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Development of chiral conducting polymers for asymmetric electrosynthesis

Yingpit Pornputtkul
University of Wollongong

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**DEVELOPMENT OF CHIRAL
CONDUCTING POLYMERS FOR
ASYMMETRIC ELECTROSYNTHESIS**

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

DOCTOR OF PHILOSOPHY

from the

UNIVERSITY OF WOLLONGONG

by

YINGPIT PORNPOTTKUL, M.Sc.(Biochemistry)

**INTELLIGENT POLYMER RESEARCH INSTITUTE
DEPARTMENT OF CHEMISTRY**

July 2005

CERTIFICATION

I, Yingpit Pornputtkul, 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.

Yingpit Pornputtkul

July 2005

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ABBREVIATIONS

μ	micro
$\Delta\epsilon$	difference in molar extinction coefficients
λ	wavelength
$^{\circ}\text{C}$	degree Celsius
$[\alpha]$	specific rotation
A	ampere
A^{-}	anion
AE	auxiliary electrodes
Ag/AgCl	silver/silver chloride reference electrode
BMI-BF ₄	1-butyl-3-methylimidazolium tetrafluoroborate
BMI-PF ₆	1-butyl-3-methylimidazolium hexafluorophosphate
C	coulomb
CD	circular dichroism
cm	centimetre
cm^{-1}	wave number
CS	chemical synthesis
CV	cyclic voltammetry
DSC	differential scanning calorimetry
E	potential
EB	emeraldine base
ECS	electrochemical synthesis
EMI-TFSI	1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
ES	emeraldine salt
g	gram
GC	glassy carbon
HA	protonic acid
HCSA	10-camphorsulfonic acid
hr	hour
I	current

IL	ionic liquid
ITO	indium-tin oxide
LB	leucoemeraldine base
LS	leucoemeraldine salt
M	molar
mA	milliampere
MBEA-TFSI	methylbenzylethylamine bis(trifluoromethanesulfonyl)imide
mdeg	millidegree
min	minute
mm	millimetre
mM	millimolar
m.p.	melting point
MNPS	methyl 4-nitrophenyl sulfide
MPTS	methyl- <i>p</i> -tolyl sulfide
mV	millivolt
nm	nanometre
NMP	1-methyl-2-pyrrolidinone
P ₁₃ -TFSI	1-methyl-1-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide
PAn	polyaniline
PB	pernigraniline base
PLL	poly-L-lysine
PMAS	poly(2-methoxyaniline-5-sulfonic acid)
PPy	polypyrrole
PS	pernigraniline salt
Pt	platinum
PVDF	Poly(vinylidene)difluoride
Q	charge
RE	reference electrode
Rs	resistivity
RVC	reticulated vitreous carbon

S/cm	siemens per centimetre
sec	second
SPAN	sulfonated polyaniline
T _g	glass transition temperature
T _m	melting temperature
TGA	thermogravimetric analysis
UV-vis	ultraviolet-visible
V	volt
WE	working electrode

Abstract

This thesis describes novel synthetic routes and characterization of chiral conducting polymers based on aniline and substituted anilines that have potential applications in the areas of asymmetric electrosynthesis and chiral separations. Ionic liquids and novel chiral ionic liquids are used as novel electrolytes for the polymer synthesis and for improvement of the electrochemical stability of chiral polyaniline doped with (+)-10-camphorsulfonic acid. Electroorganic syntheses using bare or chiral polyaniline modified electrodes in ionic liquids or chiral ionic liquid electrolytes are explored. Following an Introduction and a General Experimental Chapter, the new studies are described in Chapters 3 to 10.

Chapter 3 reports a novel route to prepare optically active emeraldine salts via thermal treatment. Emeraldine base films were prepared by alkaline de-doping of PAn.HCl emeraldine salt films electrochemically deposited or chemically prepared. Chemically prepared emeraldine base films were cast onto glass slides from NMP solution. Re-doping these films with aqueous (+)-10-camphorsulfonic acid (1.0 M (+)-HCSA) gave optically inactive PAn.(+)-HCSA films. Significantly, after heat treatment at 170°C, optically active polyaniline were generated, as evidenced by their circular dichroism spectra. This is believed to be due to the polyaniline chains preferentially adopting a one-handed helix under the influence of the chiral dopant CSA⁻ anion during heating of the films at temperatures above the glass transition temperature (T_g) of polyaniline.

An unprecedented route to optically active polyanilines from achiral reagents using a chiral emeraldine salt inducer is described in Chapter 4. This macromolecular asymmetric proliferation is performed via electrochemical polymerization of aniline in

racemic (e.g. (\pm) -HCSA) or achiral (e.g. HCl and *p*-TSA) acid solutions using a thin film of chiral PAn.(+)-HCSA or PAn.-)-HCSA pre-electrodeposited on the working electrode as a chiral inducer. The thin film of PAn.(+)-HCSA or PAn.-)-HCSA was deposited on ITO-coated glass electrodes using 25 mC/cm² electrodeposition charge, giving a thickness of *ca.* 100 nm. Remarkably, strongly optically active PAn.HA films of the same hand as the chiral inducer were produced during the second stage electrodepositions (another 100 mC/cm²) using (\pm) -HCSA or achiral acids. A possible mechanism for this chiral induction is discussed. Experiments using deposition charges of between 50 and 300 mC/cm² in the second electrodeposition showed that induction by the thin PAn.(+)-HCSA film occurred undiminished for final films as thick as 700 nm. This novel asymmetric synthesis method presents potential applications such as using thin chiral polyaniline films as inducers for the electrochemical asymmetric synthesis of other chiral conducting polymers.

The fully sulfonated polyaniline poly(2-methoxyaniline-5-sulfonic acid) (PMAS) was found in Chapter 5 to be remarkably resistant to alkaline de-doping, even in 3 M NaOH or conc. NH₄OH. Instead of de-doping to the corresponding emeraldine base, UV-visible spectral studies showed that a change of conformation for the polyaniline chains from an “extended coil” to a “compact coil” arrangement occurred. However, when the sterically crowded amines tetrabutylammonium hydroxide (Bu₄NOH) and diisopropylamine were added to aqueous PMAS, de-doping of the “compact coil” emeraldine salt to emeraldine base was observed (pH \geq 11.5), as evidenced by the appearance of a characteristic absorption band at *ca.* 630 nm. The resistance to de-doping in NaOH and NH₄OH may therefore be associated with the electrostatic binding of the relatively small Na⁺ and NH₄⁺ ions to sulfonate (SO₃⁻) groups on the PMAS chains, which is sterically hindered for the larger ammonium ions.

The redox switching properties of PMAS were also investigated in Chapter 5. The oxidation behaviour of PMAS was similar to that previously observed for unsubstituted polyaniline. However, an unexpected sharp peak at 408 nm was observed for the reduced leucoemeraldine base (LB) form of PMAS generated by treatment with aqueous hydrazine, together with the usual 330 nm peak of LB assigned as a π - π^* transition. Thermo- and solvatochromism of the reduced PMAS species was observed involving reversible interconversion between the 408 nm and 330 nm species. These phenomena may involve a rearrangement of the PMAS leucoemeraldine base chains between two conformations.

A novel chiral composite is prepared in Chapter 6 by mixing aqueous solutions of PMAS and poly-L-lysine (PLL) and casting as films. The highest degree of chiral induction in the PMAS-PLL films was observed using a PMAS/PLL molar ratio of 1. The electrical conductivity of the PMAS-PLL (1:1) films was *ca.* 4×10^{-3} S/cm, an order of magnitude less than PMAS itself. The chiral PLL in the complex is believed to induce optical activity into the main chain of the PMAS moiety, as evidenced by its CD spectrum in visible region. The observed optical activity of the PMAS-PLL films may arise from the PMAS chains adopting a one-handed helical structure due to electrostatic interactions between free sulfonic acid groups on the PMAS with ammonium side chain groups on the PLL. The PMAS-PLL composite films remained optically active during treatment with 1.0 M NH_4OH and when reduced with hydrazine or oxidized with ammonium persulfate.

The temperature employed in the electrochemical polymerization of aniline is found in Chapter 7 to have a critical effect upon the chiroptical properties of PAn.(+)-HCSA films deposited on ITO-coated glass from aqueous 0.2 M aniline/1.0 M (+)-HCSA.

Films grown at elevated temperatures (35-65°C) have inverted CD spectra compared to analogous films grown at lower temperatures (0-25°C). These observations are explained in terms of a temperature-induced interconversion between two diastereomeric emeraldine salt products during the doping of the growing polyaniline chains with the chiral (+)-CSA⁻ anion. The critical effect of polymerization temperature found in this study highlights the importance of employing a controlled temperature during electrochemical synthesis of optically active polyanilines.

The influence of solvents on the chiroptical properties of PAn.(+)-HCSA emeraldine salt films prepared in ionic liquids are explored in Chapter 8. Polymerizations at high temperature (50-55°C) are required for dissolution of the (+)-HCSA (0.5 M) in all ionic liquids studied, except for (-)-MBEA-TFSI in which solvent HCSA is highly soluble at room temperature. Electroactive polyaniline can be prepared from the electrochemical polymerization of aniline in the presence of (+)-HCSA in the ionic liquids BMI-BF₄, BMI-PF₆, EMI-TFSI, P₁₃-TFSI and chiral (-)-MBEA-TFSI. Raman spectra of the films generally showed characteristics of emeraldine salts, and were very similar to those previously reported for PAn.HCSA synthesized via conventional methods. However, the polymer grown from EMI-TFSI showed different features indicating the presence of unusual chemical structures. These are probably generated by *ortho*-coupling and cross-linking during electropolymerization. The optical activity of the PAn.(+)-HCSA films grown from EMI-TFSI, BMI-BF₄ and P₁₃-TFSI were relatively low, and much less than previously observed for analogous films electrodeposited from aqueous solution, while the emeraldine salt grown from BMI-PF₆ was optically inactive. This probably arises from competition between chiral (+)-CSA⁻ and the achiral anions of the ionic liquids (BF₄⁻, TFSI⁻, PF₆⁻) as the dopant incorporated into the polymer during polymerization. An attempt to prepare a chiral emeraldine salt from electrochemical polymerization of

aniline with racemic (\pm)-HCSA using the novel chiral ionic liquid (-)-MBEA-TFSI as electrolyte was unsuccessful. Anodic degradation during polymerization at high positive potential (+1.3 V) apparently generated low molecular weight polyaniline oligomers whose length may be too short to maintain a helical structure, as the green product dissolved/dispersed in the polymerization solution.

The electrochemical and chiroptical properties of chiral PAn.(+)-HCSA emeraldine salts prepared in aqueous (+)-camphorsulfonic acid and investigated in ionic liquids are explored in Chapter 9. The nature of the ionic liquids employed and the applied potential have a marked effect on the stability of the chiral polyaniline films. Reversible loss of the electroactivity of the PAn.(+)-HCSA films occurred when the polyaniline films were potential cycled in the ionic liquids EMI-TFSI, BMI-PF₆ and BMI-BF₄. Electrochemical degradation of the polyaniline films occurred in EMI-TFSI and MBEA-TFSI electrolytes when they were polarized at high positive potentials ($> +1.1$ V). However, significantly, in BMI-PF₆ and BMI-BF₄ electrolytes the optical activity and electrochemical stability of the polyaniline films were retained at potentials as extreme as + 2.0 V. However, cross-linking involving a phenazine-type structure occurred when the PAn.(+)-HCSA films were exposed to high positive potentials in BMI-PF₆, as evidenced by their Raman spectra. Racemization of the PAn.(+)-HCSA films occurred when electrochemical reduction was carried out in all of the ionic liquids examined except (+)-, (-)-, or (\pm)-MBEA-TFSI. In the later ionic liquid electrolyte, strong CD signals were observed for the leucoemeraldine base film formed. Incorporation of the cation from the ionic liquids during the reduction (rather than expulsion of the (+)-CSA⁻ anion) and resultant swelling of the polyaniline films may be the reason for the racemization observed in the other ionic liquids.

These are important observations, since they open the possibility of using such PAn.(+)-HCSA films as chiral electrodes in electrochemical asymmetric syntheses in appropriate ionic liquids. BMI-PF₆ and BMI-BF₄ appear to have potential as electrolytes in electrochemical asymmetric oxidations (e.g. the oxidation of prochiral sulfides to chiral sulfoxides) at high positive potentials, while MBEA-TFSI would appear useful for electrochemical asymmetric reductions (e.g. the reduction of prochiral ketones to chiral alcohols) at very negative potentials.

Electroreduction of carbonyl compounds such as acetophenone and acetylpyridine to alcohols and electrooxidation of organosulfides such as methyl 4-nitrophenyl sulfide and methyl-*p*-tolyl sulfide to the corresponding sulfoxides in ionic liquids are explored in Chapter 10. The expected alcohol products were obtained from potentiostatic reduction of acetophenone and 2-acetylpyridine in EMI-TFSI on glassy carbon electrodes at -1.9 and -1.8 V, respectively. Reduction of 4-acetylpyridine in (-)-MBEA-TFSI on a glassy carbon electrode at -1.6 V yielded 4-pyridylethanol. However, the optical rotation of the product could not be measured due to interference from the chiral ionic liquid which could not be completely separated from the product. 4-Acetylpyridine was not reduced in (±)-MBEA-TFSI on a PAn.(+)-HCSA modified ITO-Pt-coated electrode to the corresponding alcohol, the corresponding achiral pinacol being instead formed.

Oxidation of methyl 4-nitrophenyl sulfide in EMI-TFSI and methyl-*p*-tolyl sulfide in BMI-BF₄ on glassy carbon electrodes was shown to yield the corresponding sulfoxides products. However, the asymmetric electrosyntheses of these sulfoxides in ionic liquids by using a chiral polyaniline modified electrode was not successful due to oxidative degradation of the polyaniline.