ELECTROCHEMISTRY OF CHIRAL POLYANILINE IN IONIC LIQUIDS

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ABSTRACT

The electrochemical behavior and chiroptical properties of electrodeposited chiral PAN.(+)-HCSA emeraldine salt films \{HCSA = (+)-10-camphorsulfonic acid\} have been investigated in a variety of ionic liquids \{1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF6), 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF4), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI), and (+) or (-) and (±) -α-methylbenzylethylamine bis(trifluoromethyl sulfonyl)imide (MBEA-TFSI)\} using cyclic voltammetry and \textit{in situ} electrochemical UV-visible and circular dichroism spectroscopy. The electroactivity of the PAN.(+)-HCSA films was generally retained over a wide potential range. Although electrochemical degradation of the polyaniline films occurred in EMI-TFSI and MBEA-TFSI when they were held at high positive potentials (> +1.1 V), no evidence of degradation or chemical modification of polyaniline was observed when polarized at +2.0 V in BMI-BF4. Surprisingly, racemisation of the polyaniline films occurred in all of ionic liquids when they were held at negative potentials, except in chiral or racemic MBEA-TFSI. Racemisation is attributed to incorporation of the cation from the ionic liquid during the reduction (rather than expulsion of the (+)-CSA anion) and resultant swelling of the polymer film. These results open the way to the future exploration of electrochemical asymmetric synthesis using such chiral polyaniline-modified electrodes and appropriate ionic liquids.

INTRODUCTION

The electrolyte is known to play a critical role in determining the properties and performance of inherently conducting polymers such as polypyrrole, polythiophene and polyaniline when they are used in electrochemical applications (1). The fact that these polymer materials are essentially conductive ion exchange resins means that they will undergo facile exchange processes with anions present in the electrolyte. These exchange processes may be further influenced via the electrochemical oxidation/reduction of the polymer as illustrated for polyaniline (PAn) in Scheme 1.
The dopant anion has been shown to affect chemical properties (e.g., subsequent ion exchange capabilities), electrochemical switching potential, and electronic conductivity and of the polyanilines. We have also shown that unique molecular structures can be generated in polyanilines by incorporation of chiral dopant anions, with such dopants inducing macroasymmetry in the polymer backbone.

It has been shown that once this chiral structure is adopted by polyaniline films, a series of oxidation/reduction cycles can be carried out in aqueous media without a loss of chirality. However, aqueous electrolytes have a limited electrochemical potential window, which in turn limits the possible use of these novel chiral electrode materials in electrochemical applications such as asymmetric electrosynthesis. The degradation of polyaniline in aqueous electrolytes at more positive potentials has been described previously. In addition, syntheses of interest such as the oxidation of prochiral organosulfides to give chiral sulfoxides (at positive potentials) or the reduction of prochiral ketones to form chiral alcohols (at negative potentials) generally require the application of potentials that result in oxidation/reduction of water and/or other conventional electrolytes.

Ionic liquids (ILs), organic room temperature molten salts, have been shown to be extremely useful electrolytes. Their extremely low vapour pressure, wide electrochemical potential window, good ionic conductivity, and unique solvent properties make their use appealing in a number of applications. ILs have yielded some additional benefits when used with conducting polymer electrodes. The extended potential window for ILs usually results in an extended working range for the conducting polymer electrode. It has also been found that the intimate interaction of selected organic cations from IL electrolytes with the conducting polymer backbone can actually enhance electromechanical performance.

Scheme 1: Redox and pH switching between the various forms of polyaniline.
In order to further elucidate the behaviour of conducting polymer electrodes in IL electrolytes we have investigated the electrochemical and chiroptical behaviour of chiral polyaniline in the range of ionic liquids shown in Figure 1.

**EXPERIMENTAL**

*Materials.* — Aniline (Aldrich) was distilled under a nitrogen atmosphere prior to use. (1S)-(+)10-camphorsulfonic acid (HCSA) was purchased in the purest grade available from Aldrich and used as supplied. The ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆) (20), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI) (20), and the chiral (+)- or (-) and (±) -α-methylbenzylethylamine bis(trifluoromethyl sulfonyl)imide (MBEA-TFSI) (21) were synthesised in house using previously published methods. 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄) was purchased from Solvent Innovation. All ionic liquids were deoxygenated by purging with nitrogen gas for at least 30 min prior to use. Indium-tin-oxide coated glass was obtained from Delta Technology Ltd (8-12 Ω) and was sputter coated with platinum (ITO-Pt) at 30 mA for 5 sec prior to use to facilitate the deposition of uniform and strongly adhering polyaniline films on the substrate.

**Electrochemical preparation of PAN.(+)-HCSA films.** — Electrochemical polymerisations in aqueous solution were carried out at room temperature (20-25°C) using glassy carbon (0.07 cm² surface area) or platinised ITO coated glass, platinum mesh and Ag/AgCl(EMI-TFSI) as working, auxiliary and reference electrodes, respectively. The polymerisation solution was 1.0 M (+)-HCSA containing 0.2 M aniline, deoxygenated by bubbling with nitrogen gas for 15 min. The PAN.(+)-HCSA films were deposited on the GC-disk working electrode at 0.8 V for 70 mC/cm² charge passed, and on ITO-Pt coated glass at 0.9 V (120 mC/cm²), respectively, using a BAS CV-27 potentiostat. The PAN.(+)-HCSA modified electrodes were washed with methanol to remove oligomers, excess (+)-HCSA and monomer and then vacuum dried at room temperature for 3 hrs.

**Electrochemical behavior** — Cyclic voltammetry studies were carried out in a one-compartment electrochemical cell with three electrode configuration. A PAN.(+)-HCSA film deposited on glassy carbon (0.07 cm² surface area), platinum mesh and Ag/AgCl(EMI-TFSI) as working, auxiliary and reference electrodes, respectively. Ionic liquids were gently purged with nitrogen gas for at least 30 min prior to use and during the experiments. A PC-controlled CV-27 potentiostat with Mac Lab and EChem software was used for cyclic voltammetry.

**UV-visible and circular dichroism (CD) spectroscopic studies** — Spectroelectrochemical experiments were performed in a 1 cm pathlength quartz cuvette with the three electrode configuration. A PAN.(+)-HCSA film deposited on ITO-Pt coated glass was used as working electrode, installed perpendicularly to the light path. A platinum wire and ITO coated glass installed parallel to the working electrode was used as the auxiliary electrode. The reference electrode used in the ionic liquid electrolytes was Ag/AgCl(EMI-TFSI). After polarisation at a certain potential by using a BAS CV-27 potentiostat, UV-visible spectra were recorded with a Shimadzu model UV-1601 spectrophotometer, while CD spectra were measured using a Jobin Yvon Dichrograph 6.
**Raman studies** – Raman spectra of the polyaniline films were recorded using Jobin-Yvon-Horiba HR800 spectrometer equipped with an optical microscope and a CCD detector. The spectra were excited with the 632.8 nm line of a He-Ne laser. The laser beam was focused on the film by a x100 lens.

**RESULTS AND DISCUSSION**

**Cyclic voltammetry studies**

The electrochemical behaviour of the electrodeposited PAN.(+)-HCSA films on glassy carbon was characterised in each of the ionic liquids using cyclic voltammetry. Using a limited potential range (see Figure 2) only one redox process (attributed to the leucoemeraldine to emeraldine redox transition (see Scheme 1) was obvious. No significant degradation of the polymer was observed during potential cycling in these ranges for many hundred cycles in all ionic liquids used.

In all of the ionic liquids investigated this leucoemeraldine to emeraldine transition initially occurs at more positive potentials but gradually moves to less positive potentials with subsequent cycles. This suggests that the electrolyte anion is initially more difficult to incorporate. However, as it gradually replaces the (+)-CSA-anion in the polymer during CV cycling, the anion exchange process upon oxidation/reduction becomes more facile.

Extending the potential range to more positive potentials in EMI-TFSI electrolyte resulted in the appearance of a second redox response at more positive potentials (Figure 3). This latter response is attributed to the emeraldine to pemigraniline transition (see Scheme 1). Polyanilines are known to degrade rapidly in aqueous (22-23) or other organic (23-24) media when the potential is such that the pemigraniline form is produced. However, as seen in Figures 3, when using the ionic liquid electrolyte only slow degradation/decrease of current response was observed. Over this extended potential range similar results were obtained in all ionic liquids investigated.

Cycling to further extended potentials (> +1.2 V) in either EMI-TFSI or MBEA-TFSI resulted in polymer film degradation and rapid loss of electroactivity. This was not the case when BMI.PF$_6$ or BMI.BF$_4$ was used. Relatively stable electrochemistry was observed even when the positive potential limit was extended to +2.0 V (Figure 4). In contrast, using more conventional electrodes (e.g. bare GC) with ILs containing TFSI', BF$_4$' or PF$_6$' as the anion, the upper potential limit is similar for each IL. This suggests that the TFSI' anion interacts in some way with the polyaniline material causing a deterioration in mechanical properties. The effect of the electrolyte anion on the anodic degradation of polyaniline in aqueous electrolytes has been reported previously (25,26).

The effect of extending the potential range in the negative direction was then investigated. Using EMI-TFSI, BMI.BF$_4$ or BMI.PF$_6$ as electrolyte, electroactivity rapidly decreased upon extending the negative potential limit to -1.5 V. However, the polymer did not physically degrade and the normal redox responses were observed when these polymers were removed from the ionic liquid and cyclic voltammograms recorded for these polymers in aqueous HCSA. However, for the ionic liquid MBEA-TFSI (in either the optically active (+)-MBEA, (-)-MBEA or racemic (+)-MBEA form)
electroactivity was retained (Figure 5) even when potentials as negative as -2.0 V were applied. This behaviour is attributed to specific interactions of the cation of the IL with the polyaniline material. With EMI or BMI the electroactivity of the polyaniline is shut down. Redox cycling of polyanilines has been shown to involve (27, 28) the insertion/expulsion of protons, anions and water. Similarly in organic solvents the transport of protons, anions and solvent is important (24, 29, 30). It has been shown that while polyanilines are inherently more stable in organic media degradation does still occur. The degradation pathways are believed to be different (23), however some degradation may be associated with residual water trapped in polyanilines during synthesis (31). The solubility of the anion incorporated during synthesis in the organic media being used for electrochemically switching as been shown to have a profound effect (4).

In-situ spectroelectrochemical studies

In-situ spectroelectrochemical studies on PAn.(+)-HCSA films electrodeposited on ITO-coated glass electrodes were also employed to investigate the effect of oxidation and reduction on the UV-visible and CD spectra of the polyaniline in various ionic liquids. The UV-visible and CD spectra of the as-grown film are shown in Figure 6. As expected, the application of negative potentials of \( \leq -0.20 \) V in all the ionic liquids resulted in the disappearance of the UV-visible bands characteristic of the PAn.(+)-HCSA emeraldine salt and the appearance of a band at ca. 320-350 nm characteristic of the fully reduced leucoemeraldine base form of polyaniline (32).

However, to our surprise, the leucoemeraldine base formed was typically found to be optically inactive, indicating racemisation during the reduction. This contrasts with the behavior of PAn.(+)-HCSA films in aqueous electrolytes where reduction to the leucoemeraldine base form has been reported to occur with retention of optical activity (8). This was believed to be due to the severely hindered chain movement in the solid state films.

The only exception to this behaviour was observed for reduction of the PAn.(+)-HCSA film in the ionic liquid MBEA-TFSI (either in the chiral (+) or (-) -or racemic (+)-MBEA form), where reduction even at potentials as negative as -2.0 V was shown from UV and CD spectra to give the optically active leucoemeraldine base (8) (Figure 7). The leucoemeraldine base formed exhibited strong bisignate CD bands centred at ca. 360 nm, associated with the corresponding absorption band at this wavelength.

This contrasting behaviour with the different ionic liquids may be rationalised by assuming that during reduction in all the electrolytes except MBEA-TFSI, charge balance is largely achieved in the polyaniline material via incorporation of the cation from the ionic liquid rather than by expulsion of the (+)-CSA' anion. The concomitant swelling may allow the movement of the polyaniline chains required for racemisation. Evidence for such cation incorporation and consequent swelling has been recently reported in polyaniline (30). In contrast, during reduction of PAn.(+)-HCSA films in MBEA-TFSI as electrolyte, expulsion of the (+)-CSA' anion may be the dominant charge compensation mechanism. It is interesting to note that the solubility of HCSA in MBEA-TFSI (0.7 M at 20° C) is much more than in the other ILs (ca. 0.01-0.05 M at 20° C) studied. Lu and Mattes (4) have recently reported that the solubility of anion dopants in non-aqueous electrolytes has a significant impact on the electrochemistry and actuation of polyaniline.

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Application of more positive potentials in all ILs resulted in spectral changes attributed to the conversion of emeraldine salt to pernigraniline salt form (see Scheme 1). However, there was a decrease and finally a complete loss of polyaniline film optical activity at potentials > 1.1 V in (+)- or (±)- MBEA-TFSI (Figure 8) and EMI-TFSI. This might be associated with oxidative degradation of polyaniline chains as dissolution of the polymer films was observed at these very positive potentials. The degradation of polyaniline at ≥ 1.1 V in these ILs probably arises from polymer chain scission, as found in electrochemical systems containing conventional organic solvents (23).

Surprisingly, this was not the case when BMI-PF$_6$ and BMI-BF$_4$ were used as electrolyte. The optical activity of the polyaniline films was also preserved even at +2.0 V in BMI-PF$_6$ (Figure 9) and BMI-BF$_4$.

In addition, Raman spectra of the films (using the excitation line $\lambda_{\text{exc}} = 632.8$ nm) indicated that no chemical modification of the polymer backbone occurred after application of + 2.0 V in BMI-BF$_4$; whereas a cross-linked structure, with bands located at ca. 579, 1384, 1649 cm$^{-1}$ (33-35), was formed after holding at + 2.0 V in BMI-PF$_6$. Crosslinking of polyaniline to form a structure containing phenazine rings has been previously observed when polyaniline was held at high anodic potential (36-39) or treated at high temperature (34, 40-43). It appears that similar crosslinking occurs when exposed to high positive potentials in BMI-BF$_4$ ionic liquid.

CONCLUSIONS AND FUTURE DIRECTIONS

The electrochemical stability and chiroptical properties of electrodeposited PAn.(+)-HCSA films in ionic liquid electrolytes are strongly dependent on the applied potential and on the nature of the ionic liquid used. Although electrochemical degradation of the polyaniline films occurs in EMI-TFSI and MBEA-TFSI when they are polarized at high positive potentials (> +1.1 V), significantly, in BMI-PF$_6$ and BMI-BF$_4$ the optical activity and electrochemical stability of the polyaniline films are retained at potentials as extreme as + 2.0 V. Undesirable racemisation occurs when electrochemical reduction (- 2.0 V) is carried out in all of the ILs examined except MBEA-TFSI. where in a strong CD signal is observed for the leucoemeraldine base formed. BMI-PF$_6$, BMI-BF$_4$ and MBEA-TFSI therefore appear to have useful potential as electrolytes in electrochemical asymmetric synthesis using chiral polyaniline-modified electrodes. This aspect of their use is the subject of ongoing investigations.

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| Ionic liquids          | Cation                          | Anion                          |
|----------------------|---------------------------------|--------------------------------|
| BMI-BF₄              | ![Cation Structure](image1)    | BF₄⁻                           |
| BMI-PF₆              | ![Cation Structure](image2)    | PF₆⁻                           |
| EMI-TFSI             | ![Cation Structure](image3)    | CF₃O₂S⁻N⁻SO₂CF₃                |
| ((+)-(-)- or (±)- MBEA-TFSI | ![Cation Structure](image4) | CF₃O₂S⁻N⁻SO₂CF₃                |

Figure 1. Structures of ionic liquids used in this work.
Figure 2. CVs of PAn.(+)-HCSA deposited on to GC, carried out in: (a) BMI-BF₄, 40 cycles, 50 mV/s; (b) BMI-PF₆, 40 cycles, 50 mV/s; (c) EMI-TFSI, 50 cycles, 100 mV/s; (d) (-)-MBEA-TFSI, 20 cycles, 25 mV/s. * Arrows indicate increasing number of scans.

Figure 3. Cyclic voltammograms obtained in EMI-TFSI using PAn.(+)-HCSA deposited on to GC as the working electrode. Scan rate = 50 mV/sec: (a) 20th cycle, (b) 50th cycle, (c) 100th cycle.
Figure 4. Cyclic voltammograms obtained for PAn.(+)-HCSA deposited on to GC. Electrolyte was BMI-PF$_6$. Scan rate = 50 mV/s.

Figure 5. Cyclic voltammograms obtained for PAn.(+)-HCSA deposited on to GC. Electrolyte was (-)-MBEA-TFSI. Scan rate = 50m V/s. Cycle numbers 41-60 shown.
Figure 6. Typical UV-vis and CD spectra for a PAn.(+)-HCSA film electrodeposited on ITO glass.
Figure 7. *In situ* UV-visible spectra (a) and CD spectra (b) of a PAn.(+)-HCSA film after being held at -2.0 V for 30 min in (-)-MBEA-TFSI.
Figure 8. *In situ* UV-visible spectra (a) and CD spectra (b) of a PAn.(+)-HCSA film after being held at various positive potentials for 5 min in (-)-MBEA-TFSI.
Figure 9. *In situ* UV-visible spectra (a) and CD spectra (b) of a PAn. (+)-HCSA film after being held at +2.0 V for 5 min in BMI-PF$_6$. 