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Development of conducting polymers for separations

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DEVELOPMENT OF CONDUCTING POLYMERS FOR SEPARATIONS

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

DOCTOR OF PHILOSOPHY

from the

UNIVERSITY OF WOLLONGONG

by

DAVID ANDREW REECE, B.Sc. (Hons) Adv, Grad. Cert. Bus.

INTELLIGENT POLYMER RESEARCH INSTITUTE

DEPARTMENT OF CHEMISTRY

October 2003

This work is dedicated to my family and to Rachael as a thank you for all their support and encouragement.

CERTIFICATION

I, David Andrew Reece, 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.

David Reece

2 October 2003

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LIST OF ABBREVIATIONS

| | |
|-------------------|--|
| Å | Angstrom |
| A ⁻ | Anion |
| AAS | Atomic absorption spectroscopy |
| ADP | Adenosine-5'-diphosphate |
| AFM | Atomic force microscopy |
| AMP | Adenosine-5'-monophosphate |
| ATP | Adenosine-5'-triphosphate |
| BCS | Bathocuproinedisulfonic acid |
| BOX | Bilirubin oxidase |
| C6S | Calix[6]arene-4-sulfonic acid |
| cAMP | Cyclic adenosine-5'-monophosphate |
| CD | Circular dichroism |
| CDS | Cyclodextrin sulfate |
| cm ² | Square centimetre |
| CSA ⁻ | 10-camphorsulfonate ion |
| CV | Cyclic voltammetry |
| Da | Dalton |
| DBSA | Dodecylbenzenesulfonic acid |
| °C | Degrees celcius |
| DMF | <i>N,N'</i> -dimethylformamide |
| DMSO | Dimethyl sulfoxide |
| DNA | Deoxyribonucleic acid |
| EB | Emeraldine base |
| ES | Emeraldine salt |
| ESI | Electrospray ionisation |
| FTIR | Fourier transform infrared |
| g | Gram |
| g L ⁻¹ | Grams per litre |
| HA | Generic acid |
| HCSA | 10-camphorsulfonic acid |
| HPLC | High performance liquid chromatography |

| | |
|--------------------------------------|--|
| HQS | 8-hydroxyquinoline-5-sulfonic acid |
| HRP | Horseradish peroxidase |
| ICP | Inherently conducting polymer |
| ITO | Indium tin oxide |
| keV | Kiloelectron volt |
| kN | Kilonewton |
| kPa | Kilopascal |
| M | Molar |
| M ⁺ | Cation |
| μA | Microamp |
| mA cm ⁻² | Milliamps per square centimetre |
| MAS | 2-methoxyaniline-5-sulfonic acid |
| mg | Milligram |
| MHz | Megahertz |
| min | Minute |
| mL | Millilitres |
| mM | Millimolar |
| mm | Micrometre |
| mm | Millimetre |
| mm ² | Square millimetres |
| μm ² | Square micrometre |
| mol | Mole |
| mol s ⁻¹ cm ⁻² | Moles per second per square centimetre |
| mV | Millivolt |
| mV s ⁻¹ | Millivolts per second |
| mΩ | Milliohms |
| NIR | Near infrared |
| nm | Nanometre |
| NMP | <i>N</i> -methylpyrrolidinone |
| PAC | Polyacetylene |
| PAn | Polyaniline |
| PE ⁻ | Polyelectrolyte |
| PMAS | Poly(2-methoxyaniline-5-sulfonic acid) |

| | |
|--------------------|-----------------------------------|
| PPy | Polypyrrole |
| PSS | Poly(styrene sulfonate) |
| PTh | Polythiophene |
| PTS | <i>para</i> -toluenesulfonate |
| PVA | Poly(vinyl alcohol) |
| PVDF | Poly(vinylidene fluoride) |
| PVP | Poly(vinyl pyrrolidinone) |
| PVPh | Poly(vinyl phosphate) |
| RO | Reverse-osmosis |
| s | Second |
| S cm ⁻¹ | Siemens per centimetre |
| SEM | Scanning electron microscopy |
| SPAN | Sulfonated polyaniline |
| THF | Tetrahydrofuran |
| UV-Vis | Ultraviolet-visible |
| UV-Vis-NIR | Ultraviolet-visible-near infrared |
| V | Volt |
| v/v | Volume/volume |
| Ω | Ohm |
| w/v | Weight/volume |
| X ⁺ | Cation |

ABSTRACT

This thesis describes the synthesis and characterisation of a range of novel conducting polymer materials with potential applications in the area of separations. Both polypyrroles and polyanilines are examined. Following a General Introduction and an Experimental Chapter, the new studies are described in Chapters 3 to 7.

In Chapter 3 it is shown that polypyrrole doped with either α -cyclodextrin sulfate (α -CDS) or β -cyclodextrin sulfate (β -CDS) is readily deposited electrochemically. Electrodeposited polypyrrole has been characterised using UV-Vis spectroscopy, cyclic voltammetry, AFM, SEM, microanalysis, and electrical conductivity measurements. This electrodeposited polypyrrole can easily be prepared as a composite membrane (with Pt-coated PVDF) for use in metal ion transport experiments. Transport of metal ions across PPy. β -CDS is shown to be significantly greater than across PPy. α -CDS, and also greater than that previously observed with related polypyrroles. However, the increased flux results in a loss in the selectivity that the membrane shows between different metal ions.

Chapter 4 describes a novel electroless polymerisation of pyrrole in the presence of the sulfonated calixarene, calix[6]arene-4-sulfonic acid (C6S). A solution containing pyrrole and C6S undergoes a slow polymerisation reaction in the absence of any added chemical oxidant or electrochemical oxidation. A specific host-guest interaction between pyrrole and C6S is thought to be an important part of the reaction mechanism. The product of this reaction is an insulating black powder. However, it is electroactive

and exhibits spectral features similar to conducting polypyrroles and is doped with C6S. On the basis of the obtained data, a structure consisting of small conducting regions of polypyrrole isolated by insulating pyrrolidine and ring-opened products is proposed. The addition of polymeric stabilisers such as poly(vinyl alcohol), poly(vinyl pyrrolidinone) or poly(styrene sulfonate) results in the formation of stable colloidal dispersions of the polypyrrole.

The interaction of polyaniline and some biological phosphates (particularly adenosine-5'-triphosphate (ATP)) is reported in Chapter 5. When ATP is included as a dopant during the electrosynthesis of polyaniline, highly optically active films with chiral anisotropy factors as high as 1.9 % are obtained. It is believed that this optical activity arises from interactions between hydrogen- and ionic-bonding sites of the ATP dopant with the amine nitrogen (NH) and radical cation ($+ \cdot \text{NH}$) centres on the polyaniline chains. These highly optically active polyaniline films retain their optical activity upon de-doping, re-doping, oxidation and reduction. Initial investigations into potential applications for these polyanilines show that the release of ATP from the polymers cannot be electrochemically or pH controlled; and no chiral discrimination towards 10-camphorsulfonic acid is observed.

The covalent attachment of a chiral substituent to nitrogen centres of polyaniline is examined in Chapter 6. 10-camphorsulfonyl chloride readily reacts with polyaniline emeraldine base in solution to form a weakly optically active emeraldine salt. This substituted polyaniline retains its optical activity in solution even upon alkaline de-doping. However, optical activity is lost upon oxidation and reduction. An analogous reaction can also be performed on leucoemeraldine base to form a virtually identical

optically active emeraldine salt. Alternatively, a similar reaction on aniline monomer forms a substituted chiral monomer. However, this monomer cannot be polymerised, presumably due to the steric and/or electron withdrawing effects of the 10-camphorsulfonyl substituent.

In the final chapter, Chapter 7, the induction of chirality into poly(2-methoxyaniline-5-sulfonic acid) (PMAS) via acid-base interactions with a range of chiral bases is investigated. Films evaporatively cast from aqueous solutions of PMAS mixed with alkaloids, amino acids or adenosine are all found to be optically active, confirming induction of chirality into the PMAS chains. The origin of this chiral induction is discussed on the basis of the chiroptical properties of the PMAS.Chiral Base species obtained.

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