoxidising the polymer. For the deposition of PDPA, PNMA and synthesis of PAMP, only the potentiostatic method has been used, the particular potential value being chosen after electrochemical characterisation of monomers by cyclic voltammetry.
2.3.2 Chemical synthesis

Poly\{(S)-(+)\)-(anilinomethyl)-pyrrolidine\} \{(+)\)-PAMP\} was synthesised using procedures similar to those developed earlier for polyaniline[139]: (+)-AMP monomer (100 mg) was dissolved in 3 ml of 1.0 M aqueous HCl solution and placed in an ice bath. Ammonium persulfate (104 mg) was dissolved in 2.7 ml of 1.0 M aqueous HCl, giving an oxidant/monomer molar ratio of 0.8, and the oxidant was added dropwise to the monomer solution under continuous stirring. After 4 hrs a green soluble polymer formed.

Figure 2.1 Electrochemical cell for polymerisations.
Spin-cast films of PMAS were prepared as follows: the chiral amine was added in the molar ratios detailed in Chapter 4 to 3 ml of a 5% (w/v) aqueous PMAS solution. When the amine was insoluble in water, it was dissolved in acetone or acetonitrile prior to mixing with the aqueous PMAS solution. The mixed solutions, containing PMAS and amine, were left to stand for 1 - 2 hrs and then spin-cast onto glass slides using a Photo-Resist Spinner (Headway Research Inc), with a spinning speed of 2000 rpm. The glass slides were prepared as for electrochemical deposition.

When a larger amount of the PMAS.(+)-PhEA was required (as for conductivity measurements) the polymer was deposited on a Pt plate (16 cm²) by CV, sweeping the potential from -0.2 to 1.0 V for a prolonged period of time (20 cycles). The working solution contained 0.10 M MAS and 0.10 M (+)-PhEA. The polymer was then scraped off the electrode and dried in a desiccator over silica under vacuum.

2.4 Polymer Characterisation

2.4.1 UV-visible-NIR Spectroscopy

The UV-vis-NIR spectra of the polymer films electrodeposited or spin-cast onto glass were recorded between 300 and 1100 nm using a Shimadzu UV-1601 spectrophotometer and between 300 and 2600 nm using a Cary 500 spectrophotometer (Varian).

In cases when aqueous polymer solutions were investigated, the samples were filtered through a 0.45 µm syringe filter prior to recording their spectra. The latter spectra were
recorded between 250 and 1300 nm, water absorption preventing measurements beyond
1350 nm.

The concentrations of aqueous PMAS (NH$_4^+$) solutions employed in Chapters 5 and 6
were estimated from their absorbances at 473 nm, the $\lambda_{\text{max}}$ of PMAS, by reference to the
Beer’s Law plots shown in Figures 2.2a and 2.2b below. These plots were constructed
by adding increasing amounts (5 µl to 250 µl) of a 0.5 % (w/v) PMAS (NH$_4^+$) solution
to 10 ml of water and recording the UV-vis spectrum. Beer’s Law is seen to be obeyed
over a wide PMAS concentration range from $6 \times 10^{-6}$ to $3 \times 10^{-4}$ M.

![Figure 2.2a Beer’s Law plot for aqueous PMAS (NH$_4^+$) solution.](image-url)
2.4.2 Circular Dichroism Spectroscopy

Circular dichroism (CD) spectroscopy is among the most sophisticated techniques for the analysis of chiroptical properties of chiral compounds. In chiral media, left- and right-hand circularly polarised beams of light are absorbed to a different extent. This results in the outcoming beam possessing ellipticity, which is determined (in radians) as

$$\Psi = \frac{\pi d (k_L - k_R)}{\lambda}$$

where $d$ is the pathlength in centimetres, $k_L$ and $k_R$ are the absorption coefficients of the left- and right-hand circularly polarised light, respectively, and $\lambda$ is the wavelength (in nm) at which the ellipticity is measured.

The mean molar absorptivity may be expressed as

$$\varepsilon = \frac{4 \pi k}{(2.303 \lambda c)}.$$

For convenience the signal $\Theta$ is presented in degrees:

$$\Theta = \Psi \frac{360}{2\pi}.$$
The chiral anisotropy coefficient $\Delta \varepsilon / \varepsilon$ is then expressed as

$$\frac{\Delta \varepsilon}{\varepsilon} = \frac{\Theta}{(3298 \text{ Abs})},$$

where Abs is the absorbance of the sample at the wavelength of measurement.

The particular feature determining the usefulness of CD spectroscopy is the existence of Cotton effects at the wavelengths of the absorption maxima even when absorbance is very low. In conducting polymers the electronic transitions at wavelengths above 300 nm are associated with excitations from the conjugated electron system. Such excitations inherently possess transition electric and magnetic dipole moments, which means that in helical conjugated polymers the chromophore itself is chiral.

The CD spectra of the polymer films and solutions in this thesis were recorded on a Jobin Yvon Dichrograph 6 and, in a few instances, on a Jasco 500 Spectropolarimeter. All solutions were filtered through a 0.45 $\mu$m filter prior to spectral measurements.

### 2.4.3 Electrical conductivity

The electrical conductivities of the as received PMAS and the new polymers described in Chapters 3-6 were determined using the Van der Pauw method [140]. The method has been developed for measuring the conductivity of a sample of an arbitrary shape. For the particular case when the sample is round and the contacts are applied symmetrically (Figure 2.3), this method determines the conductivity as

$$\sigma = \ln 2 \frac{I}{(\pi d E)} \text{ [}\Omega \text{ cm}^{-1}],$$

where $I$ is the current passed between contacts A and B, $E$ is the potential drop measured between contacts C and D, and $d$ is the thickness of the polymer disc (in cm).
The measurements were carried out on compressed polymer powder pellets. These pellets were made using a 6-ton KBr press, the thickness of pellets being determined using a digital micrometer. A current of 10 μA was applied with a PAR 363 Potentiostat and the potential drop was measured with a HP 34401A Multimeter.

2.4.4 Electrochemical Characterisation - Cyclic Voltammetry

Cyclic voltammetry was a preferred electrochemical method for characterisation of the polymers produced in this study, because this technique clearly shows the formation of a conducting polymeric film, and indicates the potential range of its charging and discharging. In this work, cyclic voltammetry was used for both deposition of the polymer films and for characterisation of the grown films.

Potentiodynamic deposition of PMAS.(+)-PhEA and PMAS.(-)-PhEA films was carried out in an electrochemical cell described in Section 2.2.1. Their cyclic voltammograms were recorded by scanning the potential usually between -0.20 V and 0.80 V (vs Ag/AgCl); particular details of the scan rate and potential limits are discussed in
Chapter 3. Electrochemical characterisation of the PMAS.(+)-PhEA films crosslinked with PVA was carried out by cycling the potential between -0.20 V and 1.10 V at a scan rate of 100 mV/s in 1.0 M KCl solution. Films of PDPA.(+)-HCSA and PNMA.(+)-HCSA were characterised be cycling from -0.20 V to 1.50 V at a scan rate of 100 mV/s in 1.0 M (+)-HSCA.

2.4.5 Gel Permeation Chromatography (GPC)

GPC analyses were performed on a Waters Millenium 32 GPC system, with an Ultragel 250 column and 20% methanol / 80% aqueous 0.20 M NaNO₃, 0.01 M NaH₂PO₄ as the mobile phase. Polystyrene standards (MW = 1,800 to 100,000 Da) were used for calibration. Samples were filtered through a 0.2 µm filter prior to analysis.

2.4.6 Atomic Force Microscopy

Surface morphology is an important issue for the applications of chiral conducting polymers. When a polymeric film is used in a sensor, as a separation medium or for electrode modification, it is desirable to have a smooth, continuous film of controlled thickness. As two main methods of chiral polyaniline deposition have been explored in this study, it is important to compare the morphologies of the resultant films.

Atomic Force Microscopy (AFM) images of the films were obtained using the tapping technique on a Nanoscope from Digital Instruments Inc. A commercially available gold tip was used. Samples of polyaniline were prepared by potentiodynamic electrochemical deposition of PMAS.(+)-PhEA onto an ITO-coated glass.
2.4.7 Atomic Absorption Spectroscopy

The metal ion content of the barium and sodium salts of PMAS prepared in Chapters 5 and 6, respectively, were estimated by atomic absorption spectroscopy. The PMAS (M\(^{n+}\)) polymers were readily dissolved in 0.1 M HCl and the metal ion content measured using a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer.
CHAPTER 3

ELECTROCHEMICAL SYNTHESIS OF CHIRAL PMAS
IN THE PRESENCE OF (+)- AND (-)-1-PHENYLETHYLAMINE

3.1 Introduction

One of the major drawbacks in the development of applications for polyaniline is that this polymer is insoluble in most common solvents. One way to improve solubility in organic solvents is the use of large organic dopant anions, such as dodecylbenzenesulfonic acid or camphorsulfonic acid. An alternative approach is the introduction of alkyl or alkoxy substituents into the polymer chain. Despite improved solubility, processing in these cases is still environmentally unfriendly, as it requires organic solvents. A way to overcome this drawback is sulfonation of the arene rings in polyaniline, to produce sulfonated polyanilines (SPANs). This latter class of polymers has three main distinctive features: they are soluble in water, they are self-doped and they possess relatively low electrical conductivity.

The majority of SPANs reported to date have been prepared via the sulfonation (with fuming sulfuric acid) of pre-formed emeraldine base or leucoemeraldine base [74, 141, 142]. This has provided polymers in which 50-75 % of the aniline rings have sulfonic acid groups attached. The UV-vis absorption spectra of these partially sulfonated SPANs are similar to the spectrum of parent PAN emeraldine salts. For example, the spectrum of a 75 % sulfonatedSPAN cast from solution has three absorbance bands
The first absorption band at ca. 320 nm can be assigned to \(\pi-\pi^*\) transitions of the arene rings, while the 420-435 nm and ca. 800 nm bands are assigned to localised polaron transitions [143]. There is opinion based on ESR studies that interchain polarons may form as well [144-146].

![Absorption spectra](image)

**Figure 3.1** Absorption spectra of the cast films of a partially ring-sulfonated PAn in a self-doped form (solid line) and of the unsubstituted PAn.HCl salt (dashed line) [140].

Deprotonation of these SPANs with NaOH gives the EB form of the SPAN, which has two absorption bands: at ca. 320 nm \((\pi-\pi^*\) transition) and ca. 650 nm, similar to the parent PAn. In this emeraldine base form, the absorption at 650 nm has been assigned to an exciton band associated with the quinoid rings [143, 147], as for the parent PAn.

This Chapter concentrates on a recently reported representative of the sulfonated polyanilines class, namely poly(2-methoxyaniline-5-sulfonic acid) (PMAS, 4). It is unique in that, unlike the previous SPANs, it is fully sulfonated - i.e. all the aniline rings bear a sulfonic acid substituent. PMAS was first synthesised by chemical oxidation of
the monomer, 2-methoxyaniline-5-sulfonic acid (MAS), by Shimizu et al. in 1997 [80].

Previous attempts to polymerise anilines with a sulfonic acid substituent failed due to very low reactivity of the monomers towards oxidation, but introduction of the electron-donating methoxy group compensated the electron-withdrawing effect of the sulfonic acid group, increasing the monomer reactivity.

\[
\begin{align*}
\text{MeO} & \quad \text{SO}_3^+ \\
\text{MeO} & \quad \text{SO}_3^- \\
\end{align*}
\]

The monomer is poorly soluble in water at its natural pH (ca. 2), so polymerisation was carried out under basic conditions. Introduction of the sulfonate group gave the resultant polymer an excellent (≥ 10% w/v) solubility in water. This chemical oxidation process gave a polymer with an average molecular weight of 10,000 Da and a conductivity of 0.01 S cm⁻¹.

Later PMAS was synthesised by Innis et al. [81] electrochemically under hydrodynamic conditions (in a flow-through cell). In this process ammonia was again added to the polymerisation solution with the pH adjusted to ca. 4.

Cyclic voltammograms of the sulfonated polyanilines obtained by these routes were similar to that of parent polyaniline. They showed two well resolved redox peaks [141] corresponding to the sequential formation of semiquinone radical cations (emeraldine salts) and to formation of the fully oxidised pernigraniline form. The diffusion of the charge-balancing anions into the polymer is often the rate-determining step in kinetics
of redox switching in solid polyaniline films. However, redox switching of a self-doped polymer, such as PMAS, involves only diffusion of protons and may have a superior rate compared to that of the parent polyaniline.

Theoretical studies [143] show that the bandgap and bandwidth in polyaniline depend on the dihedral angle between adjacent arene rings in the polymer main chain. Bulky substituents increase the dihedral angles and thus reduce the degree of conjugation and conductivity of the polymer. Despite the resultant relatively low conductivity, PMAS is important in that the conductivity is pH independent over a broad pH range [141]. This is caused by formation of a stable six-membered ring involving the sulfonic acid group, nitrogen and hydrogen participating in doping.

Induction of optical activity in polymers through acid-base interactions has been recently reported for some pre-formed polymers. Interaction of carboxylic acid derivatives of polyacetylene, polycarbodiimide and polyisocyanate with chiral bases (amines and amino alcohols) has been studied by Okamoto et al. [111-114]. The presence of the chiral bases induced intense Cotton effects in the visible region CD spectra of these polymers. The Cotton effects were mirror images in cases when enantiomeric chiral compounds were used, which was interpreted as evidence for the formation of either a left- or a right-handed helix by the polymer main chain.

The CD spectra of the substituted polyacetylenes showed exciton-coupled Cotton effects, the sign and intensity of which depended on the configuration and bulkiness of the particular amine or amino alcohol employed. The nature of the split-type CD signals in chiral polythiophenes has been similarly attributed to interchain exciton interactions
This suggestion is supported by experiments showing the existence of the interchain excitons in conjugated polymers [148, 150-154].

The solubility of a polymer is an important factor in the formation of a one-handed helix, and in determining the presence of exciton-split Cotton signals. In poor solvents the polymers are believed to form microcrystallites, within which intermolecular excitons are responsible for the bisignate Cotton effect [111].

In this Chapter we explore the possibility that replacing the ammonia by the optically active amine (R)-(+)1-phenylethylamine or (S)-(−)-1-phenylethylamine (PhEA) during electrochemical polymerisation of MAS could lead to formation of an optically-active PMAS polymer with main-chain chirality. The chiral induction is postulated to arise from the respective amine inducing a preferred one-hand-sense helicity to the PMAS chains via electrostatic interactions between the chiral amine and sulfonic acid groups on the polymer rings. As far as we are aware, this is the first study of polymerisation and concomitant chiral induction via acid-base interaction in conducting polymers.

3.2 Experimental

3.2.1 Cyclic Voltammetry of Aqueous MAS Solutions
The electrochemical behaviour of MAS in the presence of (+)-PhEA was studied by cyclic voltammetry over the potential range -0.25 to +1.10 V (vs Ag/AgCl). The MAS concentration was always 0.1M, but the (+)-PhEA concentration was varied between 0.010 M and 0.10 M. For the solutions with 0.01 M, 0.05 M and 0.07 M (+)-PhEA,
ammonium hydroxide was added to adjust the pH to 5.0. A Pt disc electrode with a diameter of 1.0 mm was used as the working electrode.

3.2.2 Potentiodynamic Polymerisation of MAS in the Presence of (+)- or (-)-PhEA

Thin films of PMAS.PhEA were deposited on ITO-glass electrodes (surface resistivity 10 or 20 ohm/S, surface area 2.5 cm$^2$) from aqueous solutions containing MAS and chiral PhEA. The methods explored included cyclic voltammetry (CV) and the square-wave potential pulse method. All thin films produced were dried before recording their UV-vis-NIR and CD spectra and later stored in a desiccator over silica gel.

During cyclic voltammetry the potential limits were set between -0.3 and -0.1 V for the reductive limit and between 0.8 V and 1.1 V for the oxidative limit. The scan rate was varied between 10 and 200 mV/s. The influence of the monomer and amine concentrations was explored by varying the MAS concentration between 0.10 M and 0.16 M, and using PhEA concentrations between 0.050 M and 0.13 M.

In the square-wave potential pulse method, oxidative potentials were varied between 0.9 V and 1.1 V during 1 to 20 sec, while reductive potentials were varied between -0.3 V and 0.0 V during 1 to 10 sec.

3.2.3 Potentiostatic Polymerisation of MAS in the Presence of (+)-PhEA

Potentiostatic polymerisation of MAS was carried out in a 30 ml stationary cell, using a solution containing 0.10 M MAS and 0.10 M (+)-PhEA. As working electrode, ITO-coated glass slides were used (surface area 2.5 cm$^2$). The potential applied was varied between 0.5 and 0.9 V.
3.2.4 Immobilisation of PMAS.(+)-PhEA with Poly(4-vinylpyridine)

To produce water-insoluble films, the deposited PMAS.(+)-PhEA polymers were subsequently immobilised on the electrode surface with protonated poly(4-vinylpyridine) (PVP). Following the method described by Tallman et al. [160], the electrochemically prepared films of PMAS.(+)-PhEA on ITO-coated glass were dipped into a 1% (w/v) solution of PVP in 0.10 M HCl and then dried using a hair drier for approximately 30 sec.

3.2.5 UV-vis-NIR and Circular Dichroism Spectroscopy

After drying, the UV-Vis-NIR spectra of the films were recorded using a Cary 500 spectrophotometer, while CD spectra were recorded using a Jobin Yvon Dichrograph 6. Chiral anisotropy factors \( g = \Delta \varepsilon / \varepsilon \) for the optically active PMAS.(+)-PhEA and PMAS.(-)-PhEA films were calculated from the intensities of the absorption and CD bands at 480 nm, the \( \lambda_{\text{max}} \) for the PMAS polymer.

3.2.6 Interaction of PMAS.(+)-PhEA with HCl and Ammonia

Films of PMAS.(+)-PhEA were prepared as above by potentiodynamic deposition on ITO-coated glass slides. The glass slide with dried polymer film on it was inserted into a quartz rectangular cuvette and secured in the vertical position against the wall. On the bottom of the cuvette a small amount of concentrated hydrochloric acid or concentrated ammonia solution was placed, and the cuvette was closed hermetically. UV-Vis-NIR spectra were then recorded between 300 and 2600 nm, and CD spectra were measured between 300 and 700 nm.
3.3 Results and Discussion

3.3.1 Cyclic Voltammetry of Aqueous MAS Solutions

The electrochemical behaviour of the MAS monomer has been studied by Guo et al. [155]. The CV of MAS in the presence of NaOH, NH₄OH or pyridine revealed only one oxidation peak at 1.0 V, indicating oxidation of the monomer. The polymerisation of MAS was carried out at applied potentials no higher than 0.9 V to avoid overoxidation of the polymer. The magnitude of the current did not increase with time and no redox peaks for a polymer were observed, presumably due to the fact that the PMAS formed was soluble in water.

3.3.2 Potentiodynamic Polymerisation of MAS in the Presence of (+)-PhEA.

In the present study, introduction of the chiral PhEA amine into the polymerisation solution instead of NH₄OH made a major difference. Attachment of PhEA to sulfonic acid groups on the PMAS chains should lead to increased hydrophobicity of the polymer. As a result, an insoluble polymer grew on the ITO-glass electrode surface upon cycling the potential between -0.2 and 1.0 V. Cyclic voltammetry during deposition showed, apart from the monomer oxidation peak, two reduction peaks and two oxidation peaks (one of them superimposed with the monomer oxidation peak), which may be assigned to the polymer (Figure 3.2). The magnitude of the current increased with successive scans, confirming deposition of a conducting polymer.
Figure 3.2. Cyclic voltammetry of aqueous 0.10 M MAS / 0.10 M (+)-PhEA on an ITO-coated glass electrode (2.5 cm²); 1st, 3rd and 5th scans only shown. Scan rate 50 mV/s.

When compared with the reported CVs of other water-soluble sulfonated polyanilines at pH 3 [71], the PMAS.(+)-PhEA polymer showed similar electroactivity during growth. Weakly resolved oxidation peaks were observed at 0.3 V and 0.9 V (on the 5th scan), and reduction peaks at 0.20 V and 0.0 V. This compares with partially (75 %) sulfonated polyaniline at pH 3, which exhibited [71] oxidation peaks at 0.18 V and 0.60 V and reduction peaks at 0.45 V and 0.0 V.

The MAS monomer oxidation started at 0.60 V, but a peak current value could not be reached due to overoxidation of the polymer at potentials above 1.10 V. The first polymer oxidation peak at 0.40 V is assigned to oxidation of the leucoemeraldine form of PMAS to the emeraldine salt, while the second oxidation peak at 0.90 V is attributed to further oxidation to the pernigraniline salt form. Reduction peaks are well seen only
on the early scans. Peaks at 0.20 V and 0.0 V are attributed to the corresponding reductions.

3.3.3 Polymerisation Mechanism for PMAS

By analogy with the mechanism accepted for aniline polymerisation, the mechanism for PMAS.(+)-PhEA formation may be presented as shown in Scheme 3.1.

**Step 1. Oxidation of monomer**

![Step 1 Diagram]

**Step 2. Radical coupling and re-aromatisation**

![Step 2 Diagram]
Scheme 3.1 Proposed mechanism for electrochemical polymerisation of MAS in the presence of (+)-PhEA.

Differences between the aniline and MAS polymerisation include the absence of dopant anion incorporation and association with the chiral (+)-PhEA ammonium ion for MAS. The PMAS.(+)-PhEA precipitation may be facilitated by screening of the hydrophilic external surface (SO₃⁻ groups) of the PMAS chains with the hydrophobic benzyl rings of (+)-PhEA.
3.3.4 Chiroptical Properties of PMAS.(+)-PhEA

A typical UV-vis-NIR spectrum for PMAS.(+)-PhEA deposited potentiodynamically on ITO-coated glass is presented in Figure 3.3. It showed poorly resolved bands at ca. 350 and 380 nm, and a sharp characteristic peak at 483 nm. It also exhibited a broad absorption band above 1000 nm, sometimes showing a maximum at ca. 2300 nm. These features differ significantly from those reported [70, 71] for partially-sulfonated polyanilines (SPANs) and for poly(2-methoxyaniline). The latter polymers exhibit similar absorption bands to the emeraldine salt of parent PAn. For PAn and SPANs, an absorption band between 300 nm and 330 nm has been assigned to $\pi-\pi^*$ transitions in the benzenoid rings of the polymer [146], while bands at 420-435 nm and ca. 800 nm have been assigned to localised polaron transitions [143] of the polymer when in a “compact coil” conformation. When PAn is in an “extended coil” conformation, a broad band at wavelengths above 1000 nm replaces the 800 nm band [33, 34].

The broad bands observed at 350 - 380 nm in the PMAS.(+)-PhEA films may be $\pi-\pi^*$ transitions that are red-shifted compared to these transitions in the parent polyaniline. By analogy, it is reasonable to suggest that the sharp peak at 483 nm in PMAS.(+)-PhEA (cf. 473 nm in PMAS (NH$_4^+$)) is a red-shifted polaron band transition.
Figure 3.3 UV-vis-NIR spectrum of a PMAS.(+)-PhEA film deposited on ITO-coated glass electrode by CV from -0.20 to 1.00 V (scan rate 50 mV/s).

The CD spectra of PMAS.PhEA films deposited on ITO-coated glass from polymerisation solutions containing enantiopure (+)-PhEA and (-)-PhEA are presented in Figure 3.4. The spectra exhibit an intense bisignate Cotton effect centered at 480 nm associated with the 483 nm absorption band and less intense, broad CD bands between 300 and 400 nm associated with the 350 - 380 nm absorption band. These Cotton effects for the PMAS.PhEA films in the 300 - 700 nm region may be attributed to the optical activity of the PMAS polymer itself, since PhEA does not absorb in the visible region.
Figure 3.4 CD spectra of PMAS.(+)-PhEA and PMAS.(-)-PhEA films deposited potentiodynamically on ITO-coated glass from aqueous 0.10 M MAS / 0.10 M (+)- or (-)-PhEA.

**Origin of Chiral Induction**

The induction of optical activity in the polymer chains of PMAS is believed to arise from electrostatic binding of the chiral ammonium ion of (+)-PhEA (or (-)-PhEA) to ionised sulfonate groups along the polymer backbone, as depicted in Scheme 3.2, resulting in the polyaniline preferentially adopting a one-handed helical structure.

The CD spectra of PMAS.(+)-PhEA and PMAS.(-)-PhEA films grown under identical potentiodynamic conditions are mirror images (Figure 3.4). This indicates the adoption of the opposite helical screw by the PMAS chains in the two forms, arising from stereoselectivity in the acid-base interaction between the originally optically inactive sulfonated polyaniline and the chiral amines, as shown in Scheme 3.2. The polymer is assumed to adopt a *cis-cisoid* conformation in this helical arrangement.
The acid-base interaction of the enantiomeric amines (+)- and (-)-PhEA with the sulfonated polyaniline PMAS is expected, on steric grounds, to involve a staggered arrangement of the amine substituents, with the bulky phenyl substituent on the stereogenic carbon centre remote from the polymer, as shown in Scheme 3.3. The difference in the steric effects of the amine’s methyl and hydrogen substituents will presumably determine the helical hand adopted by the polymer chains.
Such induction of helical chirality into optically inactive polymers via acid-base interactions is rare, having only recently been demonstrated by Okamoto et al. [111-114] and Maeda et al. [156] for poly{(4-carboxyphenyl)acetylene} and poly(3-carboxyphenylisocyanate). The present study represents the first such report for conducting polymers. Our approach is also different in that the chiral amine inducing agent PhEA was present during the polymerisation process itself rather than added post-polymerisation as in the earlier studies. The required acid-base interaction may also be facilitated in the present case by the strongly acidic nature of the sulfonic acid substituents (compared to carboxylic acid groups) on the polyaniline chains.

From Figures 3.3 and 3.4, a chiral anisotropy factor $g (\Delta \varepsilon/\varepsilon)$ of 0.50 ($\pm$ 0.03 %) may be calculated for both PMAS.(+)-PhEA and PMAS.(-)-PhEA enantiomers associated with their characteristic 483 nm absorption band. These relatively high $g$ values (which may be compared with the highest $g$ value of 2 % reported [157] to date for a conducting
polymer) suggest a strong degree of chiral induction by the chiral PhEA amines during the electrosynthesis of the sulfonated polyanilines.

When shaken in water, the PMAS.(+)-PhEA films were easily removed from the electrode surface. Some of the polymer dissolved during shaking, but after filtration through a 0.20 μm filter such a solution/displacement did not possess optical activity. This indicates that only in the solid state (as a film) do the PMAS.(+)-PhEA and PMAS.(-)-PhEA polymers retain a one-handed helical structure, giving rise to optical activity. Meijer et al. [148, 149] have similarly suggested for chiral substituted polythiophenes that aggregation of the polymer is required for them to exhibit optical activity.

3.3.5 Influence of Various Parameters on Polymer Deposition and Chirality

In a separate set of experiments, a series of PMAS.(+)PhEA and PMAS.(-)-PhEA films were deposited using a range of MAS and PhEA concentrations.

(i) Monomer Concentration

Variation in the MAS monomer concentration was limited by solubility on the one hand and rate of polymerisation on the other. For this reason only a small range of MAS concentrations was explored (0.10 M to 0.16 M), while the (+)-PhEA concentration was kept constant at 0.10 M. A low amine concentration results in a low pH and poor MAS solubility as a consequence. All films were deposited by CV, scanning from -0.20 V to 1.00 V at a scan rate of 50 mV/s.

With all conditions investigated, growth of uniform films was observed. However, their optical activity (as determined from their chiral anisotropy factors calculated at 480 nm)
was highest when using MAS concentrations between 0.11 and 0.12 M, i.e. slightly higher than the (+)-PhEA concentration employed (see Figure 3.5). Significantly, the $g$ factor for a PMAS.(+)-PhEA film grown using 0.11 MAS (and 0.10 M (+)-PhEA) was as high as 0.75 %.

![Figure 3.5](image)

**Figure 3.5** Dependence of the chiral anisotropy factor ($\Delta \varepsilon / \varepsilon$) on the MAS concentration for PMAS.(+)-PhEA polymers deposited by CV from -0.20 V to 1.00 V, scan rate 50 mV/s, using 0.10 M (+)-PhEA.

(ii) PhEA Concentration

Similarly, variation of the (-)-PhEA concentration between 0.05 M and 0.13 M, while maintaining [MAS] = 0.10 M during CV polymerisation, allowed the determination of the optimal amine concentrations for chiral polymer deposition to be between 0.80 M and 0.10 M (Figure 3.6). Films were deposited by scanning from -0.20 to 1.00 V at a scan rate of 50 mV/s.
Figure 3.6 Dependence of the chiral anisotropy factor ($\Delta\varepsilon/\varepsilon$) on the (-)-PhEA concentration for PMAS. (-)-PhEA polymers deposited by CV from -0.20 V to 1.00 V, scan rate 50 mV/s, using 0.10 M MAS.

(iii) Scan Rate for Potentiodynamic Polymerisation

It was interesting to find that the scan rate significantly affected the chiral anisotropy factor of deposited PMAS. (+)-PhEA polymers. This was established from the CV polymerisation of solutions containing 0.10 M MAS and 0.10 M (+)-PhEA, scanning between -0.20 and 1.00 V with scan rates of 10, 25, 50, 80, 100 and 200 mV/s. The film deposited using a scan rate of 10 mV/s was very uneven, of a grey colour and its UV-vis spectrum lacked the characteristic PMAS peak at 480 nm. At the other extreme, with a scan rate of 200 mV/s virtually no deposition was observed. With scan rates between 25 and 100 mV/s, even yellow-brown films were produced. The UV-vis spectra of these films exhibited similar characteristic features, i.e. weakly resolved
bands at 330 and 380 nm and a sharp peak at 483 nm. The chiral anisotropy factor was highest for a scan rate of 50 mV/s (Figure 3.7).

![Graph showing the dependence of the chiral anisotropy factor on the scan rate for PMAS.(+)-PhEA polymer films deposited by CV.]

**Figure 3.7** Dependence of the chiral anisotropy factor on the scan rate for PMAS.(+)-PhEA polymer films deposited by CV.

**(iv) Potential Limits During Cycling**

When polymeric films were deposited from 0.10 M MAS / 0.10 M PhEA solution by CV, faster growth was observed with a higher oxidation limit. A PMAS.(+)-PhEA grown by cycling (again at 50 mV/s) to a cathodic potential of 1.10 V also exhibited a very high $g$ value of 0.72%.

Further increase of the oxidation limit led to overoxidation of the polymer and loss of conductivity. A lower (0.90 V) oxidation limit slowed polymer growth, but did not
have a significant effect on the polymer film quality. Similarly, decreasing the reduction limit to -0.30 V (rather than -0.20 V) had little effect.

On the basis of the above studies, the optimal conditions for polymer growth were determined as 8 cycles of the potential scan from -0.20 V to 1.00 V using a scan rate of 50 mV/s.

### 3.3.6 Deposition of PMAS-(+)-PhEA Films using the Square-Wave Potential Pulse Method

Similar PMAS.(+)-PhEA films could be electrochemically deposited under a range of square-wave conditions, as long as the reductive potential was below the second reduction peak for PMAS.PhEA (0.00 V) and the oxidative potential was between the second oxidation peak for PMAS.PhEA (0.90 V) and its overoxidation limit (1.10 V).

All films deposited were yellow-brown and even. Three regimes required very long times for deposition and gave poor quality films with substantially lower optical activity. These included: (i) fast switching of the applied potential between -0.20 V and 1.00 V, (ii) slow switching of the potential between 0.00 and 1.00 V, and (iii) using a short time for reduction compared with longer oxidation.

The PMAS.(+)-PhEA films deposited by the square-wave method gave UV-Vis and CD spectra (Figures 3.8 and 3.9) similar to those deposited previously (Section 3.3.4) via CV polymerisation. The absorption band at 330 nm was decreased compared to that of the CV-deposited polymer, and the Cotton effect at 400 nm (Figure 3.9) associated with this absorption band was not as well defined. Also, a shoulder at ca. 450 nm appeared in
the absorption spectrum, and an associated band appeared in the CD spectrum. The absence of a high wavelength polaron band in the 750-850 nm region and the presence of absorption in the near infrared region again suggested an “extended coil” conformation for the PMAS.(+)-PhEA polymers deposited by this square-wave method.

Figure 3.8 UV-vis spectrum of a PMAS.(+)-PhEA film deposited by the square-wave potential pulse method from aqueous 0.10 M MAS / 0.10 M (+)-PhEA (potential applied: 1.0 V for 10 s, -0.2 V for 5 s).
Figure 3.9 CD spectrum of the PMAS.(+)-PhEA film from Figure 3.8.

The chiral anisotropy factors measured for the PMAS.(+)-PhEA films deposited with the different square-wave regimes are compiled in Table 3.1. These confirm lower optical activity for the films obtained by this technique to those deposited previously via the CV method (see Section 3.3.4). The highest optical activity for the films deposited by the square-wave method was achieved when an oxidative potential (0.90 V to 1.10 V) was applied to the working electrode for 16 or 20 sec, followed by the reductive potential (-0.20 V) for 8 or 10 sec, provided that oxidation time was kept twice as long as the reduction time. Between 6 and 10 pulses were required for deposition of films suitable for the spectroscopic studies.
Table 3.1 Chiral anisotropy factors (Δε/ε) for PMAS.(+)-PhEA films deposited by the square-wave potential pulse method (calculated at 480 nm).

<table>
<thead>
<tr>
<th>Oxidation potential, V</th>
<th>Time, sec</th>
<th>Reduction potential, V</th>
<th>Time, sec</th>
<th>(Δε/ε), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1</td>
<td>-0.20</td>
<td>1</td>
<td>0.01</td>
</tr>
<tr>
<td>1.00</td>
<td>4</td>
<td>-0.20</td>
<td>4</td>
<td>0.28</td>
</tr>
<tr>
<td>1.00</td>
<td>10</td>
<td>-0.20</td>
<td>10</td>
<td>0.26</td>
</tr>
<tr>
<td>1.00</td>
<td>10</td>
<td>-0.20</td>
<td>5</td>
<td>0.21</td>
</tr>
<tr>
<td>1.00</td>
<td>5</td>
<td>-0.20</td>
<td>10</td>
<td>0.20</td>
</tr>
<tr>
<td>1.00</td>
<td>10</td>
<td>-0.10</td>
<td>5</td>
<td>0.18</td>
</tr>
<tr>
<td>1.00</td>
<td>10</td>
<td>-0.30</td>
<td>5</td>
<td>0.16</td>
</tr>
<tr>
<td>0.90</td>
<td>10</td>
<td>-0.20</td>
<td>5</td>
<td>0.19</td>
</tr>
<tr>
<td>1.10</td>
<td>10</td>
<td>-0.20</td>
<td>5</td>
<td>0.18</td>
</tr>
<tr>
<td>1.00</td>
<td>16</td>
<td>-0.20</td>
<td>8</td>
<td>0.37</td>
</tr>
<tr>
<td>1.00</td>
<td>16</td>
<td>0.00</td>
<td>8</td>
<td>0.04</td>
</tr>
<tr>
<td>1.00</td>
<td>16</td>
<td>-0.10</td>
<td>8</td>
<td>0.27</td>
</tr>
<tr>
<td>0.90</td>
<td>16</td>
<td>-0.20</td>
<td>8</td>
<td>0.38</td>
</tr>
<tr>
<td>1.00</td>
<td>20</td>
<td>-0.20</td>
<td>10</td>
<td>0.34</td>
</tr>
<tr>
<td>1.00</td>
<td>20</td>
<td>-0.20</td>
<td>5</td>
<td>0.13</td>
</tr>
</tbody>
</table>

3.3.7 Potentiostatic Polymerisation of MAS in the Presence of (+)-PhEA

MAS has been shown to be readily polymerised at potentials between 0.50 and 0.90 V, giving a water-soluble polymer which diffused from the working electrode surface [155]. In the present work, potentiostatic polymerisation of MAS in the presence of (+)-PhEA led to slow deposition of a polymer on the electrode surface. After two hours of potentiostatic oxidation at 0.90 V using a Pt electrode, a brown polymer was
deposited on the electrode surface. This polymer was removed from the electrode and redispersed in water. After filtration through a 0.45 μm filter, the solution had a UV-Vis spectrum very similar to that of PMAS produced previously in the presence of ammonium hydroxide.

When an ITO-coated glass electrode was used, an uneven grey-green polymer deposit was observed after 2 hours under applied potentials between 0.80 V and 1.00 V. However, these latter films did not show the characteristic sharp PMAS peak at 483 nm in their electronic spectra, though a broad absorption “tail” was still observed in the NIR region (Figure 3.10). The potentiostatically deposited films did not exhibit optical activity.

![Figure 3.10 UV-vis spectrum of a polymeric film potentiostatically deposited on ITO-coated glass with an applied potential of 0.90 V during 2 hrs (from aqueous 0.10 M MAS / 0.10 M (+)-PhEA).](image-url)
3.3.8 Surface Morphology of a Potentiodynamically Deposited PMAS.(+)-PhEA Film

An Atomic Force Microscopy study of the surface morphology of a potentiodynamically polymerised PMAS.(+)-PhEA film showed a rough surface consisting of irregularly packed particles of ca. 5 - 15 µm in size (Figure 3.11). This result is consistent with the above observation that the PMAS.(+)-PhEA films were readily redispersed in water upon shaking.

![AFM image of PMAS.(+)-PhEA surface](image)

Figure 3.11  AFM image of the PMAS.(+)-PhEA surface.

3.3.9 Molecular Weight of PMAS-(+)-PhEA

The gel permeation chromatography (GPC) analysis of an aqueous solution of potentiodynamically deposited PMAS.(+)-PhEA (Figure 3.12) has shown the main fraction to have a molecular weight of 7,400 Da, with a polydispersity of 1.52. This
molecular weight is somewhat lower than that (10,000 Da) reported [80] for a chemically produced PMAS grown in the presence of ammonia.

Figure 3.12 The GPC molecular weight profile for PMAS deposited potentiodynamically in the presence of (+)-PhEA.

Figure 3.13 UV-vis spectra recorded during the GPC analysis in Figure 3.12.
A 3-dimensional plot showing the UV-vis spectrum of each polymer fraction from the GPC analysis (Figure 3.13) confirmed that there was only one polymeric species in solution (with some distribution of molecular weights), exhibiting the same spectrum as recorded previously for the PMAS.(+)-PhEA polymeric films and solutions.

3.3.10 DC Conductivity of PMAS.(+)-PhEA.

The electrical conductivity of potentiodynamically deposited PMAS.(+)-PhEA pressed into a powder pellet, was found to be 0.01 S cm\(^{-1}\). This is the same as the conductivity recently measured [80] for a PMAS sample polymerised chemically in the presence of ammonia (0.01 S cm\(^{-1}\)). When considering the potential influence of the formation of a helix on the conductivity of a conducting polymer, a number of factors may be taken into account. Formation of a one-handed helix should bring more order into the polymer and increase its crystallinity; and experiments with hot-drawn parent polyaniline films [158, 159] show that conductivity rises with increased crystallinity. On the other hand, the introduction of the bulky (+)-PhEA ammonium ions into the polymer may increase separation of the chains and increase the dihedral angles between the benzene rings in PMAS, so that the conjugation suffers, lowering the conductivity. In the particular case of the optically-active PMAS.(+)-PhEA prepared here, these factors may largely counteract with each other.

3.3.11 Interaction of PMAS.(+)-PhEA Films with Gaseous HCl and Ammonia

For the purpose of potential applications, it is important to know whether the PMAS film retains its chirality after removal of (+)-PhEA. PMAS.(+)-PhEA films were therefore exposed to either gaseous HCl or ammonia vapour in the expectation that this
would lead to substitution of the chiral amine in PMAS with a proton or ammonium cation, respectively.

3.3.11.1 Exposure to Hydrochloric Acid Vapour

Figure 3.14 shows the UV-vis spectra of a PMAS.(+-)PhEA film before and after exposure to HCl vapour for 5 min. The decreased absorption in the 500-1000 nm region and growth of the 350 nm peak relative to the 380 nm peak after HCl exposure are characteristic for the anticipated acidification of the “free” sulfonate groups on the PMAS chain (see Chapter 6).

![Figure 3.14](image)

**Figure 3.14** UV-vis-NIR spectra of a PMAS.(+-)PhEA film exposed to HCl vapour: (1) original film; (2) after 5 min exposure to HCl vapour (over conc. HCl).

The CD spectrum was not changed upon initial exposure to HCl, indicating no immediate racemisation. However, as the film became wet at longer times and the
polymer presumably partially dissolved, the optical activity decreased and disappeared completely after ca. 30 min (Figure 3.15). This is attributed to replacement of the chiral inducing (+)-PhEA cations by protons, and subsequent racemisation of PMAS chains that dissolve in the small amount of water condensed on the surface of the film.

![Figure 3.15](image)

**Figure 3.15** CD spectra of a PMAS.(+)-PhEA film exposed to HCl vapour: (1) original film; (2) after 5 min exposure to HCl vapour (over conc. HCl).

### 3.3.11.2 Exposure to NH₃ Vapour

Ammonia vapour affected PMAS.(+)-PhEA films immediately, causing the polymer to change colour from yellow-brown to blue. The UV-vis-NIR spectra of a PMAS.(+)-PhEA film before and after 30 min exposure to ammonia are presented in Figure 3.16. The colour change was reversible, the film returning to its original yellow-brown colour within 1-2 min after removal from the ammonia vapour.
Although a similar colour change is observed in parent emeraldine salt PAN.HA films treated with base due to dedoping to emeraldine base, it is extremely unlikely that the ammonia vapour caused dedoping of the PMAS. As shown in Chapter 6, fully sulfonated PMAS retains its conductivity (and, consequently, doping) up to pH 14.

Three major changes were observed upon exposure of PMAS.(+)-PhEA to NH₃ vapour: (i) disappearance of the original broad, strong absorption band above 1500 nm as well as the 483 nm peak; (ii) growth of a peak at ca.740 nm; (iii) growth and a red shift of the π→π* transition peaks at 350 and 360 nm and the appearance of a 404 nm peak (that is typical for neutralisation of the “free” sulfonic acid groups in PMAS, see Chapter 6). The spectral changes may be explained in terms of a conformational change of the PMAS chains from an “extended coil” to a “compact coil” conformation. The position of the newly appeared peak at 740 nm may be compared to the 750-800 nm peak

Figure 3.16 UV-vis-NIR spectra of a PMAS.(+)-PhEA film: (1) original film; (2) after 30 min exposure to NH₃ (over conc. NH₃).
normally observed for polyaniline emeraldine salts in a “compact coil” conformation. Similar spectroscopic changes have been observed for aqueous PMAS solutions in the presence of metal salts (see Chapter 5), which we attributed to a similar conformational change of the PMAS main chain.

The CD spectrum of the PMAS.(+)-PhEA film (Figure 3.17) revealed corresponding marked changes during exposure to the NH$_3$ vapour. The original bisignate Cotton effect centered at 480 nm was replaced by more intense bisignate CD bands at 397 and 412 nm, associated with the strong absorption band that appeared at 404 nm. The chiral anisotropy factor increased from 0.56 % at 480 nm in the original film to 1.22 % (at 412 nm) in the ammonia atmosphere. The largest effect was observed after 30 min exposure to NH$_3$; after this time the new CD signals started to diminish, presumably because of racemisation of the polymer as it became wet and partially dissolved. If the film was returned to an ammonia-free atmosphere after a short exposure to NH$_3$, the original CD spectrum (trace 1 in Figure 3.17) was quantitatively restored.
In summary, interaction of a dry PMAS.(+)-PhEA film with NH₃ vapour does not cause immediate racemisation of the polymer, but rather mutarotation to a new conformation / structure with distinct CD signals. This is important for applications where the chiral PhEA amine may be removed allowing another chiral species to access the PMAS surface.

### 3.3.12 Immobilisation of PMAS.(+)-PhEA on Poly(4-vinylpyridine)

PMAS has been shown [160] to form a water-insoluble film with protonated poly(4-vinylpyridine) (PVP) via ionic crosslinking. Using a similar approach, we have now successfully immobilised PMAS.(+)-PhEA as an insoluble film by binding to PVP.
However, when PMAS.(+)-PhEA is used as substrate instead of PMAS, the ionic crosslinking will involve substitution of some of the (+)-PhEA ammonium ions with the protonated PVP. The UV-vis-NIR and CD spectra of the crosslinked PMAS.(+)-PhEA.PVP product (Figures 3.18 and 3.19) were similar to those of the original PMAS.(+)-PhEA film. Nevertheless, the decrease in the number of chiral (+)-PhEA moieties bound to the PMAS chains, together with partial dissolution of PMAS.(+)-PhEA during dipping, caused some racemisation of the chiral PMAS. This is evidenced by the decreased chiral anisotropy factor ($\Delta\varepsilon/\varepsilon$) of 0.27 % for the immobilised PMAS.(+)-PhEA.PVP film (measured at 480 nm) compared to the value (0.35 %) prior to immobilisation.

The UV-Vis spectrum of the immobilised PMAS.(+)-PhEA film (Figure 3.18) also showed some changes, particularly in the $\pi-\pi^*$ transition region. A hypsochromic shift of the absorption in the NIR region suggested a decrease in conjugation length for the immobilised polymer.
Figure 3.18 UV-vis spectra of a potentiodynamically deposited PMAS.(+)-PhEA film: (1) original film; (2) after crosslinking with protonated PVP.

Figure 3.19 CD spectra of the potentiodynamically deposited PMAS.(+)-PhEA film from Figure 3.18: (1) original film; (2) after crosslinking with protonated PVP.
A cyclic voltammogram of the ionically crosslinked PMAS.(+)-PhEA.PVP film in 0.1 M NaN03 (Figure 3.20) showed that the PMAS polymer retained its electroactivity upon immobilisation. Broad oxidation peaks were observed at ca. 0.10 V and 0.45 V, and reduction peaks at ca. 0.20 V and −0.05 V, typical of polyanilines. The immobilised PMAS oxidised more easily than the polymer during growth, as the latter exhibited oxidation peaks at 0.4 and 0.9 V.

![Cyclic voltammogram](image)

**Figure 3.20** Cyclic voltammogram of an immobilised PMAS.(+)-PhEA.PVP film in 0.1 M NaN03 (scan rate 100 mV/s).

### 3.4 Conclusions

The substituted polyaniline, poly(2-methoxyaniline-5-sulfonic acid) (PMAS), can be deposited in a highly optically active form via the potentiodynamic polymerisation of 2-methoxyaniline-5-sulfonic acid in the presence of (R)-(+) or (S)(−)-1-phenylethylamine. Either cyclic voltammetry or square-wave potential pulse
methods may be employed. The enantiomeric amines induce intense, mirror imaged CD spectra for the respective polymer films PMAS.(+)-PhEA and PMAS.(-)-PhEA. This suggests the adoption of preferred one-handed helical structures by the polyaniline chains arising from enantioselective acid-base interactions between the amines and ionised sulfonic acid substituents on the polymer. The polymer after dissolution in water has a molecular weight of 7400 Da, while a dried pellet exhibits a moderate conductivity of 0.01 S cm\(^{-1}\).

Exposure of optically active PMAS.(+)-PhEA films to ammonia vapour leads to major changes in the UV-vis-NIR and CD spectra, which are interpreted in terms of a rearrangement of the PMAS chains from an “extended coil” to a “compact coil” conformation. Chiral PMAS.(+)-PhEA may also be immobilised on protonated PVP while retaining its optical activity and electroactivity.
CHAPTER 4

CHIRALITY INDUCTION IN PRE-FORMED PMAS
VIA ACID-BASE INTERACTION WITH CHIRAL AMINES

4.1 Introduction

As shown in Chapter 3, the presence of the chiral amines \((R)\)\((+)\)- or \((S)\)(-)1-phenylethylamine (PhEA) during electropolymerisation of 2-methoxyaniline-5-sulfonic acid (MAS) resulted in optically active PMAS.(+)-PhEA films. The polymer main chain was believed to be arranged predominantly in either a left- or right-handed helix, depending on the hand of the PhEA employed. This was the first known case of a conducting polyaniline adopting a preferential one-handed chiral conformation during polymerisation as a result of acid-base interactions.

Previously, chiral induction in polymers through acid-base interactions had only been reported for pre-formed polymers, being observed recently with carboxyphenyl substituted polyacetylenes, polyisocyanates and polycarbodiimides [111-114, 148, 149] in solution or in the solid state. Okamoto et al. [111-114] showed that the presence of chiral amines and amino alcohols induced intense, exciton-coupled Cotton effects in the CD spectra of the polymers. The Cotton effects were mirror images in cases when enantiomeric chiral compounds were used, this being attributed to the preferential formation of a left- or right-handed helix by the polymer backbone. The sign and
intensity of the CD bands depended on the configuration and bulkiness of the particular amine or amino alcohol used to induce polymer chirality.

The nature of the split-type CD signals in chiral polythiophenes has been explained by Meijer et al. [148, 149] in terms of interchain exciton interactions. This suggestion was supported by experiments showing the existence of the interchain excitons in conjugated polymers [148, 150-154]. The solubility of a polymer was also found to be an important factor in the formation of a single-handed helix and in the appearance of the exciton-type split CD signals. In a poor solvent Meijer et al. proposed that the polymers form microcrystallites, within which intermolecular excitons are responsible for a bisignate Cotton effect.

In fully sulfonated polyanilines, such as PMAS (4), approximately half of the sulfonic acid groups along the polymer chains do not participate in self-doping, and may form an acid-base association with a chiral base. The purpose of the work described in the present Chapter was to determine whether such acid-base interactions would induce preferential one-handed helical formation in pre-formed PMAS, either in solution or in the solid state.

\[
\begin{align*}
\text{SO}_3^\text{H} & \quad \text{SO}_3^- \\
\text{MeO} & \quad \text{MeO}
\end{align*}
\]

4

A range of chiral amines were examined, namely \((R)-(\pm)\)- and \((S)-(\pm)\)-1-phenylethylamine (PhEA), \((S)-(\pm)\)-N\(\alpha\)-dimethylbenzyl-amine (DMBA), \((S)-(\pm)\)-1-
cyclohexylethylamine (CHEA), (R)-(+)-1-(1-naphthyl)ethylamine (NEA), (S)-(−)-1,1′-binaphthyl-2,2′-diamine (BNDA), as well as the amino alcohols (R)-(−)-2-amino-1-propanol (AP) and (1S,2R)-(−)-2-amino-1,2-diphenylethanol (ADPE). Each of these compounds bears a stereogenic carbon centre adjacent to the amine functional group, except for (S)-(−)-BNDA which possesses axial chirality associated with the carbon-carbon bond linking the two naphthyl moieties.

If successful, such chiral induction would provide a very facile way of preparing optically active polyanilines.
4.2 Experimental

4.2.1 Materials

PMAS (in the ammonium salt form) was obtained from Mitsubishi Rayon Ltd. (Japan) and used as received. The chiral amines (S)-(−)-N,α-dimethylbenzylamine, (S)-(+) -1-cyclohexylethylamine, (R)-(+) - and (S)-(−)-1-phenylethylamine, (R)-(+) -1-(1-naphthyl)ethylamine, (S)-(−)-1,1'-((+)-binaphthyl-2,2'-diamine, and the amino alcohols (1S,2R)-(+) -2-amino-1,2-diphenylethanol and (R)-(−)-2-amino-1-propanol were obtained from Aldrich Chemical Co. and used without further purification.

Glass slides were cleaned with detergent, rinsed with isopropanol and after drying exposed to a UVO-cleaner (Jelight Co., Inc.) for 5 min.

4.2.2 Preparation of PMAS.(RNH₂) Films

PMAS.(RNH₂) films (where RNH₂ = a range of chiral amines and amino alcohols) were cast onto glass slides from an aqueous solution of 3 - 5 % (w/v) PMAS mixed with a chiral amine, as described below. In the case of amines with poor water solubility, the amine was dissolved in an organic solvent prior to addition to the aqueous PMAS solution.

4.2.2.1 Evaporatively Cast Films

(R)-(+) -1-Phenylethylamine was added to a 5 % (w/v) aqueous solution of PMAS in the proportion of 1 amine molecule per two arene rings of PMAS (1:2). This mixture was spread onto glass slides after standing for 1, 10, 30 and 60 min and evaporatively cast as PMAS.(+) -PhEA films via gentle heating with a hair drier for ca. 15 min.
4.2.2.2 Spin-Cast Films

For spin-casting a Photo-Resist Spinner (Headway Research Inc), was used, with a spinning speed of 2000 rpm.

(i) (+)-PhEA, (-)-PhEA, (-)-AP and (+)-CHEA have good water solubility. These were mixed with 5 ml of an aqueous 5% (w/v) PMAS (NH$_4^+$) solution in a 1:2 amine : PMAS ratio. After 2 hrs, the PMAS.(RNH$_2$) polymer films were spin-cast onto glass slides.

(ii) (-)-DMBA was dissolved in 0.5 ml acetone and (+)-ADPE was dissolved in 1 ml acetone, and then each separately mixed with 5 ml of a 5% (w/v) PMAS solution, in a 1:2 amine : PMAS ratio. Samples were spin-cast onto glass slides after 2 hrs.

(iii) 10 mg of (-)-BNDA was dissolved in 1.5 ml acetonitrile and mixed with 1.5 ml of aqueous 3 % PMAS, giving an amine : PMAS ratio of 0.35. The solution was spin-cast after 2 hrs.

(iv) To study the influence of the chiral amine concentration on chirality induction by (+)-PhEA and (-)-DMBA, the amine : PMAS arene ring ratio was decreased from 1:2 to 1:4, 1:8 and 1:16. The rest of the procedure was carried out as described above.

4.2.2.3 Preparation of PMAS. (+)-NEA Films via Dipping Method

When prepared as described in (ii), films with (+)-NEA were opaque due to crystallisation of the amine. For this reason a very thin amine layer was first cast on the glass slide from a solution of 10 mg of (+)-NEA in 1 ml acetone. Then the slide was dipped into a 1 % (w/v) aqueous PMAS solution for 10 min and dried in air.
4.2.3 Crosslinking of PMAS.\(+\)PhEA Films

\(+\)-PhEA was added to PMAS (5 \% \(w/v\)) in the ratios 1:2, 1:4, 1:8 and 1:16, and the solutions made up to 1 \% \(w/v\) PVA (MW 70,000-100,000). Another sample with a PhEA : PMAS ratio of 1:8 was prepared containing 2\% \(w/v\) PVA, 5\% \(w/v\) PMAS. After spin-casting, these films were thermally treated at 150°C for 5 – 10 hrs to induce crosslinking.

4.2.4 UV-vis-NIR and CD Spectroscopic Studies

The glass slides covered with the above PMAS.\(\text{(RNH}_2\) polymer films were kept in a desiccator over silica gel. Their UV-vis-NIR spectra were recorded at room temperature using a Cary 500 spectrophotometer. CD spectra were recorded using a Jobin Yvon Dichrograph 6.

4.3 Results and Discussion

4.3.1 Chiroptical Properties of PMAS.\(+\)PhEA in Solution

An aqueous mixture of PMAS with \(+\)-PhEA \((\text{amine : PMAS ratio 1:2})\) had a UV-vis-NIR absorption spectrum (Figure 4.1) very similar to that of PMAS.\(\text{(NH}_4^+)\), showing a characteristic intense band at 483 nm. The spectrum was little affected by filtration. However, the corresponding CD spectrum (Figure 4.2) was dramatically affected by filtration through 0.45 \(\mu\)m filter. The unfiltered solution exhibited a CD spectrum similar (but of lower intensity) to that found in Chapter 3 for PMAS.\(+\)-PhEA films. Bisignate CD signals were seen centered at ca. 500 nm, associated with the PMAS absorption band at 483 nm, together with weaker CD signals at lower wavelengths.
associated with the broad absorptions of PMAS in the 330 – 380 nm region. In marked contrast, the filtered solution of the PMAS.(+)-PhEA polymer did not exhibit optical activity. This observation supports the conclusions of Meijer [148, 149] that helical π-conjugated polymers exhibit Cotton effects only in a microcrystalline form, as a result of poor solubility. Presumably, filtering removes microparticles of PMAS.(+)-PhEA responsible for the optical activity observed in the unfiltered mixture. Data obtained by Okamoto et al. [111-114] for the magnitude of the Cotton effect in chiral polyacetylenes in different solvents also agree with this idea.

![Figure 4.1 UV-vis-NIR spectra of an aqueous PMAS.(+)-PhEA solution: (1) unfiltered and (2) filtered.](image-url)
Figure 4.2 CD spectra of the PMAS.(+)-PhEA solution from Figure 4.1 recorded ca. 1 hr after mixing: (1) unfiltered and (2) filtered.

4.3.2 Chiroptical Properties of PMAS.(+)-PhEA Films Cast on Glass

(i) Evaporatively cast films

The UV-vis-NIR spectra of PMAS.(+)-PhEA films evaporatively cast onto glass were essentially the same as the spectra obtained for evaporatively cast PMAS.(NH₄⁺). The spectra observed for films cast 1, 10, 30 and 60 min after mixing were virtually superimposable. The most characteristic features (Figure 4.3) were a sharp, intense peak at ca. 480 nm and a strong broad absorption band above 1000 nm (sometimes having a maximum at 1500 - 2000 nm), associated with the PMAS polymer. The π–π* transition peaks for the PMAS between 300 and 400 nm were not clearly identified because of the substrate absorption increasing non-linearly below 350 nm.
The CD spectra of the evaporatively cast PMAS.(+)-PhEA films (Figure 4.4) were qualitatively similar to the electrochemically deposited PMAS.(+)-PhEA films described in Chapter 3. Bisignate exciton-coupled Cotton CD bands were observed at 505 nm and 475 nm associated with the PMAS absorption band at 480 nm, together with CD bands at ca. 405 nm and 310 nm associated with the absorption bands of PMAS at 330-380 nm. These CD bands do not arise from the chiral (+)-PhEA ammonium ion present in the films, as this only absorbs in the UV region. The visible region CD spectra of the PMAS.(+)-PhEA films may therefore be attributed to macroasymmetry in the sulfonated polyaniline chains of PMAS. As proposed in Chapter 3 for the electrochemically deposited PMAS.(+)-PhEA films, the induction of optical activity in PMAS is believed to arise from electrostatic bonding of the chiral ammonium ion of (+)-PhEA to ionised sulfonate groups along the PMAS backbone, causing the polymer to preferentially adopt a one-handed helical structure.

Comparison of Figure 3.4 in Chapter 3 and Figure 4.4 does, however, reveal some differences between the CD spectra of the evaporatively cast films of PMAS.(+)-PhEA and those grown electrochemically. Most notable are (i) the increased relative intensity of the CD signals in the 300-430 nm region for the cast films, and (ii) the relatively weak high wavelength component of the bisignate CD signals centered at ca. 500 nm. These differences presumably reflect differences in molecular structure. In this respect, it may be noted that GPC measurements in Chapter 3 have shown the molecular weight of electrochemically produced PMAS.(+)-PhEA (ca. 7,400 Da) to be lower than the 10,000 Da reported [80] for the as received PMAS (NH₄⁺) used in this Chapter.
Figure 4.3 UV-vis-NIR spectrum of a PMAS.(+)-PhEA film evaporatively cast onto a glass slide.

Figure 4.4 CD spectra of the PMAS.(+)-PhEA films evaporatively cast onto glass slides. Times shown are the periods between mixing and casting.
A striking feature of Figure 4.4 is the marked increase in optical activity of the PMAS.(+)-PhEA films with an increase in the time that the PMAS / (+)-PhEA mixtures were allowed to stand before casting. Films cast immediately after mixing were only mildly optically active. These results indicate that the rearrangements (perhaps involving aggregation of PMAS chains) that lead to chiral induction are relatively slow. In contrast, the time passed after the films were cast did not affect their optical activity.

The increase in optical activity with the delay time before casting is quantified in Table 4.1 in terms of the chiral anisotropy coefficients \( g = \Delta \varepsilon / \varepsilon \) for the PMAS.(+)-PhEA films. The \( g \) values were calculated for the CD band at 475 nm in each case using data from Figures 4.3 and 4.4. They are seen to increase from 0.12 % at 1 min to 0.60 % at 30 min, with a further small increase in optical activity at 60 min. These latter \( \Delta \varepsilon / \varepsilon \) values are similar to those obtained for potentiodynamically deposited PMAS.(+)-PhEA films described in Chapter 3. For this reason, in all following experiments the films of polymer were spin-cast onto glass some 1 to 2 hrs after mixing with a chiral amine.

Table 4.1 Chiral anisotropy factor (\( \Delta \varepsilon / \varepsilon \)) for PMAS.(+)-PhEA films evaporatively cast after various lengths of time.

<table>
<thead>
<tr>
<th>Time, min</th>
<th>( \Delta \varepsilon / \varepsilon ) (at 475 nm), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.12</td>
</tr>
<tr>
<td>10</td>
<td>0.24</td>
</tr>
<tr>
<td>30</td>
<td>0.60</td>
</tr>
<tr>
<td>60</td>
<td>0.66</td>
</tr>
</tbody>
</table>
(ii) Spin-cast films

Spin-casting of similar aqueous PMAS / PhEA solutions gave more even polymer films than those evaporatively cast as above. The UV-vis-NIR spectra of spin-cast films of PMAS.(+)-PhEA and PMAS.(-)-PhEA (Figure 4.5) were similar to the spectrum of evaporatively cast PMAS.(+)-PhEA (Figure 4.3).

![UV-vis-NIR spectra](image)

Figure 4.5 UV-vis-NIR spectra of PMAS.PhEA films spin-cast from aqueous 5 % (w/v) PMAS / (+)-PhEA (1) and PMAS / (-)-PhEA (2) (amine : PMAS ratio 1:2). The films were spin-cast 1 hr after mixing.

The CD spectra of the spin-cast PMAS.(+)-PhEA and PMAS.(-)-PhEA films (Figure 4.6) differed in an important manner from analogous evaporatively cast and electrochemically deposited films (see Figures 3.4 and 4.4), namely the almost complete disappearance of the high wavelength component of the previously observed bisignate CD signals at ca. 500 nm. This Cotton effect is associated with the PMAS polaron absorption band observed at 480 nm. The failure to observe significant Davydov
splitting of the CD band indicates only minor exciton coupling between the responsible chromophores, either on the same or adjacent PMAS chains. One may therefore conclude that the polaron chromophores in PMAS are more separated in spin-cast films. It is uncertain at present why spin-casting should cause this effect, although MacDiarmid et al. [161] have recently suggested that the shear forces in spin-casting can lead to disentanglement of polyaniline chains and a more “extended coil” conformation.

Figure 4.6 CD spectra of the PMAS.(+)-PhEA and PMAS.(-)-PhEA films from Figure 4.5.

A spin-cast PMAS.(-)-PhEA film exhibited the expected mirror image CD spectrum to PMAS.(+)-PhEA, indicating that the enantiomeric (+)- and (-)-PhEA amines induce opposite helical senses in the PMAS chains.
4.3.3 Chiroptical Properties of Other Spin-Cast PMAS.(RNH$_2$) Films

4.3.3.1 Chiral Amines as Inducing Agents

(i) UV-Vis-NIR spectra of spin-cast films of PMAS associated with (S)-(−)-DMBA and (S)-(−)-CHEA are shown in Figure 4.7. Both films displayed characteristic features of PMAS cast on glass, having a sharp peak at ca. 465 nm and a broad, strong band in the NIR region with $\lambda_{\text{max}}$ at ≥ 2050 nm.

![Figure 4.7 UV-vis-NIR spectra of PMAS.(RNH$_2$) films spin-cast from mixtures of PMAS with (+)-CHEA (1) and (-)-DMBA (2) (amine : PMAS ratio 1:2).](image)

The CD spectra of the spin-cast PMAS.(+)-CHEA and PMAS.(−)-DMBA films (Figures 4.8 and 4.9) showed similar features to the PMAS.(+)-PhEA film, including a virtual absence of bisignate CD bands. Their most characteristic feature was a negative CD band at ca. 480 nm and 495 nm, respectively. Interestingly, this is the same sign as for
the PMAS.(+)-PhEA film, despite the opposite configuration (S) of the (+)-CHEA and (-)-DMBA amines compared to (R)-(+)PhEA.

The PMAS.(+)-CHEA film had a similar $\Delta \varepsilon/\varepsilon$ value (0.23 %) to that of PMAS.(+)-PhEA (0.22 %) (see Table 4.2), indicating that the presence of a saturated cyclohexyl ring in the incorporated amine instead of a phenyl ring had little influence on the magnitude of chiral induction in the PMAS chains. The PMAS.(-)-DMBA film was the most optically active of the spin-cast polymers, with a $\Delta \varepsilon/\varepsilon$ value (at 495 nm) of 1.09 % (see Table 4.2). The marked increase in chiral induction caused by the $N$-methyl substituent in this secondary amine compared to (+)-PhEA has parallels in other studies of chiral discrimination [177].

![Figure 4.8 CD spectrum of the PMAS.(+)-CHEA film from Figure 4.7.](image)
(ii) In contrast, PMAS.(-)-BNDA was the least optically active of the spin-cast polymers obtained. Its UV-vis-NIR spectrum (Figure 4.10) was similar to that of PMAS (NH₄⁺) and other spin-cast PMAS.(RNH₂) films, and was not affected by the presence of acetonitrile in the casting mixture. From its CD spectrum (Figure 4.11), a Δε/ε value of 0.07 % was calculated for the weak CD band at ca. 485 nm.
Figure 4.10 UV-vis-NIR spectrum of a spin-cast PMAS.(-)-BNDA film.

Figure 4.11 CD spectrum of the PMAS.(-)-BNDA film from Figure 4.10.
The source of chirality in (S)-(-)-BNDA is the chiral axis between the two naphthylamines moieties, rather than the stereogenic centre present in the other amines examined. In addition, it possesses two amine centres, which may give enhanced possibilities for acid-base interactions with SO$_3$H groups on PMAS chains. Nevertheless, chiral induction by this diamine is apparently hindered by its bulky nature.

(iii) The PMAS.(+)-NEA film had to be prepared differently, namely via adsorption of PMAS onto (+)-NEA cast on a glass slide. The difference in method again did not significantly affect the UV-vis-NIR spectrum of the resultant polymer (Figure 4.12), and its CD spectrum (Figure 4.13) showed the film to be optically active with a spectrum broadly similar to that obtained above for the spin-cast film formed from PMAS.(+)-PhEA. However, its $\Delta\epsilon/\epsilon$ value was much lower (Table 4.2). Since Okamoto et al. [113] found the more sterically demanding naphthylamine (+)-NEA to be a better chiral inducing agent for poly{(4-carboxyphenyl)acetylene} than the related phenylethylamine (+)-PhEA, the lower chiral anisotropy factor found here for PMAS.(+)-NEA probably arises from the different method employed for its preparation.
Figure 4.12  UV-vis-NIR spectrum of a PMAS.(+)-NEA film prepared via adsorption of PMAS onto a (+)-NEA film.

Figure 4.13  CD spectrum of the PMAS.(+)-NEA film from Figure 4.12.
4.3.3.2 Chiral Amino Alcohols as Inducing Agents

The UV-vis-NIR spectra of PMAS.(-)-AP and PMAS.(+)-ADPE films spin-cast onto glass slides (Figure 4.14) were similar to the spectra of the previous PMAS.(RNH₂) films, with characteristic peaks at ca. 470 nm. Their CD spectra (Figures 4.15 and 4.16) exhibited well-defined bands at 480 nm and broad weak bands in the 350-450 nm region. The absence again of bisignate CD signals indicated no exciton coupling between the responsible chromophores, either on adjacent or the same PMAS chains.

Okamoto et al. [113] reported that chiral amino alcohols induced substantially stronger signals in the CD spectra of poly{(4-carboxyphenyl)acetylene} than did amines. They attributed this to additional H-bond formation between the hydroxy group and the carboxyl substituent of the polyacetylene. This trend was not confirmed in the present study with (-)-2-amino-1-propanol, which exhibited a lower Δε/ε value (0.13 %) than found with (+)- or (-)-PhEA (see Table 4.2). However, the amino alcohol (+)-ADPE did show significantly enhanced chiral induction compared to all the amines studied (except the secondary amine (-)-DMBA), the PMAS.(-)-ADPE film having a chiral anisotropy factor of 0.57 %.
Figure 4.14 UV-vis-NIR spectra obtained for PMAS,(amino alcohol) films formed from mixtures of PMAS with (-)-AP (1) and (+)-ADPE (2) (with an amino alcohol : PMAS ratio of 1:2).

Figure 4.15 CD spectrum of the PMAS,(-)-AP film from Figure 4.14.
There was no obvious correlation between the configuration at the stereogenic centre of each chiral amine and amino alcohol and the sign of the CD signal for PMAS. (RNH$_2$) films. For example, although (R)-PhEA, (R)-NEA and (R)-AP each led to polymer films exhibiting a negative CD band at ca. 480 nm, so did (S)-CHEA and (S)-DMBA with the opposite configuration.

**Figure 4.16** CD spectrum of the PMAS.(+)-ADPE film from Figure 4.14.
Table 4.2 Chiral anisotropy factors ($\Delta \varepsilon / \varepsilon$) obtained for chiral PMAS,(RNH$_2$) films
{with amine(amino alcohol) : PMAS ratio of 1:2}.

<table>
<thead>
<tr>
<th>Amine (amino alcohol) employed</th>
<th>$\Delta \varepsilon / \varepsilon$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-NEA (amine : PMAS ratio unclear)</td>
<td>0.01</td>
</tr>
<tr>
<td>(-)-BNDA</td>
<td>0.07</td>
</tr>
<tr>
<td>(+)-PhEA</td>
<td>0.22</td>
</tr>
<tr>
<td>(-)-PhEA</td>
<td>0.21</td>
</tr>
<tr>
<td>(+)-CHEA</td>
<td>0.23</td>
</tr>
<tr>
<td>(-)-DMBA/acetone</td>
<td>1.09</td>
</tr>
<tr>
<td>(-)-AP</td>
<td>0.13</td>
</tr>
<tr>
<td>(+)-ADPE/acetone</td>
<td>0.57</td>
</tr>
<tr>
<td>(+)-PhEA, 1% PVA</td>
<td>0.22</td>
</tr>
<tr>
<td>(-)-DMBA/acetone, 1% PVA</td>
<td>0.37</td>
</tr>
</tbody>
</table>

4.3.4 Influence of the Amine : PMAS Ratio

It was found that a 4-fold decrease in the amine concentration did not reduce the degree
of chirality induced in the PMAS polymer. The results for films prepared with (+)-
PhEA and (-)-DMBA are presented in Table 4.3.
Table 4.3 Chiral anisotropy factors ($\Delta \varepsilon / \varepsilon$) obtained for PMAS.(RNH$_2$) films for different amine : PMAS ratios.

<table>
<thead>
<tr>
<th>Amine employed</th>
<th>amine : PMAS ratio</th>
<th>$\Delta \varepsilon / \varepsilon$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-PhEA</td>
<td>1:2</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>1:4</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>1:8</td>
<td>0.57</td>
</tr>
<tr>
<td>(-)-DMBA</td>
<td>1:2</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>1:4</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>1:8</td>
<td>0.31</td>
</tr>
</tbody>
</table>

4.3.5 Crosslinking of PMAS.(+)-PhEA with PVA

PMAS may be crosslinked with polyvinylalcohol (PVA) when spin-cast films are heated at 150°C for at least 5 hrs [162]. Chemically synthesised PMAS from Mitsubishi Rayon Ltd is largely in the ammonium salt PMAS (NH$_4^+$) form (see Chapter 5). During heating the ammonia from the PMAS is removed, leaving the sulfonic acid groups available for bonding with PVA.

With the PMAS.(+)-PhEA films obtained in the present Chapter, all sulfonic groups not participating in self-doping are believed to be bound to PhEA. It was therefore necessary to reduce the PhEA content to leave sites for reaction with PVA. Fortunately, it has been shown earlier (Section 4.3.4) that even quite low (+)-PhEA content does not lead to reduced optical activity in the PMAS.(+)-PhEA films.
It was found that samples with (+)-PhEA:PMAS ratios of 1:2 and 1:4 cast from 5% (w/v) PMAS / 1 % PVA solution did not crosslink even after 24 hr heating at 150°C. However, using samples with a 1:8 PhEA:PMAS ratio resulted in formation of an insoluble film after 10 hrs heating, and the 1:16 ratio sample after 5 hr heating. When the concentration of the PVA crosslinker was raised to 2 % (w/v), 5 hrs heating became sufficient to obtain an insoluble film. The UV-vis-NIR spectra of the above PMAS.(+)-PhEA films are shown in Figure 4.17, while the CD spectra before and after crosslinking are given in Figure 4.18.

The spectral characteristics of PMAS changed in the presence of PVA, though thermal treatment alone did not affect either the absorption or CD spectra substantially. The original sharp absorption band at 483 nm became significantly reduced, while absorption in the region between 500 and 800 nm was increased (Figure 4.17). In addition, the broad delocalised polaron band with a $\lambda_{\text{max}}$ at ca. 2300 nm in untreated PMAS.(+)-PhEA was strongly blue shifted to ca. 1500 - 1600 nm in the presence of PVA.

The CD spectra showed only one broad Cotton effect at ca. 400 nm after crosslinking and there was a marked drop in ellipticity (Figure 4.18) compared to the films without PVA.
Figure 4.17 UV-vis-NIR spectra of crosslinked PMAS.(+)-PhEA.PVA films (with PhEA:PMAS ratio of 1:8), spin-cast from aqueous: (1) 5% PMAS / 1% PVA; (2) 5% PMAS / 2% PVA.

Figure 4.18 CD spectra of the PMAS.(+)-PhEA.PVA films (with PhEA:PMAS ratio 1:8): (1) 5% PMAS / 1% PVA, before crosslinking; (2) same film, crosslinked; (3) 5% PMAS / 2% PVA, before crosslinking; (4) same film, crosslinked.
4.4 Conclusions

It has been shown that in aqueous solution PMAS bonds to the chiral amine, (+)-PhEA, and exists as a racemic mixture of presumably left- and right-hand oriented helices of PMAS.(+)-PhEA. However, after casting upon a substrate, a preference for one hand of the helical chains appears, giving a polymer with main chain chirality.

A wide range of chiral amines and amino alcohols are similarly found to associate with PMAS in aqueous solution, from which chiral PMAS.(RNH₂) films can be evaporatively or spin-cast. The CD spectra of these PMAS.(RNH₂) polymer films show Cotton effects in the region between 300 and 700 nm, where the amines and amino alcohols have no electronic absorption. This confirms induction of chirality in the PMAS chains by the incorporated amines and amino alcohols. The CD spectra of the spin-cast films studied, however, are different from those of the electrochemically polymerised PMAS.(+)-PhEA and PMAS.(-)-PhEA, studied in Chapter 3, since the latter exhibit bisignate Cotton effects. The absence of bisignate CD bands indicates that spin-casting causes the loss of exciton coupling between chromophores on either the same or adjacent PMAS chains.

Employment of the secondary amine (-)-DMBA instead of the related primary amine (-)-PhEA, leads to significantly increased chiral induction in the PMAS chains. The presence of bulky substituents, such as in the binaphthyl diamine (-)-BNDA, however, apparently interferes with the chiral induction and gives less optically active films. With chiral amino alcohols an increasing effect upon the induced chirality in PMAS is observed with increased bulkiness of the amino alcohol molecule and/or the
introduction of a second chiral centre. Overall, there is no clear correlation between the sign of the CD signals for spin-cast PMAS. (RNH₂) films and the configuration of the stereogenic centre of the chiral amine employed.

Although losing their optical activity when dissolved in water, the chiral PMAS.(+)-PhEA films may be crosslinked with PVA after thermal treatment, making them insoluble in water. The presence of PVA in the casting solution, however, significantly lowers the intensity of optical activity in the resultant PMAS.(+)-PhEA.PVP films.
5.1 Introduction

Polyelectrolytes are known to have a variable degree of chain extension depending on their interaction with solvents [163, 164]. A low net charge on the polymer, e.g. when ionisable functional groups are weakly dissociated, decreases solubility in polar solvents, giving the polymer a “compact coil” shape. When the degree of dissociation of the functional groups attached to the polymeric backbone increases, this leads to the growth of the polymer charge, and electrostatic repulsion between the functional groups causes the polymer to adopt an “extended coil” conformation.

The hydrocarbon backbone of a polyelectrolyte such as poly(styrenesulfonate) (PSS) is hydrophobic. Insolubility is a result of the increased order of the water structure around a hydrocarbon polymeric backbone. The entropy of the system decreases upon dissolution of a hydrophobic backbone, so the Gibbs energy of the dissolution is positive. The dependence of the Gibbs energy of dissolution on the degree of order of the solvent has an important implication when we consider an electrolyte solution as a solvent for the polyelectrolyte. Very dilute solutions of polyelectrolytes in aqueous electrolytes often exhibit a behaviour closely resembling that of neutral polymers in solution [165].

The addition of a low molecular weight electrolyte, such as a metal salt, has a two-fold effect upon a polymeric electrolyte in solution. Cations screen electrostatic repulsion of
the ionised functional groups along the polymer chain, thus favouring the contraction of the chain. The influence of the anions present in solution is important in terms of their ability to modify the water structure. As the chaotropic effect of salts present in solution becomes more pronounced in the order Cl\(^-\) < Br\(^-\) < NO\(_3\)^- < I\(^-\) < SCN\(^-\), the hydrophobic assemblage of non-polar substances is disrupted, increasing their solubility in water. This chaotropic effect is extensively documented for proteins [166] and some helical polymers [167], and has a major influence on their conformation. The effect has been observed in polyacrylamide-based ionic gels, which have shown reversible volume transitions upon ionisation [168].

The influence of the anion present upon the dimensions of the polyvinylpyridine (PVP) polycation has been studied [169], the size changing dramatically with transition from F\(^-\) to I\(^-\). The counter-cation also affected the polymer conformation, in this case as a consequence of the alteration of the solvent quality; Na\(^+\) and K\(^+\) having a more prominent effect than Li\(^+\) and Cs\(^+\). It was not possible to salt out NaPSS from concentrated NaCl, neither was it possible to dissolve or precipitate PVP in concentrated NaCl solutions.

Conducting organic polymers in their oxidised state, e.g. PAn in its emeraldine salt (PAn.HA) form, may also be considered as polyelectrolytes since they bear positive charges along their polymer chains. However, unlike proteins, there have been no reports to date exploring the influence of added metal salts on the conformation of conducting polymers in aqueous solution. The insolubility of the vast majority of conducting polymers in water has precluded such studies.
However, recent studies on PAN.(+)-HCSA emeraldine salt in a range of organic solvents have shown that the conformation adopted by the polyaniline is very sensitive to its environment, such as the nature of the solvent or added “secondary dopants” [170]. The PAN.(+)-HCSA polymers are believed to adopt an “extended coil” conformation in a good solvent, while a decrease in solubility in poor solvents causes the polymer chain to contract to a “compact coil” conformation. UV-vis-NIR and CD spectra proved useful in assigning the polymer conformations. For example, based on previous studies by MacDiarmid et al. [33], an “extended coil” conformation for polyaniline is believed to be characterised by a delocalised high-wavelength polaron absorption band spread broadly above 1000 nm, while in a “compact coil” conformation this latter band appears as a relatively sharp peak between 700 and 900 nm.

In chiral polythiophenes, variations in polymer conformation with solvent have also been observed using CD spectroscopy [171]. For other polymers, e.g. polyacrylates, conformational changes may be determined only by viscosity measurements or static light scattering experiments [165].

The water-soluble self-doped polymer, poly(2-methoxyaniline-5-sulfonic acid) (PMAS) (4), has readily ionisable sulfonic acid groups on each aniline ring and resultant high solubility in water. This polymer therefore appears to provide an excellent material with which to explore the influence of added metal salts on the conformation of conducting polymers. The results described in this Chapter indeed reveal remarkable and unprecedented ionochromism when a range of metal salts are added to aqueous solutions of PMAS. The normally yellow/brown colour of PMAS in aqueous solution
changes to blue or green, the extent and rate of the colour change varying with the nature of the metal cation and the anion of the added salts.

\[
\text{MeO} \quad \text{MeO} \\
\text{SO}_3\text{H} \quad \text{SO}_3^- \\
\text{NH} \quad \text{NH} \\
\text{MeO} \quad \text{MeO} \\
\text{n}
\]

4

5.2 Experimental

5.2.1 Materials

All experiments in this Chapter used chemically synthesised PMAS purchased from the Mitsubishi Rayon Ltd. Three forms of the polymer were used: the ammonium salt (as received), the acid form and dialysed polymer. The acid form of PMAS, as represented in structure 4, was prepared from the as received ammonium salt by ion exchange using an Amberlite IR-120 ion-exchange resin. A cellulose membrane with a 12,000 Da cut-off was used for the dialysis (during 3 days) of a 1 % (w/v) aqueous solution of the as received PMAS (NH$_4^+$) polymer. The alkali and alkaline earth metal salts were obtained from Ajax Ltd.

5.2.2 Ionochromism Studies with PMAS

For monitoring the spectral changes in various ionic media, aqueous PMAS was added to 1.0 M aqueous solutions of the appropriate metal salts. Typically the resultant PMAS concentration was between $4 \times 10^{-5}$ and $6 \times 10^{-5}$ M, based on a dimer repeat unit. The
PMAS concentrations were determined from the intensity of the characteristic absorption band at 473 nm (see Section 2.4.1). The electronic spectra were recorded between 250 and 1300 nm on a Varian Cary 500 spectrophotometer, generally at room temperature (ca. 21°C) unless otherwise stated.

5.2.3 Preparation of Alkaline Earth Metal Salts of PMAS
Calcium, magnesium and barium salts of PMAS were precipitated from a 1% (w/v) PMAS solution by adding sufficient MC12 to give a 1.0 M solution. After standing overnight, the precipitates were separated by centrifugation and washed with copious amounts of water. The powders were then dried in a desiccator under vacuum over silica gel.

5.2.4 Electrical Conductivity Measurements
The DC conductivity of the PMAS (Ba2+) salt was determined using the Van der Pauw method described in Chapter 2 (Section 2.4.3). The pellets for conductivity measurements were prepared by pressing the polymer powders using a 6 ton press.

5.2.6 Metal Ion Analysis
The barium ion content of the PMAS (Ba2+) sample prepared above was determined by atomic absorption spectroscopy, as described in Chapter 2 (Section 2.4.7).
5.3 Results and Discussion

5.3.1 UV-vis-NIR Spectroscopy of Aqueous PMAS

The electronic spectrum of an aqueous solution of PMAS showed four peaks (Figure 5.1). It did not change significantly after standing at room temperature for a week. Overlapping bands between 320 and 390 nm may be attributed to \( \pi-\pi^* \) transitions, their relative ratios being indicative of the proportion of sulfonic acid protons substituted with ammonia cations. In the acid form of PMAS (free of ammonium ions) only one peak at ca. 360 nm was present, while in the partially neutralised ammonium salt of PMAS both 320 and 390 nm peaks were partly observed. The characteristic sharp peak at 473 nm is assigned as a polaron band, being considerably red-shifted compared to the low wavelength polaron band observed in unsubstituted PAn.HA emeraldine salts [9, 34]. The absence of a further localised polaron band in the region 750 – 900 nm and the presence instead of a broad absorption band above 1000 nm suggests a delocalised polaron band, typical for emeraldine salts in an “extended coil” conformation.

The acidic pH (ca. 3.7) of aqueous solutions of the as received form of the PMAS polymer confirmed that only some of the “free” sulfonic acid protons were substituted with ammonium cations. On the other hand, the acid PMAS(H\(^+\)) form had a pH of 2.1, while the dialysed form of PMAS exhibited a pH of 5.9.
Figure 5.1 UV-Vis-NIR spectra of PMAS in solution: (1) acid form, (2) ammonium salt; (3) dialysed form; [PMAS] = 6 x 10^{-5} M.

5.3.2 Spectral and Associated Structural Changes for PMAS in the Presence of Metal Salts

The influence of added metal salts on the UV-vis-NIR spectrum of PMAS was monitored in 1.0 M aqueous solutions of the following salts:

LiCl, NaCl, KCl, CsCl, NaBr, NaI, KBr;

Na_{2}SO_{4};

KSCN, NaSCN;

CaCl_{2}, MgCl_{2}, BaCl_{2}.  
The presence of added metal salts generally caused the colour of dilute PMAS solution to change from yellow/brown to blue. Typical behaviour was observed in 1.0 M NaCl solution (Figure 5.2).

Figure 5.2 UV-vis-NIR spectra of PMAS (dialysed): (1) in water; (2) after 22 hrs in 1.0 M NaCl at room temperature; [PMAS] = 6 x 10^-5 M.

Within 22 hrs the original sharp band at 473 nm and the NIR absorption of the initial PMAS was replaced by a spectrum typical of PAN.HA emeraldine salts in the "compact coil" conformation. The characteristic intense band that grew at 748 nm may be assigned as the expected high wavelength polaron band, while the second polaron transition and the \(\pi-\pi^*\) transition appear as overlapping bands in the 330-390 nm region.
A closer examination of these NaCl-induced transformations of PMAS showed that they occurred in two distinct steps:

(1) A fast step (typically a few minutes) in which (i) a decrease occurred in the initial PMAS 473 nm band as well as a small decrease in the NIR region; and (ii) distinct peaks appeared at ca. 330 and 385 nm (Figure 5.3). These rapid spectral changes are extremely similar to those observed for PMAS when the pH was raised from 3.6 to 8.0 (see Chapter 6, Figure 6.3). They have therefore been tentatively attributed to replacement of protons from “free” SO$_3$H groups on the PMAS chains, leading to changes in conformation/structure arising perhaps from decreased H-bonding interactions.

![Figure 5.3 UV-vis spectra of PMAS (NH$_4^+$): (1) in water and (2) immediately after added to 1.0 M NaCl; [PMAS] = 4.0 x $10^{-5}$ M.](image)
(2) A slow step (typically a few hours to a few days) in which the 473 nm and NIR peaks vanished and a strong peak grew at 748 nm, together with further growth of peaks in the 330-390 nm region (Figure 5.4). Sharp isosbestic points were observed at 1045 nm, 500 and 395 nm throughout this slow second step, consistent with a clean interconversion from the “extended coil” to the “compact coil” conformation of the PMAS. This conversion may be facilitated by interchain binding of Na\(^+\) to “free” SO\(_3^-\) groups on the PMAS chains.

Figure 5.4 UV-vis-NIR spectral changes for PMAS (NH\(_4^+\)) in 1.0 M NaCl (slow second step); [PMAS] = 4 \times 10^{-5} \text{ M}.

The rate of spectral changes depended on the form of PMAS employed, increasing with a decrease in the polymer acidity and being largest for the dialysed PMAS, i.e. showing the overall rates: PMAS (dialysed) > PMAS (NH\(_4^+\)) > PMAS (H\(^+\)). This trend may be
clearly seen when comparing the charts obtained for the dialysed form of PMAS (Figure 5.5), PMAS (\(\text{NH}_4^+\)) (Figure 5.4) and the acid form of PMAS (Figure 5.6).

Figure 5.5 UV-vis-NIR spectral changes for PMAS (dialysed) added to 1.0 M NaCl.
Figure 5.6 UV-vis-NIR spectral changes for PMAS (H⁺) added to 1.0 M NaCl.

5.3.2.1 Influence of the Nature of the Metal Cation

The influence of the metal cation was examined using a range of alkali metal and alkaline earth metal chloride salts. In each case, the changes in the UV-vis-NIR spectra of PMAS proceeded via two distinct steps, as observed above in 1.0 M NaCl.

In the rapid first stage, the results in Figure 5.7 show that the 473 nm peak decrease became more pronounced along the series: \( \text{Li}^+ < \text{K}^+ < \text{Na}^+ < \text{Cs}^+ \).
Figure 5.7 UV-vis-NIR spectra of PMAS (dialysed) immediately after adding to 1.0 M MCl; [PMAS] = 4.0 x 10^{-5} M.

Related studies with alkaline earth metal chlorides led to the following overall order for the rapid initial decrease in the 473 nm band:

\[ \text{Li}^+ < \text{K}^+ < \text{Na}^+ < \text{Ba}^{2+} < \text{Cs}^+ < \text{Mg}^{2+} < \text{Ca}^{2+}. \]

In the slow second stage, however, the above order of cation activity was not followed, the rate of growth of the peak at 740-770 nm increasing along the series:

\[ \text{Cs}^+, \text{Li}^+ < \text{K}^+ < \text{Ca}^{2+} < \text{Ba}^{2+} < \text{Na}^+. \]

For example, examination of the spectral changes in Figure 5.8 for PMAS in 1.0 M KCl shows them to be considerably slower than the corresponding changes in 1.0 M NaCl seen in Figure 5.5. The UV-vis-NIR spectra recorded 24 hrs after mixing PMAS with each of the alkali metal salts (Figure 5.9) clearly illustrate the marked differences in the rates of spectral change with the different metal cations employed.
Figure 5.8 UV-vis-NIR spectral changes for PMAS (dialysed) added to 1.0 M KCl.

Figure 5.9 UV-vis-NIR spectra of PMAS (dialysed) recorded 24 hrs after adding to 1.0 M MCI.
Especially slow changes occurred in 1.0 M LiCl (Figure 5.10) requiring more than 20 days for completion. Between 3 and 250 hrs, isosbestic points were observed at 505 and 355 nm, again consistent with a clean interconversion between different conformations of the PMAS polymer. Similarly, in 1.0 M CsCl (Figure 5.11) it required more than 30 days to complete the conformational change in the dialysed form of PMAS.

Comparison of the spectra recorded at the same time (9 days) for different forms of PMAS in 1.0 M LiCl (Figure 5.12) confirmed the dependence of the rate of change on the acidity of PMAS, as shown earlier for 1.0 M NaCl (i.e. PMAS (dialysed) > PMAS (NH$_4^+$) > PMAS (H$^+$)).

![Figure 5.10](image.png)  
**Figure 5.10** UV-vis-NIR spectral changes for PMAS (dialysed) added to 1.0 M LiCl.
Figure 5.11  UV-vis-NIR spectral changes for PMAS (dialysed) added to 1.0 M CsCl.

Figure 5.12  UV-vis-NIR spectra of PMAS recorded 9 days after adding to 1.0 M LiCl.
Similar UV-vis-NIR spectral changes occurred for aqueous PMAS in the presence of *alkaline earth metal salts*. For example, Figures 5.13 and 5.14 show the changes observed in 1.0 M CaCl₂ and BaCl₂, respectively. The λ_{max} of the high wavelength polaron band that appeared after 24 hrs in the presence of CaCl₂ (at ca. 770 nm) was significantly higher than that observed (at ca. 730 nm) in the presence of BaCl₂. Interestingly, in 1.0 M MgCl₂ little or no growth of a high wavelength polaron band occurred, indicating that conversion to the “compact coil” conformation of PMAS did not occur (Figures 5.15 and 5.16). The colour of the solution also did not change. A flaky precipitate, presumably the Mg^{2+} salt of PMAS, began to form after several days. A gradual decrease in the intensity of the original PMAS absorption bands was consequently observed.

![Figure 5.13](image)

**Figure 5.13** UV-vis-NIR spectral changes for PMAS (NH₄⁺) added to 1.0 M CaCl₂.
**Figure 5.14** UV-vis-NIR spectral changes for PMAS (dialysed) added to 1.0 M BaCl$_2$.

**Figure 5.15** UV-vis-NIR spectral changes for PMAS (dialysed) added to 1.0 M MgCl$_2$. 
Figure 5.16  UV-vis-NIR spectra of PMAS (dialysed) recorded 24 hrs after adding to 1.0 M MCl₂.

Not only the speed of the above spectral changes, but also the position of the high wavelength polaron absorption band for the final polymer species, was found to depend on the nature of the metal cation employed. These differences are summarised in Table 5.1.
Table 5.1 Positions of the absorption peaks for the PMAS conformer formed in 1.0 M aqueous metal chlorides.

<table>
<thead>
<tr>
<th>Metal Salt</th>
<th>Peak position, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>335</td>
</tr>
<tr>
<td>NaCl</td>
<td>335</td>
</tr>
<tr>
<td>KCl</td>
<td>339</td>
</tr>
<tr>
<td>CsCl</td>
<td>340</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>324</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>329</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>329</td>
</tr>
</tbody>
</table>

5.3.2.2 Influence of the Nature of Anion

The influence of the metal salt anion on the speed and extent of the above metal-induced "extended coil" to "compact coil" conformational change for PMAS was determined by studying the effect of 1.0 M aqueous solutions of each of the following sodium salts: NaCl, NaBr, NaI, NaSCN and Na₂SO₄.

Most of these studies were carried out using dialysed PMAS. Its relatively high reactivity towards metal salts did not allow us to generally observe the first step in the overall conformational change. For example, from Figure 5.17 it is seen that substantial growth of the final product peak at ca. 750 nm had occurred for each of the NaX (X = Cl, Br, I) salts immediately after mixing. It is also seen that NaI is more effective than NaCl in promoting conversion to the "compact coil" PMAS product, while NaBr is less effective (relative rates Br⁻ < CI⁻ < I⁻ ).

125
Despite their different rates of conversion, the spectra recorded after 24 hrs (Figure 5.18) show that each of these halide salts causes complete conversion to “compact coil” PMAS. In addition, the $\lambda_{\text{max}}$ for the final product was independent of the halide ion employed, appearing at 750 nm in each case. This contrasts with the significant dependence of this $\lambda_{\text{max}}$ on the nature of the metal ion in the added salt (see Table 5.1).
Figure 5.18 UV-vis-NIR spectra of the PMAS (dialysed) added to 1.0 M NaX. Spectra obtained 24 hrs after mixing.

Related results in Figure 5.19 show that SCN⁻ is far less effective that Cl⁻ in promoting the above conformational change in dialysed PMAS. Even after 100 hrs the conversion is only ca. half complete with 1.0 M NaSCN, whereas conversion in 1.0 M NaCl required less than 24 hrs. Similarly, comparison of the spectral changes for PMAS (NH₄⁺) in 1.0 M Na₂SO₄ (Figure 5.20) with those in 1.0 M NaCl (Figure 5.4) show that the SO₄²⁻ ion is much less effective than Cl⁻.
Figure 5.19  UV-vis-NIR spectra of PMAS (dialysed) recorded 24 hr after adding to 1.0 M NaCl and 100 hr after adding to 1.0 M NaSCN.

Figure 5.20  UV-vis-NIR spectral changes for PMAS (NH$_4^+$) in 1.0 M Na$_2$SO$_4$ (slow second step); [PMAS] ca. 5 x 10$^{-4}$ M.
The above results with various NaX salts provide the following overall trend for the influence of the anions on the rate of conformational change:

\[ \text{SCN}^-, \text{SO}_4^{2-} < \text{Br}^- < \text{Cl}^- < \text{I}^- \].

The low effectiveness of SCN\(^-\) compared to the halide ions is consistent with its position in the chaotropic series. Studies with proteins have shown the following order for anions in their ability to promote protein folding ("compact coil") and aggregation:

\[ \text{SCN}^- < \text{I}^- < \text{Br}^- < \text{Cl}^- < \text{SO}_4^{2-} \] [166, 167]. However, the low effectiveness of SO\(_4\)^{2-} and the high ability of I\(^-\) in promoting a "compact coil" conformation for PMAS do not correlate with their positions in the chaotropic series. The origin of the observed trend in anion reactivities towards PMAS must therefore involve other specific interactions.

5.3.2.3 Influence of the Metal Salt (Electrolyte) Concentration

The reason why added salts cause coil collapse (i.e. "compact coil formation") in polyelectrolytes is that the metal cations act as point charges and screen intra- and intermolecular electrostatic repulsions. A number of theoretical models of electrolyte-polyelectrolyte interaction in solution has been developed [172, 173] describing the coil collapse and precipitation of a polyelectrolyte from an electrolyte solution with increase in the electrolyte concentration or/and decrease in the polyelectrolyte concentration.

In the present study, the conditions of precipitation with the alkali metal salts have not been achieved. Instead, only chain contraction ("compact coil" formation) is believed to happen. The speed of these UV-vis-NIR spectroscopic changes for dialysed PMAS was found to depend upon the salt concentration employed. For example, the rate of
conversion to the “compact coil” form of PMAS ($\lambda_{\text{max}}$ 750 nm) decreased markedly when the added NaCl concentration was decreased from 1.0 M to 0.5 M and 0.25 M.

5.3.2.4 Influence of the Polymer Concentration

Folding (i.e. “compact coil” formation) and aggregation of polyelectrolytes generally happens only at a low polymer concentration [165]. An increase in the polyelectrolyte concentration overcomes the screening effect of added salts. In keeping with this, when the PMAS (NH$_4^+$) concentration was increased from $4 \times 10^{-5}$ M to $3 \times 10^{-4}$ M, the time required for completion of the colour changes in 1.0 M KCl increased from 8 to ca. 20 days (Table 5.2)

Table 5.2  Dependence of spectral changes for PMAS (NH$_4^+$) in 1.0 M KCl on the PMAS concentration.

<table>
<thead>
<tr>
<th>[PMAS], M</th>
<th>Time for rearrangement to go to completion, days</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4 \times 10^{-5}$</td>
<td>8</td>
</tr>
<tr>
<td>$9.4 \times 10^{-5}$</td>
<td>10</td>
</tr>
<tr>
<td>$3 \times 10^{-4}$</td>
<td>20</td>
</tr>
</tbody>
</table>

5.3.3 Isolation and Characterisation of Metal Salts of PMAS

When the PMAS concentration was raised from $4 \times 10^{-5}$ M typically employed in the above experiments to 1 % (w/v), a dark brown precipitate formed rapidly in 1.0 M CaCl$_2$, BaCl$_2$, or MgCl$_2$. The precipitated polymer was strongly bound to the metal cation in each case and remained insoluble in water. However, acidification with HCl
returned the PMAS (M\(^{2+}\)) salts into the soluble form. A metal analysis of the PMAS (Ba\(^{2+}\)) salt after dissolution in 0.1 M HCl, determined by atomic absorption spectroscopy, showed there to be 0.37 Ba\(^{2+}\) ions per sulfonic acid group of PMAS. This indicates that ca. three quarters of the "free" sulfonate groups have a Ba\(^{2+}\) ion attached.

The DC conductivity of the PMAS (Ba\(^{2+}\)) salt was 1.8 x 10\(^{-2}\) S cm\(^{-1}\), which is somewhat higher than the value (1 x 10\(^{-2}\) S cm\(^{-1}\)) similarly measured for the initial PMAS (NH\(_4^+\)) polymer. The PMAS (Ca\(^{2+}\)) salt could not be made into a powder pellet for conductivity measurement because of its hygroscopic nature, while the PMAS (Mg\(^{2+}\)) salt pressed into a brittle film also unsuitable for such measurements.

The results of GPC analyses of the precipitated PMAS (M\(^{2+}\)) salts and the initial as received PMAS (NH\(_4^+\)) polymer are presented in Table 5.3. These data suggest that the addition of alkaline earth metal chlorides to aqueous PMAS may be useful for the separation of the higher molecular weight fractions of PMAS.

Table 5.3  GPC and DC conductivity results for the as received PMAS (NH\(_4^+\)) and fractions precipitated by MCl\(_2\).

<table>
<thead>
<tr>
<th>Type of PMAS</th>
<th>(M_w)</th>
<th>(M_n)</th>
<th>Polydispersity</th>
<th>Conductivity, S cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMAS (as received)</td>
<td>15,500</td>
<td>10,100</td>
<td>1.52</td>
<td>1.0 x 10(^{-2})</td>
</tr>
<tr>
<td>PMAS (Ca(^{2+}))</td>
<td>28,500</td>
<td>7,240</td>
<td>3.94</td>
<td>Not available</td>
</tr>
<tr>
<td>PMAS (Mg(^{2+}))</td>
<td>23,700</td>
<td>8,340</td>
<td>2.84</td>
<td>Not available</td>
</tr>
<tr>
<td>PMAS (Ba(^{2+}))</td>
<td>21,600</td>
<td>4,020</td>
<td>5.37</td>
<td>1.8 x 10(^{-2})</td>
</tr>
</tbody>
</table>
5.3.4 Reversal of Spectral Changes with Acid

The changes observed in the spectrum of aqueous PMAS in the presence of the added salts were reversible. Addition of acid (lowering of the pH to 1.0) resulted in restoration over several hours of the original spectrum of the polymer (Figure 5.20). This presumably involves the replacement of metal ions bound to the “free” PMAS sulfonate groups by protons, and the subsequent rearrangement of the polymer backbone back to an “extended coil” conformation.

Figure 5.20  UV-vis-NIR spectra of PMAS (NH$_4^+$) in “compact coil” conformation in 1.0 M NaCl (pH 3.7) and then after pH was lowered to 1.0.
5.4 Conclusions

UV-vis-NIR spectral studies indicate that poly(2-methoxyaniline-5-sulfonic acid) (PMAS) in its as received PMAS (NH$_4^+$) form has an “extended coil” conformation in aqueous solution. The related PMAS (H$^+$) form, prepared by ion exchange, also has an “extended coil” conformation, as does dialysed PMAS.

Dilute aqueous solutions of each of these forms of PMAS exhibit remarkable and unprecedented ionochromism when 1.0 M alkali and alkaline earth metal salts are added. The colour changes from yellow/brown to blue over hours or days depending on the metal salt employed, and is seen from UV-vis-NIR spectroscopy to proceed in two distinct steps. The first rapid stage (few minutes) is attributed to replacement of protons from the “free” (i.e. not participating in self-doping) SO$_3$H groups on the PMAS chains, leading to changes in conformation/structure arising perhaps from decreased H-bonding interactions. The slow (hours/days) second step is believed to involve conversion of the PMAS from an “extended coil” to a “compact coil” conformation. This conversion may be facilitated by intrachain binding of the metal ions to “free” sulfonate groups on the PMAS chains.

The ionochromic effects are strongly dependent on the nature of the metal ion in the added metal salts. The speed/extent of the rapid first step increases along the metal ion series Li$^+$ < K$^+$ < Na$^+$ < Ba$^{2+}$ < Cs$^+$ < Mg$^{2+}$ < Ca$^{2+}$, while the slower second step reveals a differing order: Cs$^+$, Li$^+$ < K$^+$ < Ca$^{2+}$ < Ba$^{2+}$ < Na$^+$.

The second step also shows marked anion dependence, the speed of the conformational/colour change increasing along the series SCN$^-$, SO$_4^{2-}$ < Br$^-$ < Cl$^-$ < I$^-$.
This order does not correlate with the position of these anions in the chaotropic series developed for proteins, suggesting the involvement in PMAS of other specific interactions.

Calcium, magnesium and barium salts of PMAS may be precipitated when 1.0 M MX$_2$ salts are added to more concentrated (1 %) aqueous PMAS. The PMAS (Ba$^{2+}$) salt has a higher electrical conductivity than the as received PMAS (NH$_4^+$), and atomic absorption analysis shows that ca. 75 % of the “free” sulfonate groups have Ba$^{2+}$ ions attached. GPC studies also show that each of the PMAS (M$^{2+}$) salts has a higher molecular weight than as received PMAS (NH$_4^+$).

These ionochromic/conformational effects may be reversed by the addition of 0.1 M HCl, regenerating PMAS in the original “extended coil” conformation – this reversal presumably involves replacement of the polymer-bound metal ions by protons.
6.1 Introduction

Parent, unsubstituted polyaniline (PAn) is well known to undergo facile pH and redox switching between different forms as summarised in Scheme 6.1.

![Scheme 6.1](image)

**Scheme 6.1** Interconversions between different forms of polyaniline.

Films of the green, conducting emeraldine salts, PAN.HA (HA = acid) are readily dedoped to the blue insulating emeraldine base (EB) form via treatment with alkali,
commencing at pH 4. The EB is characterised by a strong exciton absorption band at ca. 600 nm. It may, in turn, be readily re-doped with acids, HA, to regenerate emeraldine salts. Chemical reduction of PAn.HA emeraldine salt films using reducing agents such as hydrazine or phenylhydrazine leads to the pale yellow leucoemeraldine form of PAn. This insulating polymer’s electronic absorption spectrum shows no high wavelength bands, exhibiting only a $\pi-\pi^*$ band at 300 - 330 nm.

Chemical oxidation (e.g. using $(\text{NH}_4)_2\text{S}_2\text{O}_8$) or electrochemical oxidation (using potentials above 0.7 V vs Ag/AgCl) of PAn.HA emeraldine salts in acid solutions (pH < 1) generates pernigraniline salts, which are characterised by a Peierl’s gap absorption band at ca. 700 nm. On the other hand, chemical oxidation in basic solution leads to the dedoped oxidised polymer, pernigraniline base, exhibiting instead an absorption band at ca. 540 nm.

The presence of the electron-withdrawing and pH-responsive sulfonic acid groups on each of the aniline rings in PMAS (4), together with its methoxy ring substituents, would be expected to influence its ability to be pH and redox switched between different forms.

![Chemical structure of PMAS](image)
This Chapter explores this aspect, revealing marked differences in behaviour compared to that previously observed with the parent unsubstituted polyaniline. In particular, PMAS was found to be remarkably resistant to alkaline dedoping, with no emeraldine base formed even in 1 M NaOH. Instead, PMAS in alkaline solutions underwent very similar, but much more rapid spectroscopic changes to those observed in Chapter 5 caused by added metal salts. That is, it is believed to undergo a similar conformational change from an “extended coil” to a “compact coil” form in the presence of NaOH or KOH.

6.2 Experimental

6.2.1 Materials

For all of the experiments in this Chapter the PMAS (NH$_4^+$ form) was used as received from Mitsubishi Rayon Ltd. Sodium and potassium hydroxides were obtained from Ajax Ltd., while ammonium persulfate and hydrazine hydrate were purchased from Aldrich Chemical Co. in the purest form available.

6.2.2 Spectroscopic Studies of Aqueous PMAS in NaOH Solutions

In studies of PMAS at increasing pH, concentrated aqueous NaOH was progressively added by microsyringe to an aqueous 3 x 10$^{-4}$ M PMAS solution and the UV-vis-NIR spectra (250-1300 nm) recorded immediately after mixing. The pH was determined using a Denver Instruments Model 20 pH/conductivity meter.
For the study of related spectral changes in concentrated NaOH (5.0 M), dialysed PMAS stock solution was added to 2.5 ml of alkali solution. UV-vis-NIR spectra were recorded immediately after mixing.

6.2.3 Electrical Conductivity Measurements

The DC conductivity of the sodium salt of PMAS was measured using the Van der Pauw method. The PMAS (Na⁺) polymer was prepared by the neutralisation of the PMAS (NH₄⁺ salt form) with aqueous NaOH using sufficient base to interact with every second sulfonate group on the PMAS chains (the remaining sulfonate groups are presumably involved in self-doping). The polymer produced had a blue colour. It was dried in a rotatory evaporator and then in a desiccator over silica gel, before being pressed into a pellet for conductivity measurement.

6.2.4 Chemical Oxidation and Reduction of the Aqueous PMAS

Chemical reduction and oxidation of PMAS was carried out on 2.50 ml samples of aqueous 3 x 10⁻⁴ M PMAS. Hydrazine hydrate (0.08 M or 0.4 M) was used as reducing agent (made by adding 10 ml or 50 ml of N₂H₄.H₂O), while ammonium persulfate (0.1 M) was used as oxidant. The pH was adjusted with potassium hydroxide or hydrochloric acid.
6.3 Results and Discussion

6.3.1 PMAS Behaviour in Basic Solutions

In the dimer repeat unit of PMAS (see Structure 4) there are two kinds of sulfonic acid groups, one that is “free”, and the other that is participating in self-doping of the polymer. In previous studies of partially (50 % and 75 %) sulfonated polyanilines (SPANs) [93], two stages of spectroscopic changes upon increasing the pH were observed. This led to the suggestion that the first stage involved neutralisation of the “free” sulfonic acid groups, while the second led to the dedoping of the polymer to give the emeraldine base form (with $\lambda_{\text{max}}$ ca. 600 nm).

The present study with PMAS is the first examination of the influence of alkaline media on a fully sulfonated polyaniline.

The addition of aqueous NaOH to dilute PMAS solution caused a rapid colour change from yellow/brown to blue. However, in marked contrast to the earlier studies [93] with partially sulfonated polyanilines, no spectroscopic evidence was observed for alkaline dedoping of PMAS even at a pH as high as 14. Rather than the appearance of an absorption band at ca. 600 nm as expected for an emeraldine base product, alkaline treatment of PMAS at pH > 9 led rapidly (in seconds) to the appearance of a band at ca. 750 nm (e.g. Figure 6.1). This alkaline solution absorption spectrum of PMAS is very similar to that observed in the previous Chapter 5 for aqueous PMAS solutions exposed for hours/days to alkali and alkaline earth metal salts (Figure 6.2), suggesting similar conformational changes in the polymer chain.
Figure 6.1 UV-vis-NIR spectrum of PMAS in 1.0 M NaOH, pH 14.

Figure 6.2 UV-vis-NIR spectra of PMAS: (1) in 1.0 M NaCl; (2) 1.0 M NaOH (after the completion of the spectral changes).
In alkaline solution one would anticipate deprotonation of each of the "free" sulfonic acid groups on the PMAS chain, generating a highly negatively charged form (5) of PMAS.

\[
\text{SO}_3^- \quad \text{SO}_3^- \\
\text{MeO} \quad \text{MeO}
\]

The remarkable resistance of the fully sulfonated PMAS to undergo alkaline dedoping may therefore arise from strong electrostatic repulsion of the negative sulfonate groups of (5) towards approaching OH\textsuperscript{-} ions.

It should be noted that partially (50 % or 75 %) sulfonated polyanilines were also found to be less readily dedoped by base than unsubstituted PAn.HA salts, deprotonation to EB not commencing until pH 6 [174] or 9 [175] or even 14 [93] (as opposed to ca. pH 4 for PAn.HA). However, the resistance to dedoping of PMAS up to ca. 2 M NaOH (see below) is unprecedented.

UV-vis-NIR spectral studies during the titration of a PMAS (NH\textsubscript{4}\textsuperscript{+}) solution with aqueous NaOH (Figures 6.3 and 6.4) revealed two stages, depending on the pH:

1. **the first stage** was observed between pH 3.7 (natural pH of the PMAS ammonium salt) and 8.0. The changes observed in the PMAS spectrum as the pH was raised from 3.66 to 8.02 were (i) a decrease in both the initial delocalised polaron band absorption above 1000 nm and the 473 nm peak, and (ii) red shifts in the 300-400 nm region involving the development of a distinct peak at 330 nm and a shoulder at ca. 385 nm.
Three isosbestic points were observed at 290, 423 and 505 nm, indicating a clean interconversion between two species. These spectral changes are believed to be associated with deprotonation of “free” $\text{SO}_3\text{H}$ groups on the PMAS chains, and may result in part from changes in the PMAS conformation/structure from decreased H-bonding interactions.

![Figure 6.3](image)

**Figure 6.3** UV-vis-NIR spectra of an aqueous $3 \times 10^{-4}$ M PMAS solution with increasing pH, Stage I.

(2) A *second stage* involved further marked spectral changes when the pH of the solution was increased to 9.15 and above. The initial peak at 473 nm and the NIR absorption band above 1000 nm were replaced by a strong band at 750 nm (Figure 6.4). Absorption bands at 330 nm and 385 nm continued to increase with increasing pH (and were slightly red-shifted). Three isosbestic points (at 410, 506 and ca. 980 nm) were observed, indicating a clean conversion between discrete forms of PMAS.
The overall changes in the absorbances at 473 nm and 750 nm of the PMAS solution with increasing pH are shown in Figure 6.5. Two stages are again apparent, with the most rapid decrease in Abs (473 nm) and increase in Abs (750 nm) occurring near pH 9.

Figure 6.4  UV-vis-NIR spectra of a $3 \times 10^{-3}$ M PMAS solution with increasing pH, Stage II.
Figure 6.5 Changes in absorbance at 473 nm and 750 nm from Figures 6.3 and 6.4 with increasing pH.

The position of the characteristic 750 nm peak of PMAS at pH 14 (in 1.0 M NaOH) is significantly different from that expected for the emeraldine base form of polyaniline (ca. 600 nm). However, it is at exactly the same wavelength as observed in Chapter 5 for PMAS in 1.0 M NaCl, and it is similar to the localised polaron band typically observed for PAN.HA salts in the “compact coil” conformation [9, 34]. The peaks at 330 and 380 nm are also consistent with a “compact coil” emeraldine salt structure, being assignable to the $\pi-\pi^*$ transition and a second polaron band transition, respectively.

These spectral changes observed in aqueous PMAS with increasing pH closely resemble those described under the influence of metal salts. As reported in Section 5.3.1, changes in the PMAS spectrum with added metal salts included a decrease in the 473 nm peak high in the rapid first stage, and the growth of a characteristic 750 nm peak in the
second stage. It therefore seems reasonable to suggest that even at pH 14 PMAS only undergoes a conformational change from an “extended coil” to a “compact coil” structure, rather than alkaline dedoping to EB.

The UV-vis-NIR spectrum of PMAS in 2.0 M NaOH was similar to that at pH 14. However, increasing the NaOH concentration to ≥5 M resulted in the 750 nm peak shifting to ca. 630 nm, closer to the position of the characteristic band observed at ca. 600 nm for unsubstituted EB (Figure 6.6). This suggests that this high base concentration caused substantial dedoping of PMAS.

The DC conductivity of a pressed pellet of the Na salt of PMAS was $4 \times 10^{-2} \text{ S cm}^{-1}$. This is significantly higher than the conductivity of the original as received PMAS ($\text{NH}_4^+$), which was only $1 \times 10^{-2} \text{ S cm}^{-1}$.  

![Figure 6.6 UV-vis-NIR spectrum of PMAS in aqueous 5.0 M NaOH.](image)
6.3.2 Redox Switching of PMAS in Aqueous Solution

PMAS was found to be readily and reversibly oxidised and reduced in aqueous solution. The reaction rates and spectral changes were found to be pH-dependent, as described in detail below.

6.3.2.1 Oxidation in Weakly Acidic Media

When aqueous (NH₄)₂S₂O₈ was added to PMAS solution (pH 3.6) to prepare 2.5 ml of 2.8 x 10⁻⁴ M PMAS / 0.1 M (NH₄)₂S₂O₈, the solution changed colour from yellow/brown to blue. The spectral changes (Figure 6.7) revealed the growth of peaks at 330 and 550 nm and the disappearance of the two original polaron bands of PMAS at 473 nm and in the NIR region. These changes indicate formation of the oxidised pernigraniline form of PMAS, as shown in Scheme 6.2. The 550 nm peak of the product is very similar in position to that previously observed [18] for pernigraniline base prepared via oxidation of unsubstituted PAN.

Unsubstituted polyaniline in the pernigraniline oxidation state may be protonated with acids at pH < 1 to give the corresponding pernigraniline salt. The failure to observe protonation of pernigraniline base here from oxidation of PMAS at pH 3.7 is therefore consistent with the behaviour of the parent PAN. It may be noted that isosbestic points were observed at 364 and 495 nm during the 25 min that the oxidation of PMAS was monitored. The failure of the initial PMAS trace to pass though the 364 nm isosbestic point suggests that there may be a rapid rearrangement or other process occurring prior to the slower final formation of the pernigraniline base product.
6.3.2.2 Oxidation of PMAS in Strongly Acidic Media (pH 1)

In order to determine whether PMAS could be oxidised to the pernigraniline salt form, 2 drops of conc. HCl were added to an aqueous PMAS solution prior to addition of the (NH₄)₂S₂O₈ oxidant. The spectral changes observed (Figure 6.8) were very different to those seen in Figure 6.7 for oxidation at pH 3.7. The 330-380 nm bands disappeared, while there was no growth of a pernigraniline base peak at 550 nm, nor of a band at ca. 700 nm anticipated for the pernigraniline salt form of PMAS. The initial 473 nm peak of PMAS decreased with time, and was broadened and blue-shifted. These changes suggest that in strongly acidic conditions, the pernigraniline salt form of PMAS is unstable and decomposes. Limited stability has also been previously noted [18] for unsubstituted pernigraniline salt in strong acid.
Figure 6.8 UV-vis-NIR spectra of PMAS (2.8 x 10^-4 M) during oxidation in 0.1 M (NH₄)₂S₂O₈, pH 1.

6.3.2.3 Reduction of PMAS at pH 9

Upon addition of ca. 0.08 M hydrazine, an aqueous PMAS solution underwent a very fast colour change from yellow-brown to pale yellow. Two distinct stages were observed via UV-vis spectroscopy. Within 1 min the initial PMAS peak at 473 nm had disappeared and was replaced with a strong peak at 408 nm (Figure 6.9). Over the following 2 hours this 408 nm peak decreased in intensity, while a strong band grew at ca. 330 nm. These latter changes are consistent with conversion to the leucoemeraldine base form of PMAS (Scheme 6.2). The 330 nm band is assigned as the π–π* transition absorption similar to that previously observed [177] for the leucoemeraldine form of unsubstituted PAN. The clean nature of the slow second step was shown by the presence of a sharp isosbestic point at 355 nm. The reaction did not proceed to completion and the 120 min spectrum shown in Figure 6.9 represents the final equilibrium position.
The observed reduction of PMAS differs from that of unsubstituted PAN in the unprecedented initial formation of a species with $\lambda_{\text{max}}$ 408 nm (Species I). The nature of this latter species is unknown, but it may be a conformer or isomer of leucoemeraldine that does not occur for the parent PAN.

![UV-vis-NIR spectrum](image)

**Figure 6.9** UV-vis-NIR of spectral changes for PMAS ($2.8 \times 10^{-4}$ M) during reduction in 0.08 M hydrazine, pH 9.

When the hydrazine concentration was increased to 0.4 M, similar spectral changes to those in Figure 6.9 were observed, but the reaction reached the equilibrium point within 1 hour.
6.3.2.4 Reduction of PMAS at pH 13

In this case an aqueous 0.1 M KOH solution was used instead of water to dissolve PMAS. At pH 13 the PMAS solution was blue and had a strong absorption peak at 748 nm as well as a broad band in the 330-380 nm region, as shown on Figure 6.10. As discussed in Section 6.3.1 above, at pH 13 PMAS is believed to be in the emeraldine salt form in a “compact coil” conformation.

After addition of hydrazine (0.08 M) to the solution, the UV-Vis spectrum started to change slowly, with the 748 nm peak decreasing and a peak growing at 405 nm (Figure 6.10). This latter peak is believed to belong to the same form of PMAS as Species I formed via reduction of PMAS with hydrazine at pH 9 (Section 6.3.2.3). However, the slow conversion of PMAS to Species I at pH 13 (3 hr to complete) contrasts with the very rapid formation of species I at pH 9 (complete within 1 min). This indicates that prior conversion of the PMAS to the “compact coil” form with strong base retards its subsequent reduction (Scheme 6.2).

Also contrasting with the reduction at pH 9 was the failure to observe subsequent conversion of the Species I (with $\lambda_{\text{max}}$ 405) nm to leucoemeraldine at pH 13.
Figure 6.10 UV-vis-NIR spectra of PMAS during reduction with hydrazine, pH 13.
Scheme 6.2  Redox and pH switching of PMAS (ES = emeraldine salt, PB = pernigraniline base, LB = leucoemeraldine base).
6.3.2.5 Reduction of PMAS in 0.5 M KCl at pH 9

The possibility of similar retardation of PMAS reduction via prior conversion of the polymer to the “compact coil” conformation by the addition of metal salts (as described in Chapter 5) was then explored. A sample of PMAS was dissolved in 0.5 M KCl and after a few days turned into the blue “compact coil” form with $\lambda_{\text{max}}$ at 750 nm. When hydrazine (0.08 M) was added, the course of the spectral changes during reduction (Figure 6.11) was indeed very similar to that described above for PMAS at pH 13. Conversion to the Species I ($\lambda_{\text{max}}$ 408 nm) was complete within 30 min. These results support our hypothesis that the difference in the reduction course at pH 9 and pH 13 is due to different conformations for the initial PMAS.

![Figure 6.11 Reduction of PMAS with hydrazine in 0.5 M KCl, pH 9, during 30 min.](image-url)
6.3.2.6 Reoxidation of the Leucoemeraldine Form of PMAS

The reduced Species I (with $\lambda_{\text{max}}$ at 405 nm) produced above by reduction with hydrazine at pH 13 did not undergo reoxidation with oxygen in the air. However, if hydrochloric acid was added lowering the pH to 1, reoxidation of the polymer started immediately (Figure 6.12). The peak at 405 nm shifted to 400 nm and decreased in intensity, disappearing completely after 1 hr. A sharp peak grew at 473 nm, consistent with aerial oxidation to reform the emeraldine salt of PMAS in the “extended coil” conformation. The clean nature of this conversion was evident from the presence of a sharp isosbestic point at 420 nm.

![Figure 6.12](image-url)  
**Figure 6.12** UV-vis-NIR spectral changes during the reoxidation of the Species I form of PMAS in air at pH 1 to regenerate PMAS.
6.4 Conclusions

PMAS is found to be remarkably resistant to alkaline dedoping, with no emeraldine base being formed even in 2.0 M NaOH. Instead, PMAS in alkaline solutions undergoes very similar, but much more rapid, spectroscopic and colour changes to those caused by adding metal salts. That is, its polymer backbone is believed to undergo a conformational change from an “extended coil” to a “compact coil” conformation. During the titration of a PMAS (NH$_4^+$) solution with aqueous NaOH, two stages are revealed by UV-vis-NIR spectroscopy. The spectroscopic changes in the first stage between pH 3.7 and 8.0 are attributed to deprotonation of “free” SO$_3$H groups on the PMAS chains, and may result from changes in the PMAS conformation/structure from decreased H-bonding interactions. The second stage between pH 9 and 14 is believed to involve rearrangement from an “extended coil” to a “compact coil” conformation.

Like unsubstituted polyaniline, PMAS is readily oxidised by ammonium persulfate at pH 3.7 to give the corresponding pernigraniline base form. Attempted oxidation at pH 1 leads to decomposition of the pernigraniline salt form of PMAS.

Chemical reduction of PMAS by hydrazine displays distinctively different behaviour to that previously reported for unsubstituted polyaniline. At pH 9, two distinct stages are observed via UV-vis spectroscopy. The first involves the rapid formation of a novel polymer (Species I) characterised by an intense, sharp absorption band at 408 nm, which is attributed to a conformer or isomer of leucoemeraldine (LB). This species then slowly converts to the leucoemeraldine base form of PMAS, with a spectrum similar to the LB form of unsubstituted PAn. In contrast, hydrazine reduction of PMAS at pH 13
or in 1.0 M KCl produces only Species I, which does not convert further to leucoemeraldine. Acidification of this reduced solution results in aerial oxidation, leading to reformation of the initial PMAS.
CHAPTER 7

SYNTHESIS AND CHARACTERISATION
OF OTHER CHIRAL SUBSTITUTED POLYANILINEs

7.1 Introduction

Since the first report of the formation of optically active polyaniline via the incorporation of the chiral dopant (+)-camphorsulfonate (CSA⁺) into the polymer chain during electrochemical polymerisation of aniline monomer [122], similar chiral induction has been described for the ring-substituted polymers poly(o-toluidine) (6a) [122] and poly(o-methoxyaniline) (6b) [123, 124]. In each of these cases, the polyaniline or ring-substituted polyaniline chains are believed to adopt a preferred one-handed helical arrangement due to the influence of the chiral (+)-CSA⁻ dopant anion.

This Chapter now explores the possibility of generating optically active polyanilines from the \( N \)-substituted aniline monomers, \( N \)-methylaniline (NMA, 7a) and diphenylamine (DPA, 7b) in the presence of the chiral (+)-CSA⁻ dopant anion.
Previous studies of poly(N-substituted anilines) include papers by Kilmartin et al. [49] and Athawale et al. [51], who have shown that poly(N-methylaniline (PNMA, 2) may be deposited electrochemically at potentials between 1.0 V and 1.2 V (vs Ag/AgCl) using an N-methylaniline monomer concentration of 1.0 M in 1.0 M aqueous HClO₄. It was reported that a blue soluble polymer formed when 0.5 M sulfuric acid or 1.0 M hydrochloric acid solutions were used.

Due to its N-alkylated nature, redox processes in PNMA are controlled by diffusion of dopant and do not involve protonation, so pH does not alter the peak currents. Unlike unsubstituted polyaniline, partially oxidised PNMA (i.e. in its emeraldine state) does not form polarons, but only dications, as indicated by magnetic studies [54].

Diphenylamine (DPA) may also be polymerised electrochemically at 1.0 V (vs Ag/AgCl) from 0.1 M monomer solution in acetonitrile with lithium perchlorate as
supporting electrolyte and dopant [59] to give poly(diphenylamine) (PDPA, 3). PDPA is more readily soluble in organic solvents than polyaniline and possesses a good resistance to long-term exposure to anodic potentials in the absence of water.

This Chapter also provides the first exploration of another new potential route to optically-active polyanilines, namely the polymerisation of an aniline monomer bearing a covalently attached chiral substituent. The monomer chosen was (S)-(+-)(anilinomethyl)pyrrolidine (AMP, 8).

Previous studies on the polymerisation of pyrrole and thiophene monomers bearing chiral substituents led to chiral polymers possessing exciton-coupled bisignate Cotton effects in their CD spectra [105, 171, 178-182]. It has been proposed that in chiral, regioregular polythiophenes the bisignate CD bands are associated with an intermolecular aggregation phenomenon and in solution strongly depend on the polymer solubility. For example, the chiral side chains of poly{3,4-bis[(S)-2-methylbutoxyl]thiophene} (PBMBT) induced strong bisignate Cotton effects in the
π-π* absorption when the polymer was in an aggregated phase. The chiroptical properties in absorption and emission of PBMBT were considered to be associated with a high degree of interchain and intrachain order as they were present in aggregated phases but absent when the polymer chains were molecularly dissolved.

Langeveld-Voss et al. [179] similarly considered optically active substituents attached as a side chain to polypyrroles to be a particularly interesting and revealing tool to study the nanoscopic and mesoscopic supramolecular organisation of π-conjugated polymers in general.

The proposed search for chiral induction in PNMA and PDPA in the presence of a chiral dopant and polymerisation of the chiral AMP monomer are important for a better understanding of the factors controlling such chiral induction. If successful, they would also provide new chiral conducting polymers that may be useful in chiral synthesis or as chiral sensors.

7.2 Experimental

7.2.1 Electrochemical Synthesis of PNMA.(+)-HCSA and PDPA.(+)-HCSA Films

The electrochemical polymerisation of the NMA and DPA monomers and the electrochemical characterisation of the resultant PNMA and PDPA films were carried out in a three-electrode cell, described in Chapter 2.

(i) In preliminary studies, the electrochemical oxidation of NMA was characterised by performing the cyclic voltammetry of NMA solutions in 1.0 M (+)-HCSA between
0.0 and 1.2 V. The NMA monomer was also polymerised potentiostatically in aqueous 1.0 M (+)-HCSA solution, employing a monomer concentration that was varied between 0.2 M and 1.0 M. A number of applied potentials between 0.6 V and 1.4 V (vs Ag/AgCl) were examined. At completion of the polymerisation the films were rinsed in distilled water and dried.

(ii) A preliminary cyclic voltammetry study of the oxidation of the DPA monomer was carried out in acetonitrile solution containing 0.2 M DPA and 0.7 M (+)-HCSA. An Ag/Ag⁺ electrode was used as reference. The PDPA.(+)-HCSA films were then prepared by polymerisation of a mixture containing 0.2 M DPA and 0.5 M (+)-HCSA in 42 % (v/v) water / acetonitrile, using an applied potential of 1.2 V. ITO-coated glass working electrodes were employed.

7.2.2 Spectroscopic Characterisation of PNMA.(+)-HCSA and PDPA.(+)-HCSA Films and Study of their Redox Reactions

(i) For the UV-Vis-NIR spectroscopic characterisation of the PNMA.(+)-HCSA and PDPA.(+)-HCSA films, the polymers were deposited onto ITO-coated glass working electrodes, and their UV-vis-NIR spectra were recorded between 300 and 2300 nm using a Cary 500 spectrophotometer.

Redox studies were carried out on PNMA.(+)-HCSA and PDPA.(+)-HCSA films (deposited on ITO-coated glass) immersed upright in a quartz cuvette. The oxidising solution contained 0.1 M ammonium persulfate in 0.1M HCl, and the reducing solution contained 0.1 M hydrazine hydrate. UV-vis-NIR spectra were recorded between 300 and 1300 nm.
The CD spectra of the above films, deposited on ITO-coated glass, were generally recorded on a Jobin Yvon CD Dichrograph 6 between 300 and 800 nm.

7.2.3 Chiral Discrimination Studies

(i) Cyclic voltammetry of PNMA.(+)-HCSA films deposited on a microelectrode (20 μm diameter) were performed in aqueous solutions containing the enantiomeric forms of HCSA and aspartic acid. The polymer was deposited potentiostatically at 1.1 V, and the subsequent CV studies were performed between -0.2 and 0.8 V using a scan rate of 100 mV/s. Electrolyte solutions contained 0.10 M (+)- or (-)-HCSA, and 0.010 M D- or L-aspartic acid.

The electrochemical responses of PNMA.(+)-HCSA films in 0.02M D- or L-Valine solutions were also studied using a small Pt disc (1.0 mm diameter) electrode, with 0.10 M NaN03 as supporting electrolyte.

(ii) For the evaluation of the chiral discriminating capability of PDPA.(+)-HCSA, cyclic voltammetry was performed on films in aqueous 0.10 M NaNO3 solutions containing alternatively 0.02 M D- or L-valine. The potential was scanned between -0.2 V and 1.2 V. The polymer for this experiment was deposited potentiostatically on a Pt disc electrode (1.0 mm diameter) at 1.2 V.

7.2.4 Synthesis of Poly{(S)-anilinomethyl}pyrrolidine} (PAMP)

PAMP was synthesised chemically according to the method previously established for polyaniline [24]. 100 mg of AMP monomer were dissolved in 3 ml of 1.0 M HCl. Ammonium persulfate (104 mg) was dissolved in a 2.7 ml of 1.0 M HCl and added to
the AMP solution dropwise with stirring at 5°C. After 2 hours a dark-green, soluble product formed.

7.3 Results and Discussion

7.3.1 Electrochemical Preparation and Properties of PNMA.(+)-HCSA

7.3.1.1 Cyclic Voltammetry of an NMA Solution in 1.0 M (+)-HCSA

Figure 7.1 shows successive CV scans for an aqueous 0.2 M NMA solution in 1.0 M (+)-HCSA performed on a Pt disc electrode. Polymerisation started at a potential of 0.50 V and a blue soluble product formed near the electrode surface. The oxidation peaks observed at 0.55 V and 0.70 V (and corresponding reduction peaks at 0.56 V and 0.48 V) are believed to be due to dissolved PNMA.(+)-HCSA polymer surrounding the electrode. The oxidation current observed between 1.0 and 1.2 V is believed to be due to the monomer oxidation and decreased with successive scans.

When the NMA monomer concentration was raised to 1.0 M a green film, believed to be the polymer product PNMA.(+)-HCSA, was deposited on the electrode surface. A cyclic voltammogram during deposition (Figure 7.2) showed current values increasing with successive scans, which indicated the deposition of a conducting polymer film.
Figure 7.1 Cyclic voltammogram of a 0.2 M NMA solution in aqueous 1.0 M (+)-HCSA on a Pt disc electrode (1 mm diameter); scan rate 100 mV/s.

Figure 7.1(a) Enlarged section of the cyclic voltammogram from Figure 7.1.
Figure 7.2 Cyclic voltammogram of a 1.0 M NMA / 1.0 M (+)-HCSA solution on a Pt disc electrode (1 mm diameter); scan rate 100 mV/s.

The cyclic voltammogram in Figure 7.2 exhibited one pair of redox peaks. The oxidation peak was observed at 0.82 V, while the reduction peak shifted with successive scans from 0.32 V during the first scan to 0.20 V during the fifth scan. This indicates that the polymer became more resistive to reduction.

A similar dependence of the CV behaviour on the monomer concentration has been described earlier by Athawale et al. [51] for N-ethylaniline. This phenomenon was believed to be the result of different rates of the competing reactions during polymerisation. At lower monomer concentrations the predominant formation of the quinoid structures was observed leading to the higher pernigraniline oxidation state, while at higher monomer concentrations the process was shifted towards formation of the emeraldine phase. Similar observations have been made for polyaniline growth.
At higher aniline monomer concentrations (≥ 0.4 M) the stability of the diradical dications was thwarted, so the second oxidation wave leading to pernigraniline was not seen at usually employed scan rates (100 or even 200 mV/s).

7.3.1.2 Potentiostatic Growth of PNMA.(+)-HCSA Films and Their Chiroptical Properties

The potentiostatic oxidation of the NMA monomer was carried out on ITO-coated glass electrodes using applied potentials of 0.6 V, 0.7 V, 0.8 V and 1.2 V. The polymer deposited on the electrode surface at an extremely slow rate when the monomer concentration was below 0.7 M, while a significant quantity of a soluble product formed. This observation confirmed the conclusions made by Athawale et al. [51] that poly(N-alkylanilines) form films only at high monomer concentrations. For all our subsequent film growth experiments, polymerisation solutions containing 1.0 M NMA and 1.0 M (+)-HCSA were therefore employed.

At lower applied potentials (e.g. 0.6 V) the polymer formed on the electrode surface had a blue colour and did not adhere well to the electrode. It therefore could not be washed with water to remove excess acid and monomer. At higher potentials, i.e. 0.8 V and 1.2 V, the polymer films deposited were green and could be rinsed with water without releasing from the ITO-coated glass electrode. The UV-vis-NIR spectra of the films grown at these applied potentials are shown in Figures 7.3 and 7.4.
**Figure 7.3** UV-vis spectra of PNMA.(+)-HCSA films deposited potentiostatically from 1.0 M NMA / 1.0 M (+)-HCSA solution at applied potentials of: (1) 0.6 V; (2) 0.8 V.

**Figure 7.4** UV-vis-NIR spectra of PNMA.(+)-HCSA deposited potentiostatically from 1.0 M NMA / 1.0 M (+)-HCSA at an applied potential of 1.2 V.
The spectra of all films exhibited a shoulder at 420 nm, as in PAN, which may be attributed to the low wavelength polaron transition in the emeraldine salt form of PNMA. The broad absorption band at \( \geq 1000 \) nm may be assigned to the high wavelength polaron band of the PNMA, its position and broadness suggesting that the polymer backbone is in an "extended coil" conformation. The PNMA(+)HCSA film grown at 1.2 V exhibited a UV-vis-NIR spectrum most characteristic of emeraldine salts, and showed a \( \lambda_{\text{max}} \) for the high wavelength polaron band at ca. 1150 nm. This latter film was optically active, exhibiting broad CD bands between 330 and 600 nm (Figure 7.5).

An interesting feature of the film deposited at 0.6 V was a broad absorption band at ca. 580 nm. The origin of this weak band is unclear. It has been observed before for alkylated polyanilines in the emeraldine base form [48], but it is extremely unlikely that PNMA would exist in the base form in 1.0 M HCl.
7.3.1.3 Electrochemical Characterisation of PNMA.(+)-HCSA Films

A PNMA.(+)-HCSA film was potentiostatically deposited at 1.2 V on ITO-coated glass, rinsed with water and air-dried, and its cyclic voltammogram recorded in 0.1M (+)-HCSA (Figure 7.6). The Scheme 7.1 proposed by Kilmartin et al. [49] for PNMA oxidation includes two stages, as for PAN. Despite this, only one redox pair was recognisable in the voltammogram for PNMA.(+)-HCSA, with the oxidation peak at ca. 0.76 V and the reduction peak at ca. 0.18 V.

Figure 7.5  CD spectrum of the PNMA.(+)-HCSA film from Figure 7.4 deposited potentiostatically at 1.2 V
Figure 7.6 Cyclic voltammogram of a PNMA.(+)-HCSA film in aqueous 0.1 M (+)-HCSA on a Pt disc working electrode (1 mm diameter); scan rate 100 mV/s.

The present results for PNMA.(+)-HCSA are somewhat similar to previous data for PNMA and poly(N-ethylaniline) grown in other dopant acids. During potentiostatic polymerisation, PNMA growing in 0.5 M Na$_2$SO$_4$, at pH 1, exhibited an oxidation peak at 0.5 V and a reduction peak at ca. 0.4 V [50]; while in 1.0 M sulfuric acid oxidation and reduction peaks were observed at 0.52 V 0.33 V, respectively [183]. An intermediate third peak recorded on some voltammograms was ascribed to degradation products. Similarly, the CV recorded during polymerisation of N-ethylaniline in 1.0 M HCl showed an oxidation peak at 0.6 V and a reduction peak at 0.2 V [40].

In contrast, the cyclic voltammogram of the unsubstituted PAN.HCl polymer in aqueous 1.0 M HCl [183] exhibited 2 pairs of redox peaks. Oxidation peaks were observed at 0.2 and 0.75 V, and reduction peaks at 0.7 and 0.1 V. The first oxidation peak corresponds to the formation of the emeraldine salt radical cation, while the second peak
corresponds to further oxidation to the pernigraniline dication. Comparison of these CV studies of PNMA and PAn shows that N-substitution of the aniline units with a methyl group leads to polymers with less resistance towards oxidation.

Scheme 7.1 Redox switching in PNMA.

7.3.1.4 Chiral Discrimination Studies with PNMA.(+)-HCSA Films

To examine the discriminative ability of the PNMA.(+)-HCSA films towards enantiomeric compounds, cyclic voltammetry was performed using PNMA.(+)-HCSA polymer-coated Pt microelectrodes (20 μm diameter) in aqueous 0.10 M (+)- or (-)-HCSA, and 0.010 M D- or L-aspartic acid. The potential was cycled between -0.2 and 0.8 V using a scan rate of 100 mV/s. Unfortunately, no clear electrochemical
response was observed in all cases, with no redox peaks being observed in the voltammograms.

The electrochemical responses of PNMA.(+)-HCSA films in 0.02 M D- or L-Valine solutions were studied using a larger electrode (diameter 1.0 mm), requiring a supporting electrolyte, so the CVs were carried out in aqueous 0.10 M NaNO₃. In this case also, no clear peaks could be determined on the CV chart, and no chiral discrimination was observed.

7.3.1.5 Chemical Oxidation and Reduction of PNMA.(+)-HCSA Films

PNMA.(+)-HCSA films prepared by potentiostatic polymerisation at 1.2 V on ITO-coated glass were subjected to chemical oxidation and reduction. The UV-vis-NIR spectra of a film before and after oxidative treatment are presented in Figure 7.7. During oxidation with 0.1 M S²O₈²⁻ the original emeraldine salt polaron band at ca. 1100 nm shifted to 745 nm, which is characteristic of polyaniline in the pernigraniline salt form (assigned [18] as the Pieirl’s gap absorption). Visually, the film changed colour from green to a dark blue-green and also partially dissolved.
Figure 7.7 UV-vis-NIR spectra of a PNMA.(+)-HCSA film: (1) as grown; (2) after oxidation in 0.1 M (NH₄)₂S₂O₈ / 1.0 M HCl for 10 min.

Upon reduction for 10 min with 0.1 M hydrazine, a similar PNMA.(+)-HCSA film became colourless, again paralleling the behaviour known for unsubstituted polyaniline. The UV-vis-NIR spectrum of the reduced PNMA (Figure 7.8) exhibited only one absorption peak at 337 nm, which may be assigned to the π–π* transition in the leucoemeraldine form.
3.5
2.5
1 2
Si
1.5
Si
0.5
0
300 500 700 900 1100 1300 1500 1700 1900
Wavelength, nm
Figure 7.8 UV-vis-NIR spectra of a PNMA.(+)-HCSA film: (1) as grown; (2) after reduction in aqueous 0.1 M N₂H₄ for 10 min.

7.3.2 Electrochemical Preparation and Properties of PDPA.(+)-HCSA

The methods for PDPA.HClO₄ synthesis described in the literature employ acetonitrile as solvent in the polymerisation, because the DPA monomer is insoluble in water. However, the choice of a dopant may strongly alter the solubility of the resulting polymer. We observed that when (+)-HCSA was used as the dopant during polymerisation, the polymer product PDPA.(+)-HCSA was soluble in acetonitrile, but not in water. This led us to use a solvent mixture that would allow the dissolution of DPA monomer, yet not dissolve the resulting polymer. A mixture of 42 % (v/v) water / 58 % acetonitrile was found suitable. After growth, the films were washed in water to remove excess monomer and HCSA, and than dried by a stream of nitrogen.
7.3.2.1 Cyclic Voltammetry of a DPA / (+)-HCSA Solution in Acetonitrile

Initial electrochemical characterisation of the DPA monomer oxidation was carried out in acetonitrile solution containing 0.2 M DPA and 0.7 M (+)-HCSA. The CV recorded (Figure 7.9) showed only one oxidation peak at 1.5 V, presumably being oxidation of the monomer. The reductive current reached a maximum at 0.35 V. The voltammogram did not show an increase in current values with increasing number of scans since the products formed are soluble.

![Cyclic voltammogram](image)

**Figure 7.9** Cyclic voltammogram of a 0.2 M DPA, 0.7 M (+)-HCSA solution in acetonitrile (vs Ag/Ag⁺). Pt disk working electrode (1 mm diameter), scan rate 100 mV/s.

Earlier CV studies of DPA oxidation in acetonitrile with [Bu₄N]PF₆ as supporting electrolyte [58, 59, 185] showed that the presence of a small amount of water in the acetonitrile led to CV with one oxidation peak at ca. 0.9 V (vs. Ag quasi-reference electrode) and two reduction peaks at ca. 0.75 V and 0.65 V. The oxidation peak was
assigned to the oxidation of DPA with formation of the DPA cation radical. There was no reduction peak corresponding to the oxidation peak, as the radical cations generated were completely consumed in the following chemical reactions. The reduction peaks were considered by the authors as related to (i) reduction of $N,N'$-diphenylbenzidine (DPB) dication to DPB cation and (ii) reduction of DPB cation to DPB. In a CV study of DPA in 1.0 M $\text{CCl}_3\text{COOH}$ in dichloroethane with $[\text{Bu}_4\text{N}]\text{PF}_6$ as supporting electrolyte [186] only one reduction peak was observed, similar to the result obtained in this work.

7.3.2.2 Potentiostatic Growth of PDPA.(+)-HCSA Films and Their Chiroptical Properties

In preliminary studies it was found that PDPA.(+)-HCSA polymer films may be grown potentiostatically on an ITO-coated glass electrode using applied potentials between 0.7 and 1.3 V. In all subsequent experiments the PDPA.(+)-HCSA films were grown at 1.2 V, with the charge passed being kept at 200 mC cm$^{-1}$. However, unlike during the deposition of PAn.(+)-HCSA, the charge passed was not a reliable measure of the quantity of the deposited polymer for PDPA, since the latter partially dissolved. The PDPA polymer was also not stable in air, and the films could be kept only for a few hours.

The UV-vis-NIR spectrum of a typical PDPA.(+)-HCSA film deposited at 1.2 V (Figure 7.10) had peaks at ca. 330, 420, 810 and 1360 nm. The 330 and 420 nm absorption band positions are similar to those reported [122] for the $\pi-\pi^*$ transition and the low wavelength polaron absorption band, respectively, in PAn.(+)-HCSA. Interestingly, high wavelength polaron bands were observed at both 805 and 1300 nm for the
PDPA.(+)-HCSA emeraldine salt, which may suggest a mixture of “compact coil” and “extended coil” conformations for the polymer chains. Alternatively, these two bands may be peculiar to the structure of PDPA.(+)-HCSA, which is intermediate between polyaniline and poly(p-phenylene) (see Structure 3).

Figure 7.10 UV-vis-NIR spectrum of a PDPA.(+)-HCSA film deposited potentiostatically at 1.2 V from 0.2 M DPA / 0.5 M (+)-HCSA in 42 % water / 58 % acetonitrile solution.

The UV-vis spectra of PDPA.ClO$_4^-$ polymer films previously deposited on ITO-coated glass electrode at 0.8 V from acetonitrile solution [56, 59] showed less defined peaks than the presently studied PDPA.(+)-HCSA, exhibiting a peak at 460 nm and broad absorption band between 500 and 650 nm. Our PDPA.(+)-HCSA film therefore appears to be more characteristic of an emeraldine salt.
The CD spectrum of the above PDPA.(+)-HCSA film is presented in Figure 7.11. The observed ellipticities were very small, and the CD spectra of PDPA films deposited with the (+)- and (-)- enantiomers of HCSA as dopants were not mirror images. The presence of the phenyl rings in the polymeric chain of PDPA (3) may give rise to a polymer with a more rigid backbone than that of PAn. As a result the chiral dopant (+)-CSA$^-$ may not be able to induce the preferential formation of a one-handed helix in the PDPA polymer.

![Chemical structure of PDPA](image)

Figure 7.11  CD spectrum of the PDPA.(+)-HCSA film  from Figure 7.10.

7.3.2.3 Electrochemical Characterisation of PDPA.(+)-HCSA
A PDPA.(+)-HCSA film similarly grown on ITO-coated glass at 0.9 V was further characterised by cyclic voltammetry in 0.10 M aqueous (+)-HCSA solution (Figure 7.12) using a Pt disc (1 mm diameter) working electrode. When the upper potential limit was between 0.9 V and 1.3 V, the electroactivity of the polymer increased with each scan, which may be seen as the current response growing. Two redox pairs were well presented when the upper potential limit was 1.2 V, with oxidation peaks observed at 0.7 V and 0.9 V (Figure 7.12 a) and reduction peaks at 0.3 V and 0.6 V. Similar results have been observed for a PDPA.ClO$_4^-$ film [56, 59], cyclic voltammogram in acetonitrile exhibiting two sets of redox peaks assigned to the sequential formation of polarons and bipolarons (Scheme 7.2). Oxidation peaks were observed at 0.5 and 0.76 V, reduction peaks at 0.68 and 0.4 V. However, the same polymer showed only one set of redox peaks when cycled in dichloroethane with [Bu$_4$N]PF$_6$ as supporting electrolyte [186].

Interestingly, when the upper potential limit was increased to 1.4 V (Figure 7.12 b), only one pair of redox peaks was seen for the PMAS.(+)-HCSA film, with an oxidation peak at 0.75 V and a reduction peak at 0.25 V.
Scheme 7.2 Redox switching in PDPA.

Figure 7.12 Cyclic voltammograms of a PDPA.(+)-HCSA film in aqueous 0.10 M (+)-HCSA on a Pt disc working electrode (1 mm diameter), scan rate 100 mV/s.
7.3.2.4 Chemical Oxidation and Reduction of PDPA.(+)-HCSA Films

PDPA.(+)-HCSA films may be oxidised or reduced chemically. After oxidation for 10 min in 0.1 M (NH₄)₂S₂O₈ / 0.1 M HCl, the polaron band of the original polymer at 845 nm had largely disappeared, being replaced with a 745 nm absorption band, characteristic for pernigraniline (Figure 7.13).

After reduction of a PDPA.(+)-HCSA film in 0.1 M N₂H₄ for 5 min, absorption at wavelengths above 400 nm became significantly weaker, as expected for the leucoemeraldine form of polyaniline (Figure 6.14). The only strong absorption peak in the reduced PDPA was at ca. 330 nm which may be assigned to a π–π* transition band. Prolonged oxidation or reduction of PDPA.(+)-HCSA films (beyond 20 min) led to decomposition of the polymer.

![Figure 7.13](image_url)  
**Figure 7.13** UV-vis-NIR spectra of a PDHA.(+)-HCSA film: (1) as grown and (2) after 10 min oxidation in 0.1 M (NH₄)₂S₂O₈ / 0.1 M HCl.
Figure 7.14  UV-vis-NIR spectra of a PDHA.(+)-HCSA film: (1) as grown and (2) after reduction in aqueous 0.1 M N₂H₄ for 5 min.

7.3.2.5 Cyclic Voltammetry of PDPA.(+)-HCSA Films in the Presence of D- and L-Valine

PDPA.(+)-HCSA films were deposited on a Pt electrode potentiostatically at 1.2 V (200 mC current passed). Cyclic voltammograms in 0.1 M NaNO₃ showed that essentially identical films could be consistently grown in this fashion. Cyclic voltammetry of a PDPA.(+)-HCSA-coated Pt electrode in 0.02 M D- or L-valine solutions (with 0.1 M NaNO₃ as supporting electrolyte) (Figure 7.15) revealed an anodic shift of the polymer oxidation potential compared with the CV’s recorded above in 0.1 M (+)-HCSA. The peak current could not be reached due to overoxidation of the polymer. On the other hand, the polymer underwent easier reduction, as the reduction potential was shifted by 0.1 V to more positive values compared with cycling in 0.1 M (+)-HCSA solution. However, the polymer did not demonstrate any significant
discrimination between the L- and D-enantiomeric forms of the amino acid valine, possibly due to lower enantiomeric purity (see Figure 7.11).

Figure 7.15 Cyclic voltammograms of a PDPA. (+)-HCSA film in aqueous 0.02 M (a) L-valine and (b) D-valine; 0.1 M NaNO₃ supporting electrolyte.

7.3.3 Synthesis and Properties of Poly{(S)-(+-)(anilinomethyl)pyrrolidine} (PAMP)

7.3.3.1 Cyclic voltammetry of (S)-(+-)(anilinomethyl)pyrrolidine) (AMP)

A preliminary study of the oxidation of the (+)-AMP monomer (8) was carried out by cyclic voltammetry of a 0.35 M AMP / 1.0 M HCl aqueous solution (Figure 7.16).

![Structural formula of 8](image)

The CV was performed on an ITO-coated glass electrode between -0.2 V and 1.2 V with a scan rate 100 mV/s. It showed two redox pairs, with oxidation peaks at 0.6 and ca. 1.0 V and reductions waves at 0.2 and 0.0 V. The current did not increase with
successive scans due to the solubility of the polymer. As both monomer and polymer may have redox responses in this potential region, it was not possible to unequivocally identify their separate oxidative processes.

![Graph](image)

**Figure 7.16** Cyclic voltammetry of a 0.35 M (+)-AMP / 1.0 M HCl aqueous solution on an ITO-coated glass electrode; scan rate 100 mV/s.

### 7.3.3.2 Attempted Potentiostatic Polymerisation of (+)-AMP

For attempted potentiostatic polymerisation of (+)-AMP, an applied potential of 0.9 V was chosen. However, like the above potentiodynamic study, potentiostatic polymerisation led to a green, soluble product, the UV-Vis spectrum of which is shown in Figure 7.17. This exhibited peaks at ca. 400 and 830 nm, as expected for an emeraldine salt. However, the presence of the 600 nm peak is unusual for conducting emeraldine salts, whereas emeraldine base typically shows a strong band at this wavelength. However, the EB form is unlikely to be present in the 1.0 M HCl solution employed.
Figure 7.17 UV-vis-NIR spectrum of the product of potentiostatic oxidation of (+)-AMP at an applied potential of 0.9 V in 1.0 M aqueous HCl.

7.3.3.3 Chemical Synthesis of PAMP.HCl

Chemical oxidation of the (+)-AMP monomer was then examined using ammonium persulfate as oxidant. About 5 min after addition of the first drop of the oxidant solution, the reaction mixture started to turn green, suggestive of emeraldine salt formation. After 4 hrs the solution became dark green, but there was no precipitate forming. The UV-vis spectrum of the reaction mixture (diluted with 1.0 M HCl) is shown on Figure 7.18, exhibiting absorption bands at ca. 395, 415 and 580 nm. No high wavelength polaron band was observed at wavelengths above 800 nm. The spectrum was therefore inconsistent with that of the desired emeraldine salt, and the nature of the product is currently uncertain.
The product solution possessed weak optical activity. Its CD spectrum (Figure 7.19) showed a Cotton effect at 450 nm associated with the 420 - 460 nm polymer absorption band in Figure 7.18, and a broad Cotton effect at 600 – 700 nm, associated with the absorption band near 600 nm. Since the monomer only absorbs in the UV region, these Cotton effects must be associated with the polymer chains. The results therefore indicate that the presence of the chiral substituent on the nitrogen atom of AMP monomer induces a small amount of chirality into the presumably polymeric or oligomeric material formed.
7.4 Conclusions

Chiral polyanilines can be prepared via the electropolymerisation of aniline monomers bearing methyl or phenyl substituents on the aniline nitrogen atom. N-Methylaniline (NMA) forms a chiral polymer PNMA.(+)-HCSA when potentiostatically oxidised in the presence of the chiral dopant anion (+)-camphorsulfonate. The optical activity of the polymer is believed to arise from chiral induction by the (+)-CSA\(^-\) dopant to give one-handed helical fragments in the \(N\)-substituted polyaniline chains. Deposition of a PNMA.(+)-HCSA film on the electrode surface requires a high concentration of monomer (1.0 M). The UV-vis-NIR spectra of the films produced have a broad polaron band at ca 1150 nm, suggesting that the polymer chains are in an “extended coil” conformation. The PNMA.(+)-HCSA films are electroactive, exhibiting one redox pair,
and the electroactivity range is extended to 1.3 V which is significantly higher than that known for PAN.

Poly(diphenylamine) (PDPA.(+)-HCSA) polymers can also be electrodeposited potentiostatically at 1.2 V from a 42 % (v/v) water / 58 % acetonitrile mixture containing (+)-HCSA. The UV-vis-NIR spectra of these polymer films show absorption bands at 420 nm and ca. 810 nm, characteristic for emeraldine salts in the “compact coil” conformation. However, the PDPA backbone, being intermediate between those of polyaniline and poly(p-phenylene), apparently does not form a one-handed helix in the presence of (+)-HCSA, since the PDPA.(+)-HCSA films are only weakly optically active in the visible region. The polymers are electroactive, exhibiting two pairs of redox peaks when cycled between 0.2 and 1.2 V. PDPA.(+)-HCSA does not show discrimination towards enantiomers of the amino acid valine.

The chiral monomer, (S)-(+-)(anilinomethyl)pyrrolidine (AMP), bearing a chiral substituent on the nitrogen atom of aniline, polymerises chemically or electrochemically in 1.0 M HCl, but the resultant product is soluble and is possibly an oligomer. The presence of the chiral substituent presumably leads to formation of some one-handed helical fragments in the polymer product, as evidenced from the CD spectrum. However, the UV-vis-NIR spectrum of the product is inconsistent with that of an emeraldine salt, and the nature of this product is uncertain.
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