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

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ABSTRACT: The electropolymerization of *o*-methoxyaniline in the presence of (+)-(1*S*)- or (−)-(1*R*)-camphorsulfonic (HCSA) provides a route to optically active poly(*o*-methoxyaniline) (POMA). The green emeraldine salt films POMA·(+)-HCSA (**1a)** and POMA·(−)-HCSA (**1b**) deposited on ITO-coated glass working electrodes exhibit mirror imaged circular dichroism spectra in the visible region, indicating diastereoselection in the electrochemical deposition. Their chiroptical properties 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 **1a** along the solvent series NMP < $CHCl_3$ < DMSO, DMF < MeOH indicates a concomitant increase in the conjugation length of the polymer chains. The **1a** and **1b** films may also be dedoped in aqueous 1.0 mol dm^{-3} NH_4OH to give optically active POMA emeraldine base. Redoping of these latter blue films with 1.0 mol dm^{-3} HCl regenerates the circular dichroism spectra of the original **1a** and **1b** films, confirming retention of configuration during reversible dedoping/redoping cycles in the solid state.

Introduction

Recent research into conducting polyaniline materials has targeted improving the solubility, and hence processability, of these polymers by the polymerization of ring-substituted aniline monomers. These include alkyl,[1,2] alkoxy,[3,4] sulfonate,[5−7] and carboxylate[8,9] substituents. The alkyl and alkoxy substituents enhance organic solubility, while the presence of a sulfonate or carboxy group results in water-soluble polyanilines. The improved solubility of substituted polyanilines results from the incorporation of flexible groups into the polymer chains that decrease the rigidity of the polymer backbone and/or the presence of polar substituents increasing the overall polarity of the polymer chain. However, the steric effect of such substituents, resulting in a twisting of the polyaniline chains from planarity, may have a detrimental effect on the electrical properties of the polymer.

The emeraldine salt of poly(*o*-methoxyaniline) (POMA) was first prepared[10] in 1988 via the oxidation of *o*-methoxyaniline with $(NH_4)_2S_2O_8$ in aqueous HCl. The POMA·HCl obtained, unlike the analogous polyaniline PAn·HCl salt, is soluble in a range of organic solvents. The successful electrochemical preparation of poly(*o*-methoxyaniline) films doped with HCl has also been recently reported by Mattoso et al.[3], the POMA·HCl salts formed again showing higher solubility than the similarly prepared polyaniline salts in common organic solvents.

In this paper we report the synthesis of optically active poly(*o*-methoxyaniline) salts, namely POMA·(+)-HCSA (**1a)** and POMA·(−)-HCSA (**1b**), via the electropolymerization of *o*-methoxyaniline on platinum or indium−tin−oxide- (ITO-) coated glass electrodes in the presence of (+)-(1*S*) or (−)-(1*R*)-10-camphorsulfonic acid (HCSA). These salts, like the parent chiral polyanilines PAn·(+)-HCSA and PAn·(−)-HCSA recently prepared by a similar route,[11] may have potential as new electroactive stationary phases and chiral membranes for the separation of enantiomeric molecules or as novel chiral electrodes in electrochemical asymmetric synthesis. The poly(*o*-methoxyaniline) salts are more soluble in a range of organic solvents than the parent polymers, permitting a detailed examination of their chiroptical properties. Of particular interest was to establish the influence of the methoxy substituent on the conformation of the polymers, as revealed by circular dichroism (CD) and UV−visible spectroscopy.

The dedoping of the electrochemically deposited POMA·(+)-HCSA salt film (**1a)** with aqueous NH_4OH has also been explored (Scheme 1) in order to ascertain whether the chirality of the poly(*o*-methoxyaniline) chains is altered by the removal of the dopant (+)-CSA anion. Retention of optical configuration in reversible dedoping/redoping sequences of the type in Scheme 1 is important if the emeraldine base forms are to be used as chiral ion exchange materials for enantiomeric separations.

Experimental Section

Materials. Aniline and *o*-methoxyaniline (purchased from Aldrich Chemical Co.) were distilled under vacuum and stored below −10 °C before use. Other reagents and solvents were of analytical grade from Aldrich Chemical Co. and were used without further purification. Solutions were freshly prepared using Milli-Q deionized water. Indium−tin−oxide- (ITO-) coated glass was obtained from Delta Technology, while reticulated vitreous carbon (RVC) was purchased from ERG Aerospace Ltd.

Electrochemical Polymerization. The electropolymerization studies were performed in a three-electrode cell at room temperature using a 20 cm^3 aqueous solution containing 0.2 mol dm^{-3} *o*-methoxyaniline (or aniline) and 1.0 mol dm^{-3} (+)- or (−)-HCSA as the supporting electrolyte. Nitrogen gas was flushed through the electrochemical cell and polymerization solution prior to all experiments in order to minimize the influence from oxidation products.

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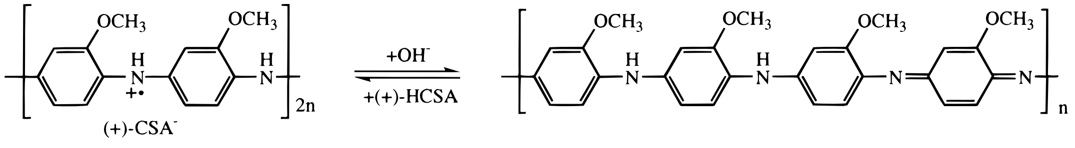
Scheme 1



POMA.(+)-HCSA 1a

EB

In all cases, a Ag/AgCl reference electrode was employed as well as a reticulated vitreous carbon (RVC) auxiliary electrode. The working electrode was either platinum or indium−tin−oxide- (ITO-) coated glass. Both potentiostatic and potentiodynamic polymerizations were employed, with the potential being controlled or varied using a BAS CV-27 connected to a MacLab and chart recorder.

(i) Potentiostatic Polymerization. The majority of electropolymerizations were carried out potentiostatically. For the deposition of the POMA·HCSA (**1**) films, a constant potential of +0.8 V (vs Ag/AgCl) was employed for both the Pt (6.4 cm^2) and ITO-coated glass (4 cm^2) electrodes. However, in the latter case, potentials as high as +1.1 V were also examined. The charge passed (Q) was 120 mC/cm^2 in all cases.

For comparative purposes, films of PAn·(+)-HCSA were similarly deposited on ITO-coated glass using previously described potentiostatic conditions.[11]

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

Cyclic Voltammetry. The electrochemical characterization of a POMA·(+)-HCSA (**1a**) film deposited potentiostatically on Pt as described in (i) above was performed using cyclic voltammetry. The potential was cycled between −0.2 and +0.9 V (vs Ag/AgCl) at a scan rate of 50 mV/s in aqueous 1.0 mol dm^{-3} (+)-HCSA as supporting electrolyte.

Spectroscopic Studies. The UV−visible and circular dichroism (CD) spectra of the optically active POMA·HCSA (**1**) films (and of related PAn·HCSA films) deposited potentiostatically on ITO-coated glass were recorded using a Shimadzu UV-1601 spectrophotometer and a Jobin Yvon Dichrograph 6, respectively. The near-infrared spectra of the films were recorded with a Bomen MB 154 Fourier transform spectrophotometer. Solution UV−visible and CD spectra were also recorded for the POMA·(+)-HCSA (**1a**) samples following dissolution of the electrochemically deposited films (480 mC) in a range of organic solvents (5 cm^3 of $CHCl_3$, DMSO, DMF, NMP, or methanol). These solutions were filtered through a 0.45 μm syringe filter before measuring their spectra ca. 5 min after dissolution.

Chemical Dedoping/Redoping of the POMA·HCSA Films. These POMA·(+)-HCSA (**1a**) and POMA·(−)-HCSA (**1b**) films were dedoped to give emeraldine base films by suspending them in 30 cm^3 of aqueous 1.0 mol dm^{-3} NH_4OH for 30 min and drying in the air. The EB films were then redoped with HCl to give the corresponding POMA·HCl films by suspending them in 30 cm^3 of 1.0 mol dm^{-3} HCl for 30 min.

Results and Discussion

Electrochemical Polymerization of *o*-Methoxyaniline. The electropolymerization of *o*-methoxyaniline in the presence of various acids (eg. HCl, $HClO_4$, H_2SO_4) to produce conducting poly(*o*-methoxyaniline) films has been extensively studied.[3,10,12−20] These electrochemically deposited POMA·HA films were found to have similar electroactivity and electrochromism, but they generally had an order of magnitude lower conductivity, compared to the parent polyaniline PAn·HA films. This reduced conductivity was attributed to steric hindrance by the methoxy group causing adjacent phenyl rings in the polymer chains to twist from a coplanar arrangement. Also, Jackowska et al.[15] have shown that the type of dopant acid influences the rate of *o*-methoxyaniline polymerization, with the oxidation rate increasing in the order $HClO_4 < HCl < H_2SO_4$. They also found that the mechanisms for nucleation and growth were dependent on the dopant acid, as has been observed for the electrochemical polymerization of the parent aniline with these acids.[16]

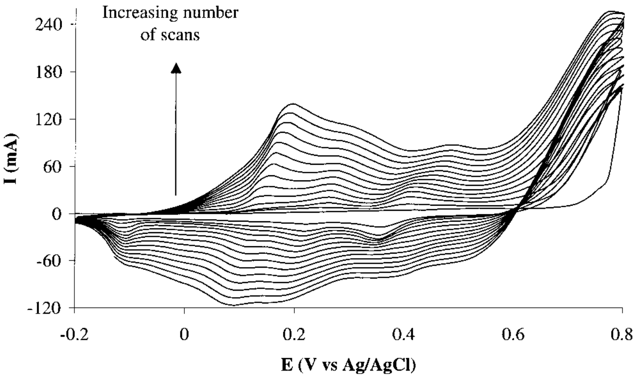


Figure 1. Cyclic voltammogram during the potentiodynamic growth of POMA·(+)-HCSA (**1a**) from an aqueous solution of 0.2 mol dm^{-3} *o*-methoxyaniline and 1.0 mol dm^{-3} (+)-HCSA (Pt electrode, scan rate 20 mV/s).

In the present study, the optimal potential for the potentiostatic polymerization of *o*-methoxyaniline in the presence of (+)-HCSA on different substrates was determined using cyclic voltammetry. The cyclic voltammogram for the *potentiodynamic deposition* of a green POMA·(+)-HCSA (**1a**) film on a Pt electrode from aqueous 0.2 mol dm^{-3} *o*-methoxyaniline and 1.0 mol dm^{-3} (+)-HCSA is shown in Figure 1. The current (charge) passed during the deposition of the POMA·(+)-HCSA film was considerably less than for the parent PAn·(+)-HCSA film grown under identical conditions. This indicates that the POMA·(+)-HCSA salt is either less conducting than the parent polyaniline film or that less polymer was deposited on the electrode.

During the first anodic sweep, the maximum current observed at +0.75 V (vs Ag/AgCl) is attributed to the formation of the radical cation species generated on oxidation of *o*-methoxyaniline. After the potential scan direction in the first cycle was reversed, the current remained more positive until about 0.60 V, indicative of polymer deposition and an increase in the electrode surface area. In subsequent cycles, new peaks appeared in the voltammogram attributed, as in previous studies,[3] to the electrochemical oxidation/reduction of the deposited polymer and any intermediate species formed. The increasing current magnitude for these peaks with successive cycles suggests an increase in film thickness. In similar experiments using an ITO-coated glass electrode, a higher potential (+1.05 V vs Ag/AgCl) was required to oxidize the monomer due to the need to overcome the resistance of the ITO-coated glass electrode.

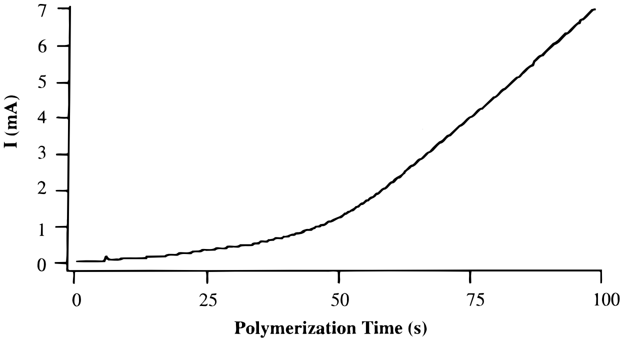


Figure 2. Chronoamperogram obtained during the potentiostatic deposition of **1a** on an ITO-coated glass electrode (+1.1 V vs Ag/AgCl).

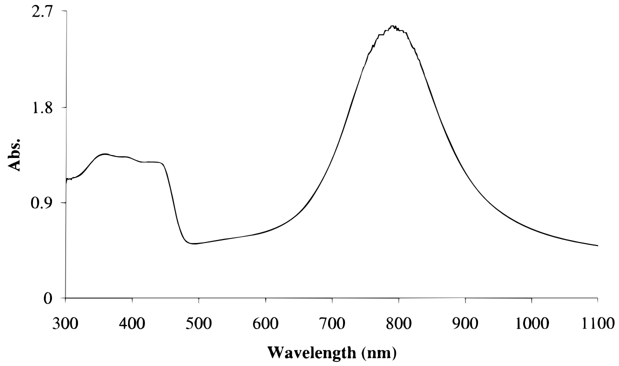


Figure 3. UV−visible spectrum of a POMA·(+)-HCSA (**1a)** film potentiostatically grown on ITO-coated glass electrode as in Figure 2.

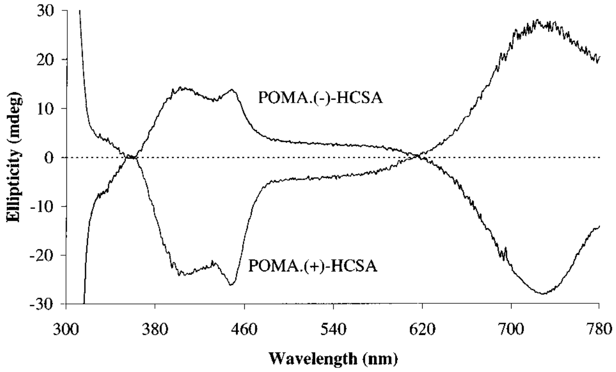


Figure 4. CD spectra of POMA·(+)-HCSA (**1a)** and POMA·(−)-HCSA (**1b**) films potentiostatically grown as in Figure 3.

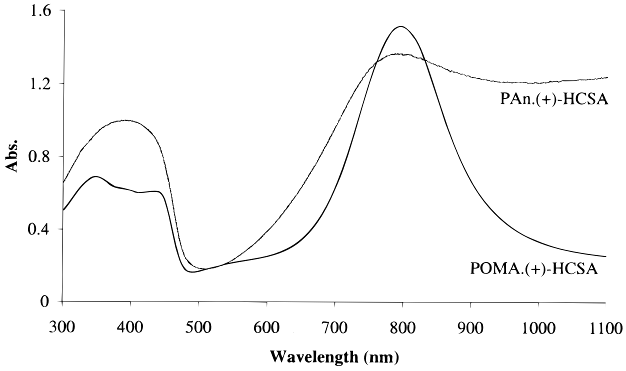


Figure 5. Comparison of the UV−visible spectra of POMA·(+)-HCSA (**1a)** and PAn·(+)-HCSA films electrochemically deposited on ITO-coated glass.

The *potentiostatic polymerization* of *o*-methoxyaniline in aqueous 1.0 M (+)-HCSA on an ITO-coated glass electrode at +1.1 V (vs Ag/AgCl) resulted in the deposition of dark green, conducting emeraldine salt POMA·(+)-HCSA (**1a)** films. Figure 2 shows a typical chronoamperogram for the deposition, revealing that polymer growth/deposition occurred in two stages. The rate of deposition was initially slow but increased as the effective surface area of the electrode increased. The slow initial stage is believed to be related to the nucleation of the polymer on the bare sections of the electrode surface, while the second stage involving rapid deposition of the polymer corresponds to the autocatalytic growth of poly(*o*-methoxyaniline). The magnitude of the currents observed for POMA·(+)-HCSA were approximately 50% lower than for the potentiostatic growth/deposition of the parent polyaniline PAn·(+)-HCSA film under identical conditions.

Chiroptical Properties of POMA·(+)-HCSA and POMA·(−)-HCSA Films. The UV−visible spectrum of the POMA·(+)-HCSA (**1a)** film potentiostatically grown on ITO-coated glass at +1.1 V (charge passed 480 mC) is shown in Figure 3. This exhibited an intense, well-defined polaron band at 785 nm, as well as two lower wavelength absorption bands at 425 and 350 nm, assigned as a second polaron band and a benzenoid $\pi-\pi^*$ transition, respectively. This absorption spectrum is nearly identical to that of electrochemically deposited POMA·HCl films[14] and is consistent with a "compact coil" conformation for the polymer chains.

The circular dichroism spectra of this POMA·(+)-HCSA (**1a)** film and an analogously deposited POMA·(−)-HCSA (**1b**) film (Figure 4) confirmed that they were optically active, with CD bands in each case at ca. 330, 400, 450, and 730 nm. The mirror imaged CD spectra observed for **1a** and **1b** films indicate that the electrochemical polymerization of *o*-methoxyaniline in the presence of (+)- or (−)-HCSA is diastereoselective. The CD peaks at 330 and 400 nm may be tentatively assigned as the bisignate, exciton-coupled bands associated with the benzenoid $\pi-\pi^*$ absorption band seen at ca. 350 nm. Partly overlapping with these is another probable pair of bisignate exciton-coupled CD bands (of which only the 450 nm band is observed) that correspond to the 425 nm polaron absorption band. The CD peak observed at 730 nm is probably the lower wavelength component of the expected pair of bisignate exciton-coupled CD bands associated with the localized polaron absorption band at 785 nm. The CD signal below 330 nm arises from the (+)-CSA$^-$ or (−)-CSA$^-$ dopant anion incorporated into the polymer.

The UV−visible and CD spectra for the POMA·(+)-HCSA (**1a)** film are markedly different from those of the parent PAn·(+)-HCSA film. In contrast to POMA·(+)-HCSA, the UV−visible spectrum for the latter parent emeraldine salt showed only a shoulder for the high wavelength polaron band at ca. 790 nm but exhibited a strong free carrier tail in the near-infrared region (see Figure 5 for comparison). As discussed earlier by us,[21] this suggests at least a partial "extended coil" conformation for the parent PAn·(+)-HCSA salt.

Similarly, the relatively complex CD spectrum for the POMA·(+)-HCSA film between 320 and 500 nm contrasts with that for PAn·(+)-HCSA, which showed only two bisignate bands in this wavelength region (see Figure 6 for comparison). Also in contrast to POMA·(+)-HCSA, the latter parent emeraldine salt exhibited no well-defined CD peak between 500 and 780 nm.

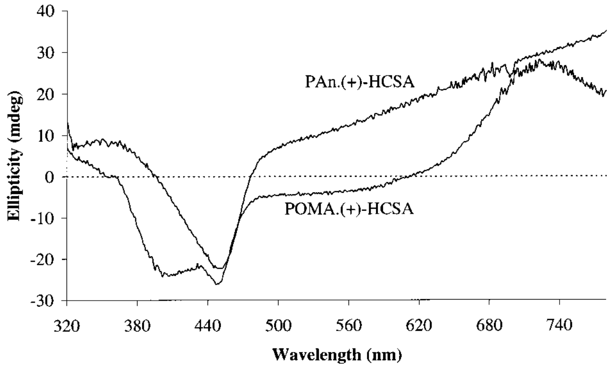


Figure 6. Comparison of the CD spectra of POMA·(+)-HCSA (**1a**) and PAn·(+)-HCSA films electrochemically deposited on ITO-coated glass.

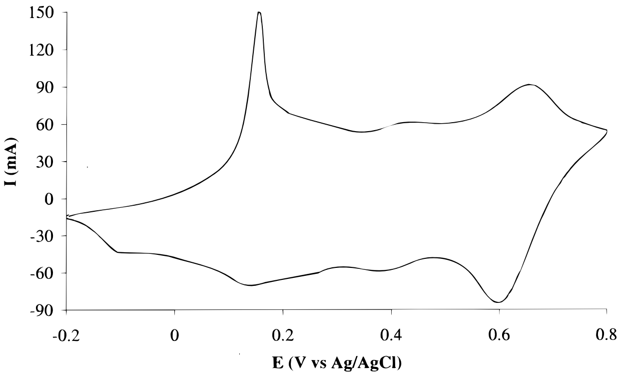


Figure 7. Cyclic voltammogram for a POMA·(+)-HCSA (**1a**) film in aqueous 1.0 mol dm^{-3} (+)-HCSA (Pt electrode, scan rate 50 mV/s, fourth cycle shown).

The different UV—visible and CD spectra for electrochemically deposited POMA·(+)-HCSA and PAn·(+)-HCSA films confirm that the poly(*o*-methoxyaniline) has a different conformation from the parent polyaniline salt. This change in conformation of the polymer backbone is presumably due to the methoxy substituent increasing the flexibility of the polymer chains thereby causing the polymer backbone to deviate from a coplanar arrangement.

Electrochemical Characterization of POMA·HCSA Films. The cyclic voltammogram (Figure 7) of the optically active POMA·(+)-HCSA (**1a**) film potentiostatically deposited on a Pt electrode (at +0.8 V with a charge density of 120 mC/cm^2) confirmed that the polymer was electroactive, with three redox couples observed at +0.15, +0.40 and +0.65 V (vs Ag/AgCl). The positions of these redox couples were nearly identical to those reported by Zotti et al.[17] for electrochemically deposited POMA·H_2SO_4 films on a Pt electrode.

The redox couples at +0.15 and +0.65 V in Figure 7 can be attributed to the redox responses of POMA·(+)-HCSA. The first (+0.15 V) anodic process is related to the oxidation of the leucoemeraldine form of POMA to the emeraldine salt, while the third (+0.65 V) anodic process corresponds to the oxidation of the emeraldine salt form to the pernigraniline state. The second reversible redox couple at +0.40 V is similar to that reported by Jackowska et al.[18] for electrochemically deposited POMA·HCl. They assigned this reversible redox couple to a cyclic or linear *o*-methoxyaniline dimer incorporated into the polymer film. However, others[19] have suggested that this redox peak is associated with degradation products arising from the overoxidation of the poly(*o*-methoxyaniline).

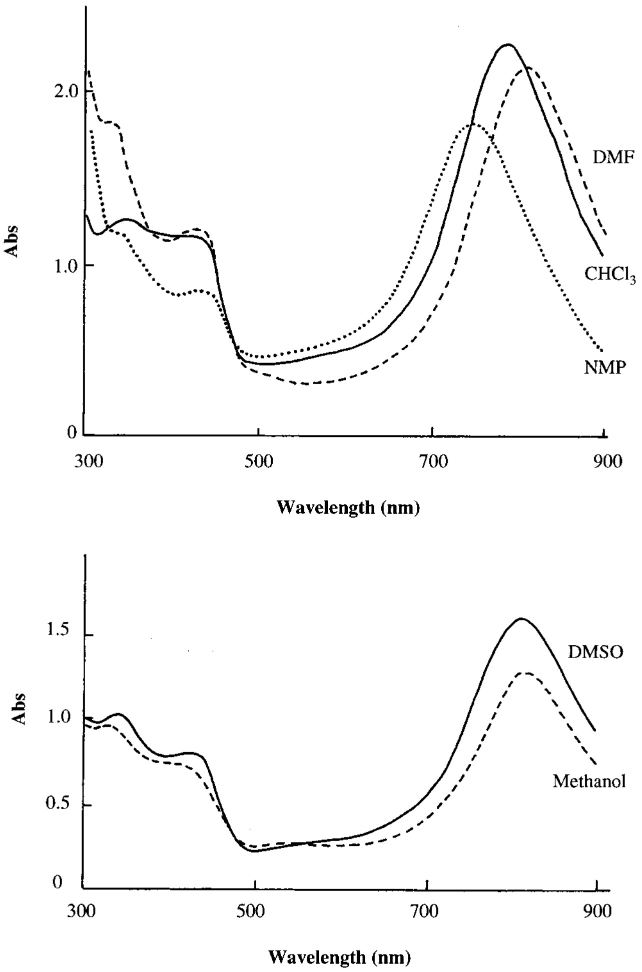


Figure 8. UV—visible spectra of electrochemically deposited POMA·(+)-HCSA (**1a**) films dissolved in (a) NMP, DMF, and $CHCl_3$ or (b) MeOH and DMSO solvents.

Chiroptical Properties of POMA·(+)-HCSA Films Dissolved in Organic Solvents. The electrochemically deposited POMA·(+)-HCSA (**1a**) films were found to be more soluble than the corresponding PAn·(+)-HCSA films in a range of organic solvents (NMP, DMSO, DMF, methanol, or chloroform), generating deep green solutions. However, the polymers were not soluble in acetone or acetonitrile. The improved solubility of these poly(*o*-methoxyaniline) films, which is a benefit for processing, is believed to be due to the methoxy group decreasing the stiffness of the polyaniline chains and the polar substituent increasing the overall polarity of the polymer chains.

UV—visible spectra recorded within 5 min of dissolution of the POMA·(+)-HCSA (**1a**) films in NMP, DMF, chloroform, DMSO, and methanol are summarized in parts a and b of Figure 8. In each solvent, the emeraldine salt exhibited three characteristic absorption bands at ca. 340, 430, and 780 (± 35) nm, which are very similar to those observed for their precursor POMA·(+)-HCSA film (see Figure 3). In particular, the presence of an intense localized polaron band at ca. 780 (± 35) nm and the absence of strong near-infrared absorption supports a “compact coil” conformation for the POMA·(+)-HCSA in each solvent.

It is interesting that similar conformations were maintained in each of these solvents which encompass both aprotic and protic solvents. However, changing the nature of the solvent had a significant influence on the

Table 1. Solvent Dependence of the UV−Visible Spectrum of Electrochemically Deposited POMA·(+)-HCSA (1a)

solvent	λ_{max} for low-energy polaron band (nm)	shift (Δ nm) in λ_{max} compared to film
NMP	745	−40
$CHCl_3$	782	−3
DMF	808	23
DMSO	808	23
MeOH	817	32

position of the low energy polaron band. (In contrast, the positions of the benzenoid $\pi-\pi^*$ transition (ca. 340 nm) and the second polaron band at ca. 430 nm were relatively unaffected by the nature of the solvent.) As summarized in Table 1, λ_{max} for this band was significantly red shifted (72 nm) along the series NMP < $CHCl_3$ < DMF, DMSO < MeOH, which is consistent with an increase in the conjugation length of the poly(*o*-methoxyaniline) chain along the series of solvents. This trend in λ_{max} may reflect a change from a “good” to a “poor” solvent for the POMA·(+)-HCSA salts along the series. As solutes, the emeraldine salts contain both polar and hydrophobic (polarizable) sites. On the basis of the dielectric constants, molar polarizabilities and dipole moments of the solvents, one may predict[22] that electrostatic interactions with the polar solute sites would decrease down the order NMP > DMF > DMSO > MeOH; while dispersion interactions would decrease in a similar order NMP > DMSO, DMF > MeOH. The exceptionally low λ_{max} observed in NMP may reflect the high basicity of this solvent, which is well-known to facilitate the partial deprotonation of emeraldine salts to emeraldine base, with a concomitant decrease in the wavelength of the highest observed absorption band.

The corresponding CD spectra of the electrochemically deposited POMA·(+)-HCSA (**1a**) films after dissolution in each of these solvents are shown in parts a and b of Figure 9. All of these solutions exhibited similar CD peaks at 345 and 400 nm which are assigned as the bisignate exciton-coupled bands associated with the benzenoid $\pi-\pi^*$ absorption band at ca. 340 nm. They also exhibited a broad shoulder at 440 nm and a well-defined peak at ca. 465 nm, which may be assigned as the bisignate exciton-coupled bands associated with the low-wavelength polaron absorption band. These spectra are very similar (apart from the 440 nm shoulder) to those attributed by us in earlier studies[22] to the parent Pan·(+)-HCSA when in the “compact coil” conformation.

However, the CD spectra for the electrochemically deposited POMA·(+)-HCSA in the above solvents are significantly different from the solid-state spectra (Figure 4), indicating that the dissolution results in some change, as yet undefined, to the polymer chain conformation.

Dedoping/Redoping of POMA·HCSA Films. We have previously shown[23] that electrochemically deposited PAn·(+)-HCSA and PAn·(−)-HCSA films can be dedoped to emeraldine base and subsequently redoped with HCl with retention of configuration. Similar behavior was found here for POMA·(+)-HCSA (**1a**) and POMA·(−)-HCSA (**1b**) films, providing a facile route to optically active films of POMA in its emeraldine base form.

Treatment of an electrochemically deposited POMA·(+)-HCSA emeraldine salt film (**1a**) with 1.0 mol dm^{-3} NH_4OH resulted in rapid deprotonation to produce a methoxy-substituted blue emeraldine base film, as shown in Scheme 1. The UV−visible spectrum of this latter film (Figure 10, curve a) exhibited two absorption bands at 330 and 590 nm characteristic of emeraldine bases. These absorption bands have been assigned[24] as the benzenoid $\pi-\pi^*$ transition and the molecular exciton associated with the quinoid group, respectively.

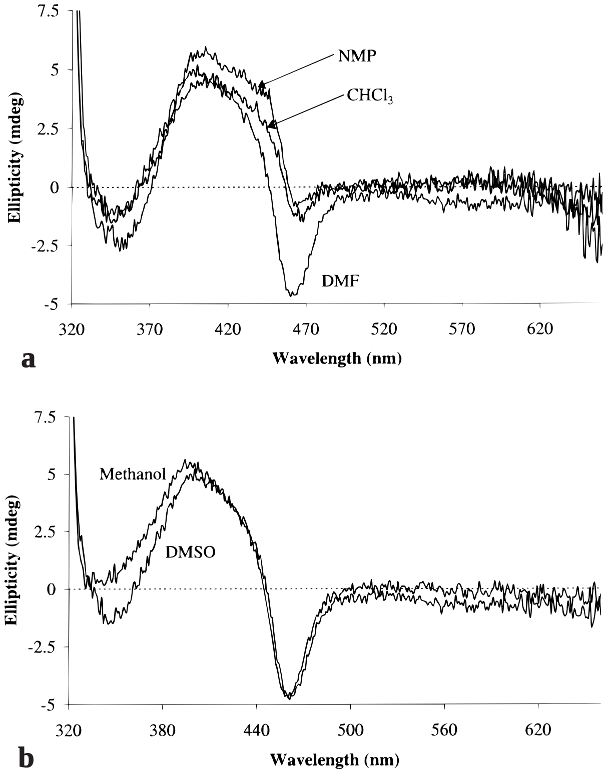


Figure 9. CD spectra of electrochemically deposited POMA·(+)-HCSA (**1a**) films dissolved in (a) NMP, DMF, and $CHCl_3$ or (b) MeOH and DMSO solvents.

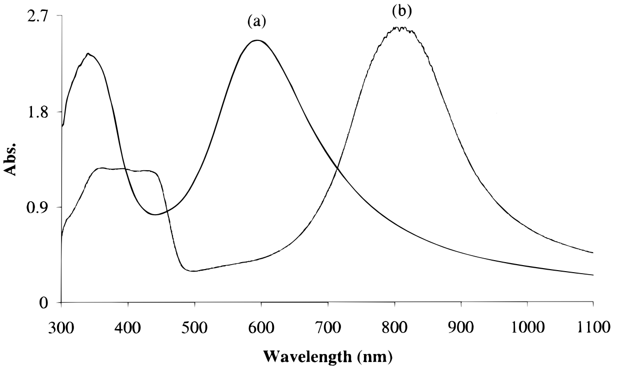


Figure 10. UV−visible spectra of a POMA·(+)-HCSA (**1a**) film (a) after dedoping with 1.0 mol dm^{-3} NH_4OH and (b) then redoping with 1.0 mol dm^{-3} HCl.

Significantly, the CD spectrum of this POMA emeraldine base film showed that it was optically active, with strong bands at <300, 375, 515, and ca. 640 nm (Figure 11, curve a). The CD peaks at <300 and 375 nm may be assigned as the bisignate exciton-coupled bands associated with the benzenoid $\pi-\pi^*$ absorption band at 330 nm, while the 515 and 640 peaks are the bisignate exciton-coupled bands arising from the absorption band at 590 nm. The retention of optical activity in the POMA emeraldine base film, despite the removal of the (+)-HCSA group, again demonstrates that the observed optical activity for the films arises from the macroasym-

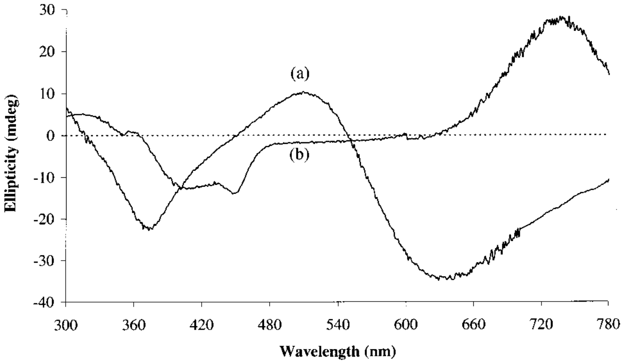


Figure 11. CD spectra of poly(*o*-methoxyaniline) films from Figure 10.

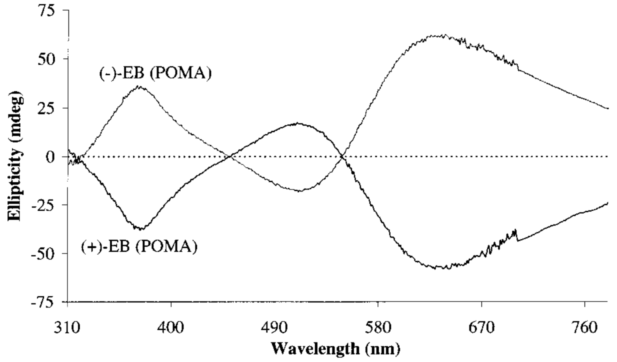


Figure 12. CD spectra of the enantiomeric forms of optically active POMA emeraldine base.

metry of the polymer backbone and not the (+)-CSA$^-$ dopant.

Redoping of the above optically active POMA emeraldine base film with aqueous 1.0 mol dm^{-3} HCl solution for 30 min regenerated a UV−visible spectrum (Figure 10, curve b) essentially identical to that of the initial POMA·(+)-HCSA (Figure 3), except that the position of the localized polaron band underwent a small red shift to 800 nm. The CD spectrum of the regenerated POMA·HCl film (Figure 11, curve b) was also identical to the initial spectrum of the POMA·(+)-HCSA film, except that the band for the incorporated (+)-HCSA was absent, and there was a slight red shift in the CD band associated with the localized polaron band from 730 to 740 nm.

Similar behavior was observed upon alkaline dedoping of a POMA·(−)-HCSA (**1b**) film. The blue emeraldine base film obtained exhibited a mirror-imaged circular dichroism spectrum (Figure 12) compared to that obtained by dedoping **1a**, confirming the enantiomeric nature of the two POMA emeraldine base films.

These chiroptical studies confirm that the electrochemically deposited poly(*o*-methoxyaniline) films retain their absolute configuration during reversible dedoping/redoping processes in the solid state. In contrast, dissolution of the optically active emeraldine base films in organic solvents such as DMF, DMSO, and NMP causes rapid racemization. Presumably, steric constraints in the solid state prevent the interconversion between enantiomeric helical forms of the POMA chains that can occur readily in solution.

Conclusions

The synthesis of optically active poly(*o*-methoxyaniline) has been achieved via the electropolymerization of *o*-methoxyaniline from aqueous solutions containing (+)- or (−)-10-camphorsulfonic acid. The green POMA·HCSA emeraldine salt films exhibit strong visible region CD bands, confirming the induction of chirality in the polymer chains by the (+)- or (−)-CSA$^-$ dopant anions. Mirror-imaged CD spectra are observed for POMA·(+)-HCSA (**1a)** and POMA·(−)-HCSA (**1b**) films, indicating diastereoselection in the electrochemical deposition.

The chiroptical properties of these POMA·HCSA salts indicate a "compact coil" conformation for the polymer chains, in contrast to the analogous parent PAn·HCSA films which are largely in the "extended coil" conformation. These differences are attributed to the steric influence of the methoxy substituent on the aniline rings. The POMA·HCSA salts are readily soluble in a range of organic solvents such as DMF, NMP, $CHCl_3$, DMSO, and methanol, and UV−visible and CD studies show that they adopt a "compact coil" type conformation in each solvent. The nature of the solvent has a strong influence on the position of the low energy, localized polaron band of the emeraldine salt, which is strongly red shifted ($\Delta = 72$ nm) along the solvent series NMP $<$ $CHCl_3$ $<$ DMF $\sim$ DMSO $<$ MeOH. This solvatochromism indicates an increase in the conjugation length of the polymer chain along this solvent series.

The POMA·(+)-HCSA (**1a**) and POMA·(−)-HCSA (**1b**) salt films may be readily dedoped in 1.0 mol dm^{-3} NH_4OH to give optically active POMA emeraldine base films with mirror imaged circular dichroism spectra. Redoping of these emeraldine base films with 1.0 mol dm^{-3} HCl regenerates the circular dichroism spectra of the original **1a** and **1b** films, confirming that the optically active POMA retains its absolute configuration during the reversible dedoping/redoping processes.

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