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Chapter 4

Asymmetric Proliferation with Optically Active Polyanilines

4.1 Introduction

In all the reported routes to optically active polyanilines, summarized in Chapter 1 (Section 1.4.2.3), a chiral dopant anion is incorporated into the polyaniline chains during growth. The chiral dopant is believed to induce optical activity in the polymer chains through electrostatic and/or hydrogen bonding interactions, leading to a preferred one-handed helical structure for the polyaniline backbone.¹⁻⁴

In this Chapter, an alternative approach to optically active polyanilines is explored. It is based on the hypothesis that an initial thin film of an optically active conducting polymer deposited on an electrode may cause asymmetric induction during the subsequent polymerization of aniline in the presence of racemic or achiral acids. Thin films of electrodeposited PAn.(+)-HCSA and PAn.(-)-HCSA are examined as the potential chiral inducer. This novel route, which will be called macromolecular asymmetric proliferation, is found to be remarkably effective using either (\pm)-HCSA, HCl or *p*-toluenesulfonic acid (*p*-TSA) as the acid dopants during the second stage of electrodeposition, yielding highly optically active emeraldine salts. The potential use of chiral polyaniline thin films as chiral inducers for the preparation of other optically active conducting polymers such as polypyrrole is also briefly studied.

4.2 Experimental

4.2.1 Chemicals

Chemical reagents were obtained as described in Chapter 2. All aqueous solutions were prepared with Milli-Q water.

4.2.2 Preparation of Optically Active Polyanilines via a Chiral Emeraldine Salt Inducer

All electrochemical polymerizations were carried out in a three-electrode cell. ITO-Pt-coated glass described in Chapter 2 was used as working electrode. Ag/AgCl (3 M NaCl) and Pt mesh were employed as reference and auxiliary electrodes, respectively. A constant potential was applied to the working electrode by means of a BAS CV-27 potentiostat and the charge passed during polymer growth also measured. Two steps of electrodeposition are required in this method:

Step 1: Electrodeposition of Chiral PAn.(+)-HCSA or PAn.(-)-HCSA Thin Film

PAn.(+)-HCSA (or PAn.(-)-HCSA) thin films were potentiostatically deposited at room temperature (18° - 20°C) from aqueous 0.2 M aniline/1.0 M (+)-HCSA (or 1.0 M (-)-HCSA), using an applied potential of 0.9 V and passing 25 mC/cm² of charge. The thin films of PAn.(+)-HCSA or PAn.(-)-HCSA were washed well with methanol to remove excess aniline monomer and unincorporated (+)- or (-)-HCSA by dipping ten times into a large amount of methanol for 15 sec. Their UV-visible and CD spectra were measured before using the chiral films as the working electrode in the second electrodeposition step.

Step 2: Further Electrodeposition of PA.HA Emeraldine Salts with Achiral or Racemic Dopants

Polyaniline emeraldine salt (PAn.HA) or polypyrrole (PPy.A) films were then potentiostatically deposited on the thin films of PAn.(+)-HCSA or PAn.(-)-HCSA

obtained from step 1, using an applied potential of 0.9 V with 100 mC/cm² of charge passed and aqueous 0.2 M aniline/1.0 M HA {HA = HCl, *p*-TSA, (±)-HCSA or (-)-HCSA} as the polymerization medium. Similar deposition of polypyrroles was carried out on thin optically active PAn.(+)-HCSA substrates from aqueous 0.2 M pyrrole/1.0 M (±)-HCSA at room temperature (*ca.* 18° - 20°C).

4.2.3 Chiral Amplification

Polyaniline emeraldine salt films were potentiostatically electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 120 mC/cm²) from aqueous 0.2 M aniline/1.0 M HA {HA = 2%(+)-HCSA/98% (±)-HCSA, 5% (+)-HCSA/95% (±)-HCSA, 2% (+)-HCSA/98% HCl, or 5% (+)-HCSA/95% HCl} at room temperature (*ca.* 18° - 20°C).

4.2.4 UV-visible and CD Spectral Measurements

UV-visible and CD spectra were recorded as described in Chapter 2. Films were washed with methanol before the measurements unless otherwise stated.

4.2.5 De-doping/Re-doping of a Polyaniline Film

A co-polymer emeraldine salt film, prepared by deposition of an initial thin film (25 mC/cm² passed) of PAn.(-)-HCSA and further depositing PAn.HCl (another 100 mC/cm² passed), was de-doped in 1.0 M NH₄OH for 30 min to give an emeraldine base film, and then re-doped to PAn.HCl emeraldine salt by treatment with 1.0 M HCl for 30 min. UV-visible and CD spectra were recorded before and after the base/acid treatments.

4.2.6 Electrochemical Studies

4.2.6.1 Cyclic Voltammetry

Polymer Synthesis: Preparation of polyaniline films was based on a procedure described in Section 4.2.2. A glassy carbon disc (surface area: 0.07 cm²) or ITO-Pt coated glass was used as working electrode. The polymerization solution was an aqueous solution containing 0.2 M aniline and 1.0 M acid HA {HA = (+)-HCSA, (±)-HCSA, or HCl}.

Cyclic Voltammograms: Cyclic voltammetric measurements were performed as described in Chapter 2. The current was measured at potentials swept between -0.2 and 1.1 V or -0.3 and 0.9 V, using a scan rate of 50 mV/s. The electrolyte (aqueous 1.0 M HCl or 1.0 M H₂SO₄) was de-oxygenated by gentle bubbling with N₂ prior to measurements.

4.2.6.2 Chronoamperometry and Chronocoulometry

Chronoamperograms and chronocoulomograms were recorded during the potentiostatic deposition of polyaniline emeraldine salts onto the glassy carbon electrode (surface area = 0.07 cm²) or ITO-Pt-coated glass (surface area *ca.* 1.0 cm²) at +0.9 V, using an eDAQ potentiostat with Chart software (version 5.1.2). The polymerizations were carried out in a three-electrode cell, using Ag/AgCl (3 M NaCl) and Pt mesh as reference and auxiliary electrodes, respectively.

4.3 Results and Discussion

4.3.1 Chiroptical Properties of Electrodeposited PAn.HA Films

Polyaniline films were deposited using the conditions described in the Experimental Section. Typical UV-visible and circular dichroism spectra of racemic PAn.(±)-HCSA and optically active PAn.(+)-HCSA films obtained by passing 125 mC/cm² charge during conventional potentiostatic polymerization of aniline in the presence of (±)-HCSA and (+)-HCSA, respectively, are shown in Figure 4.1. Similar UV-visible spectra

were obtained for both emeraldine salt films, with a broad absorption peak in the 350-450 nm region, assigned as overlapping benzenoid π - π^* and polaron bands, as well as a strong free-carrier tail in the near-infrared (Figure 4.1a). These spectra are consistent with a largely “extended coil” conformation for the polyaniline chains.⁵⁻⁷

As expected, the PAn.(\pm)-HCSA film exhibited no optical activity (curve 2-Figure 4.1b). However, the PAn.(+)-HCSA film was strongly optically active, exhibiting CD bands at *ca.* 350, 440 and 730 nm (curve 1-Figure 4.1b). Similar results have been reported previously by Kane-Maquire *et al.*^{1,3}

Polyaniline films prepared by electropolymerization of aniline in the presence of an achiral acid (e.g. HCl) exhibited similar UV-visible and CD spectra to those recorded for PAn.(\pm)-HCSA. Therefore, it can be concluded that optically active polyaniline emeraldine salt (PAn.HA) films can usually only be obtained by conventional electropolymerization in the presence of an optically active acid dopant.

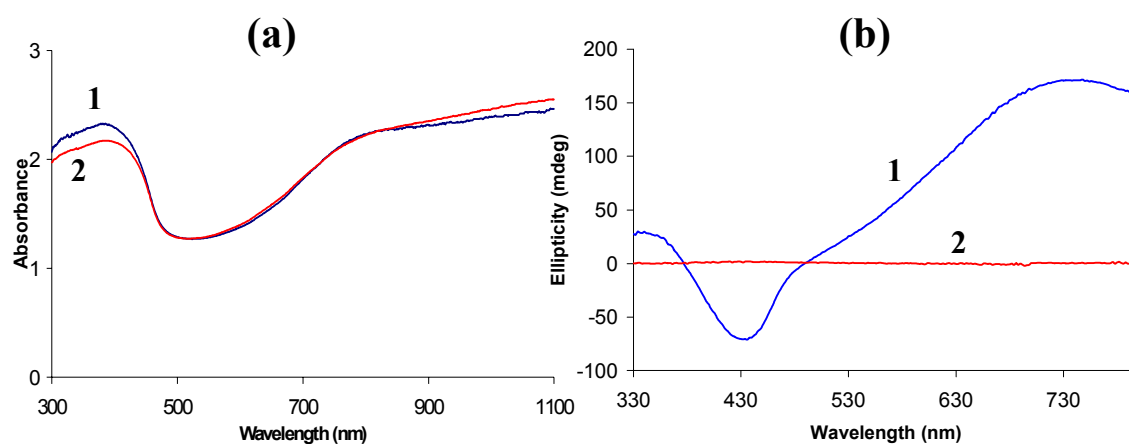
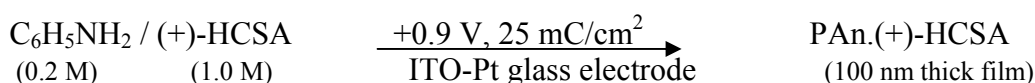


Figure 4.1 (a) UV-visible and (b) CD spectra of: (1) a PAn.(+)-HCSA film, and (2) a PAn.(\pm)-HCSA film, electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 125 mC/cm²) at room temperature.

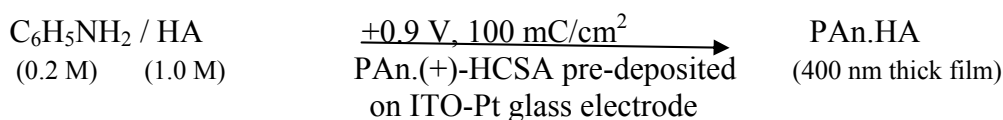
4.3.2 Synthesis of Optically Active Polyanilines Using a Thin PAn.(+)-HCSA Film as Chiral Inducer

The novel asymmetric polymerization method explored in this study involved two electrodeposition steps (Scheme 4.1). In the first step, a thin film of chiral PAn.(+)-HCSA emeraldine salt was prepared by electropolymerization of aniline in the presence of the chiral acid (+)-HCSA. The thickness of the film deposited on the ITO-coated glass working electrode was controlled by the deposition charge (25 mC/cm²). The thin PAn.(+)-HCSA film was thoroughly washed with methanol to remove excess aniline, oligomers, and unincorporated (+)-HCSA before using this as a chiral inducer in a further polymerization step. In this second stage, electrodeposition of PAn.HA emeraldine salts onto the thin chiral polyaniline film was carried out in an aqueous solution containing aniline and the racemic acid (±)-HCSA or an achiral acid such as HCl and *p*-TSA.

Step 1.



Step 2.



Scheme 4.1

(i) Using (±)-HCSA in the Second Polymerization Step

The UV-visible spectra measured for the thin initial PAn.(+)-HCSA film and for the film after further deposition of PAn.(±)-HCSA film on top, show that the absorbance intensity of the final product was much higher than that of the initiator film (Figure 4.2

a). This is consistent with the amount of charge passed during each electrodeposition step. Remarkably, the intensity of the CD spectrum also increased by a similar factor (Figure 4.2 b). That is, strongly optically active polyaniline was deposited in the second polymerization step, even though the polymerization was performed in a racemic acid solution. This indicated that the initial thin PAn.(+)-HCSA film acts to induce chirality into the final polyaniline product. In contrast, as mentioned earlier, optically inactive PAn.(±)-HCSA is obtained when this emeraldine salt is deposited on a bare ITO-Pt-coated glass electrode.

The thickness of emeraldine salt films can be estimated* from their optical absorption at 400 nm. On this basis, the film thickness of the initial thin PAn.(+)-HCSA film and of the final film after depositing PAn.(±)-HCSA on top were estimated to be *ca.* 100 and 400 nm, respectively.

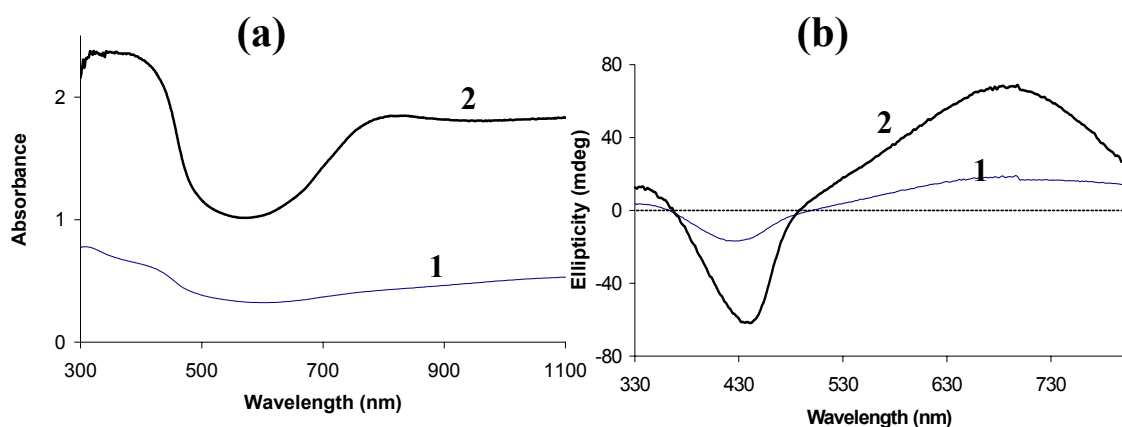


Figure 4.2 (a) UV-visible and (b) CD spectra of: (1) a PAn.(+)-HCSA film electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 25 mC/cm²), and (2) after depositing a further PAn.(±)-HCSA film (another 100 mC/cm² charge passed).

* *Footnote*: The absorbance of PAn.HA salt film was found in a study by Stejskal *et al*^{8,9} to be related to the film thickness, given by the equation: Film thickness (in nm) = 185 x Abs_(400 nm).

(ii) Using Achiral Acids in the Second Polymerization Step

In subsequent studies the achiral acids HCl and *p*-TSA were employed as the acid dopant in the second electrodeposition step. Significantly, when PAn.HCl and PAn.*p*-TSA were electrodeposited on top of the thin PAn.(+)-HCSA film, the intensity of the UV-visible absorption and CD signals of the final films (Figure 4.3 and 4.4) again increased by similar amounts.

The CD spectra obtained had the same sign and general characteristics as those observed for the PAn.(±)-HCSA film described in Figure 4.2b above. This confirms that optical activity (presumably originating from a helical chain structure) can be induced into polyanilines during electrochemical polymerization of aniline when employing optically inactive dopant anions, via the use of a chiral polyaniline-modified working electrode.

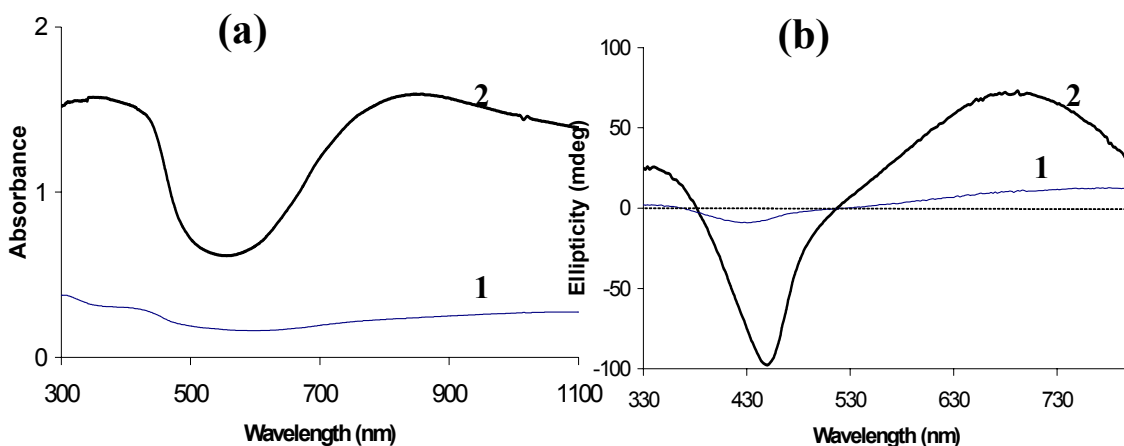


Figure 4.3 (a) UV-vis and (b) CD spectra of: (1) a PAn.(+)-HCSA film electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 25 mC/cm²), and (2) after depositing a further PAn.HCl film (another 100 mC/cm² passed).

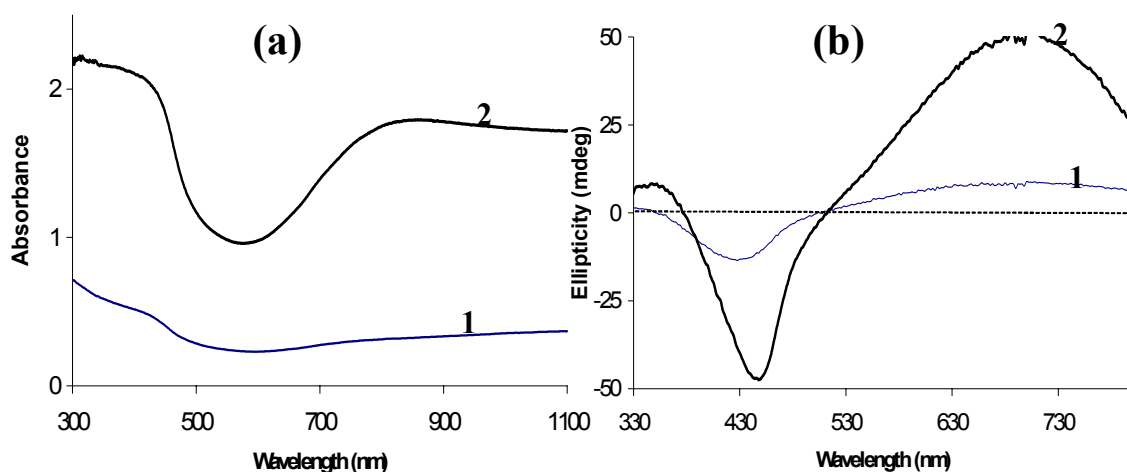


Figure 4.4 (a) UV-visible and (b) CD spectra of: (1) a PAn.(+)-HCSA film electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 25 mC/cm²), and (2) after depositing a further PAn.*p*-TSA film (another 100 mC/cm² charge passed).

(iii) Using (-)-HCSA in the Second Polymerization Step

The most striking result occurred when the enantiomeric (-)-HCSA was employed as the dopant acid in the second electropolymerization step in Scheme 4.1. The PAn.(-)-HCSA film obtained after passing 100 mC/cm² exhibited chiroptical properties (Figure 4.5) the same as those observed above when (±)-HCSA, HCl or *p*-TSA acids were employed.

Kane-Maguire *et.al.*¹ have reported that the CD spectra of emeraldine salt films electrodeposited onto ITO-coated glass in the presence of 1.0 M (+)-HCSA and 1.0 M (-)-HCSA were mirror imaged. In contrast, the result in Figure 4.5 indicates that PAn.HCSA emeraldine salts electrodeposited on an initial thin PAn.(+)-HCSA film exhibit the same CD spectra in the visible region regardless of whether the HCSA employed in the second stage deposition is the (+)- or (-)- enantiomer. This indicates that the chiroptical property of the initial thin PAn.(+)-HCSA film plays a dominant role in preferentially forming polyanilines with the same helical conformation as itself.

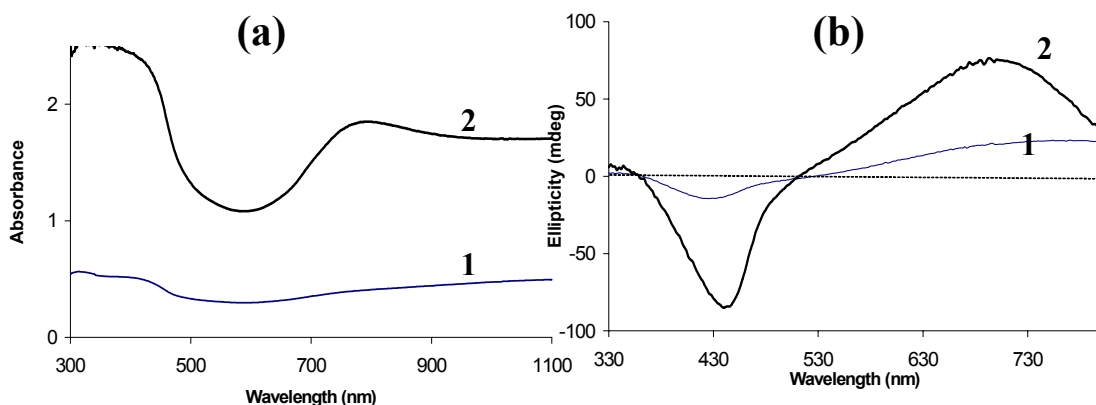


Figure 4.5 (a) UV-visible and (b) CD spectra of: (1) a PAn.(+)-HCSA film electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 25 mC/cm²), and (2) after depositing a further PAn.(-)-HCSA film (another 100 mC/cm² charge passed).

4.3.3 Synthesis of Optically Active Polyanilines Using a Thin PAn.(-)-HCSA Film as Chiral Inducer

This hypothesis was further tested by carrying out similar polymerizations in which a thin PAn.(-)-HCSA film was used as the working electrode for the second stage deposition. Thin films of PAn.(-)-HCSA were prepared as previously described in section 4.3.2 (electrodeposition charge = 25 mC/cm²), but 1.0 M (-)-HCSA was used rather than 1.0 M (+)-HCSA. The thin films were washed with methanol and then PAn.(±)-HCSA or PAn.HCl films deposited on top (step 2) using an applied potential of 0.9 V and 100 mC/cm² charge passed, employing aqueous 0.2 M aniline/1.0 M HA (HA = (±)-HCSA or HCl) as the polymerization solution.

(i) Using (±)-HCSA in the Second Polymerization Step

The UV-visible spectra measured for the initial thin PAn.(-)-HCSA film and for the film after further deposition of PAn.(±)-HCSA film on top, showed that the absorbance of the final product was markedly increased compared to that of the initial film (Figure 4.6a). This is consistent with the amount of charge passed for each electropolymerization step. The initial thin PAn.(-)-HCSA film exhibited mirror imaged

CD signals at the same wavelengths (*ca.* 350, 440 and 730 nm) as those observed for the thin PAn.(+)-HCSA films in Section 4.3.2.

Significantly, the ellipticity of the CD bands of the final product also increased by a similar factor (Figure 4.6b). This result showed that optically active polyaniline was synthesized in the second polymerization step, although it was carried out in a racemic acid solution. This indicated that the initial thin PAn.(-)-HCSA film again induces its own chirality into the final polyaniline product. The mirror imaged nature of the chiral polyaniline final products prepared by using the initial thin PAn.(-)-HCSA and PAn.(+)-HCSA films (from Figure 4.2) are seen in Figure 4.7.

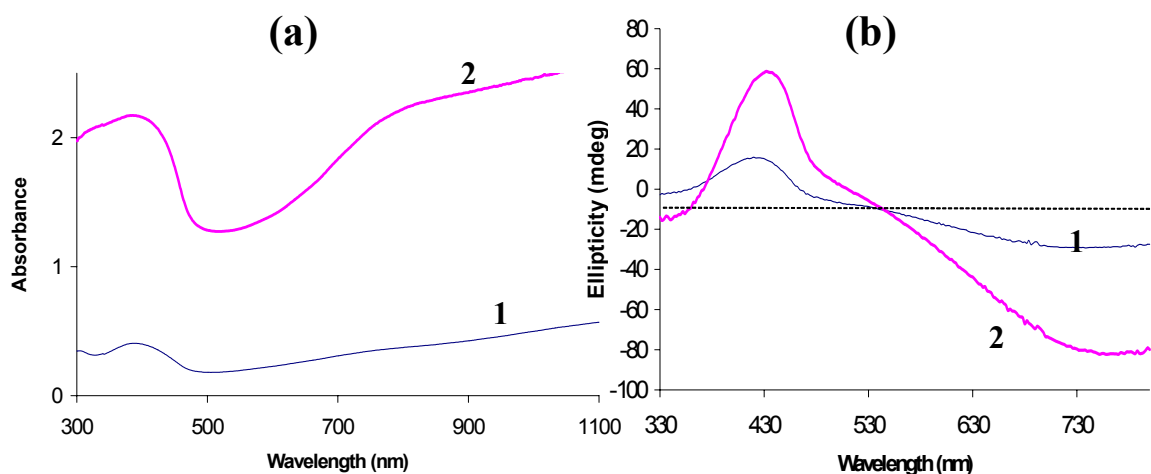


Figure 4.6 (a) UV-visible and (b) CD spectra of: (1) a PAn.(-)-HCSA film electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 25 mC/cm²), and (2) after depositing a further PAn.(±)-HCSA film (another 100 mC/cm² charge passed).

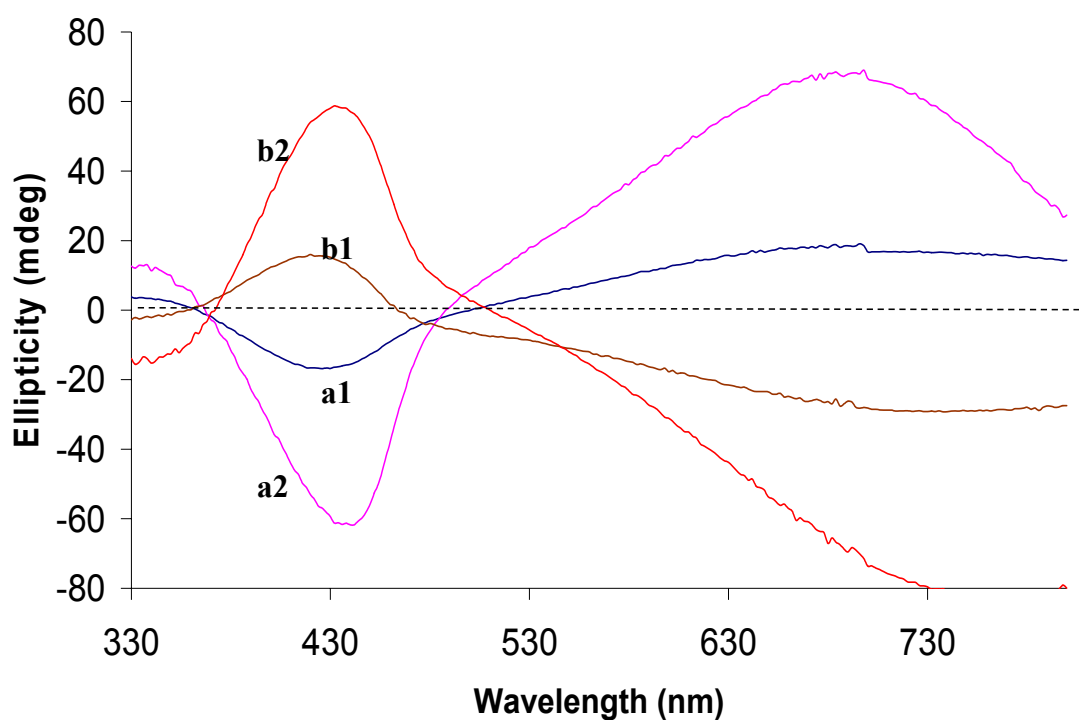


Figure 4.7 CD spectra of initial thin films (25 mC/cm^2 passed) of PAn.(+)-HCSA (a1) and PAn.(-)-HCSA (b1), and after depositing further PAn.(\pm)-HCSA films (another 100 mC/cm^2 passed) on top of each film, respectively.

(ii) *Using HCl in the Second Polymerization Step*

Very similar results were obtained when a PAn.HCl was electrodeposited upon an initial thin PAn.(-)-HCSA film. The visible region absorbance of the final product was much higher than that of the initial thin film (Figure 4.8a). Significantly, the ellipticity of the CD bands of the final product also increased by a similar factor (Figure 4.8b). This confirms that optical activity can be induced into polyaniline chains during electropolymerization of aniline when using achiral dopant anions such as Cl^- , via the use of a chiral polyaniline initiator. The CD spectrum for the final film in Figure 4.8b is again the mirror image of that previously grown on a thin PAn.(+)-HCSA film (Figure 4.3b).

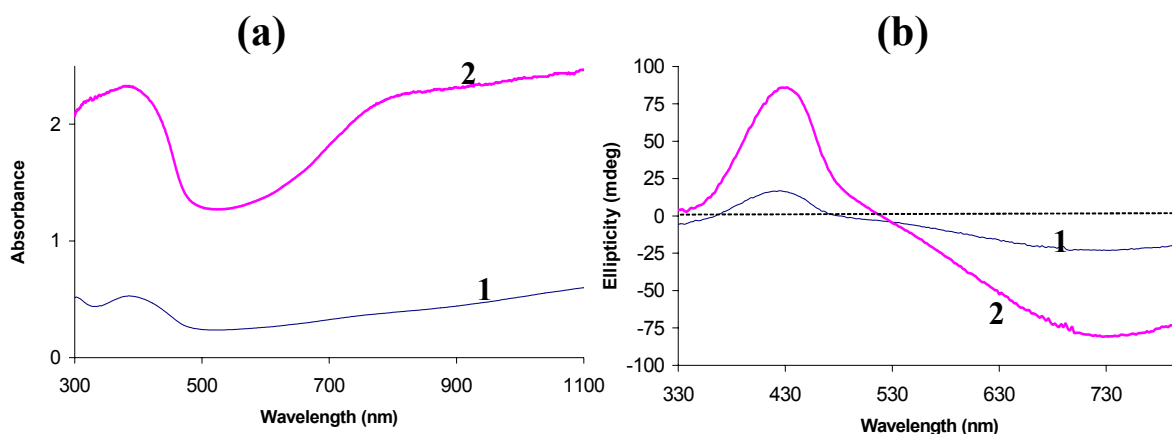


Figure 4.8 (a) UV-visible and (b) CD spectra of: (1) a PAn.(-)-HCSA film electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 25 mC/cm²), and (2) after depositing a further PAn.HCl film (another 100 mC/cm² charge passed).

4.3.4 The Origin of the Macromolecular Asymmetric Induction

Several possible mechanisms have been considered to explain the origin of the remarkable macromolecular asymmetric induction found in the above studies. One possibility is that the thin initial PAn.(+)-HCSA film may act as a chiral inducer, promoting a one-screw sense helical arrangement (the same as the chiral inducer itself) on the growing polymer chains during polymerization in the presence of racemic or achiral acid dopants. In this regard, our results may be usefully compared to the report by Maeda *et al.*¹⁰ of the asymmetric polymerization of achiral alkylisocyanate monomers to give optically active polyalkylisocyanates (-[OCNR]_n-) using optically active anionic metal complexes as catalysts. The presence of the chiral initiator on a chain terminus was believed to induce a single-screw sense on the growing poly(alkylisocyanate) chains. Recently, Samuelson *et al.*¹¹ have observed related asymmetric induction in the horseradish peroxidase catalysed synthesis of PAn.(+)-HCSA/PAA, PAn.(-)-HCSA/PAA and PAn.(± HCSA)/PAA nanocomposites {PAA = poly(acrylic acid)}; where the polyaniline chains adopted the same helical hand,

irrespective of the hand of the HCSA employed. This result contrasts with electrochemical^{1, 3, 12} and chemical¹³⁻¹⁸ polymerization of aniline where the use of opposite hands of the HCSA acid dopant gives rise to PAn.HCSA salts with opposite helical hands. The horseradish peroxidase enzyme must therefore play a critical role, as yet undefined, in inducing a constant hand on the polyaniline chains.

Another possibility that has been considered is that the (+)-CSA⁻ anion in the thin initial PAn.(+)-HCSA films could reversibly exchange on the polyaniline surface during further polymerization in the presence of racemic HCSA or achiral dopants, and that the asymmetric proliferation exhibited may then arise from cooperative effects of the “majority-rules” and “sergeant-and-soldiers” type recently observed in poly(alkylisocyanate)s^{19, 20} and poly(alkylthiophene)s.²¹ The latter mechanism appears highly unlikely on two counts: (i) the maximum possible concentration of (+)-CSA⁻ in the second-stage polymerization medium is extremely low ($\leq 10^{-4}$ M) compared to the racemic CSA⁻ or achiral anion (1.0 M); (ii) no significant chiral amplification was observed in the electrochemical synthesis of PAn.HCSA salts, as shown by chiral amplification studies that we separately carried out.

As shown in Figures 4.9 and 4.10, the observed optical activity of emeraldine salt films grown in the presence of 5% (+)-HCSA/95% (±)-HCSA (Figure 4.9-curve b) and 5% (+)-HCSA/95% HCl (Figure 4.10-curve b) were *ca.* 5/100 the intensity of an analogous film grown in 100% (+)-HCSA. No chiral amplification was observed for electropolymerizations using as the dopant acid mixtures of HCl and (+)-HCSA with only 2-5% of the chiral acid.

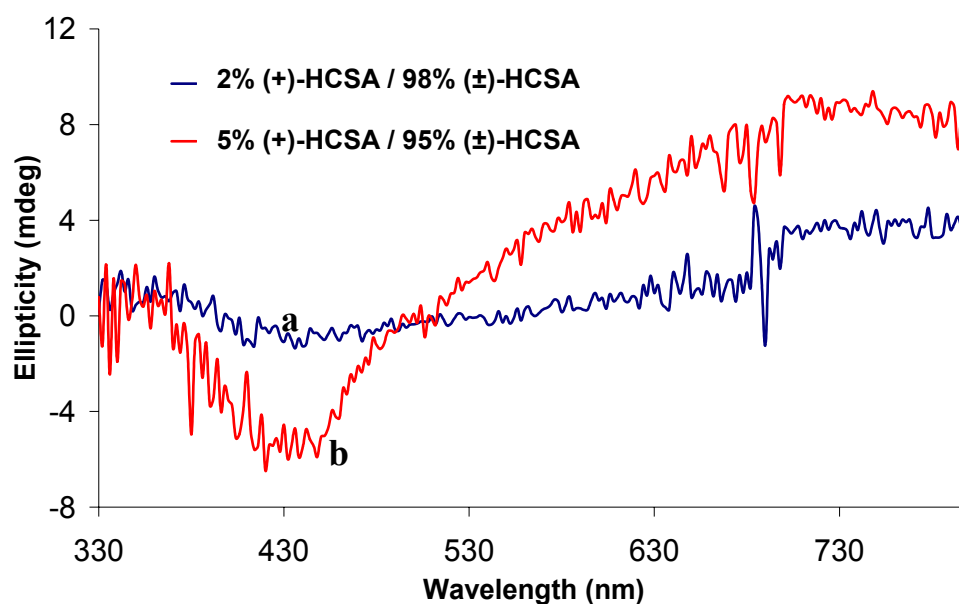


Figure 4.9 CD spectra of emeraldine salt films electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 120 mC/cm^2) from: (a) 0.2 M aniline/1.0 M HCSA (2% (+)-HCSA, 98% (±)-HCSA); and (b) 0.2 M aniline/1.0 M HCSA (5% (+)-HCSA, 95% (±)-HCSA).

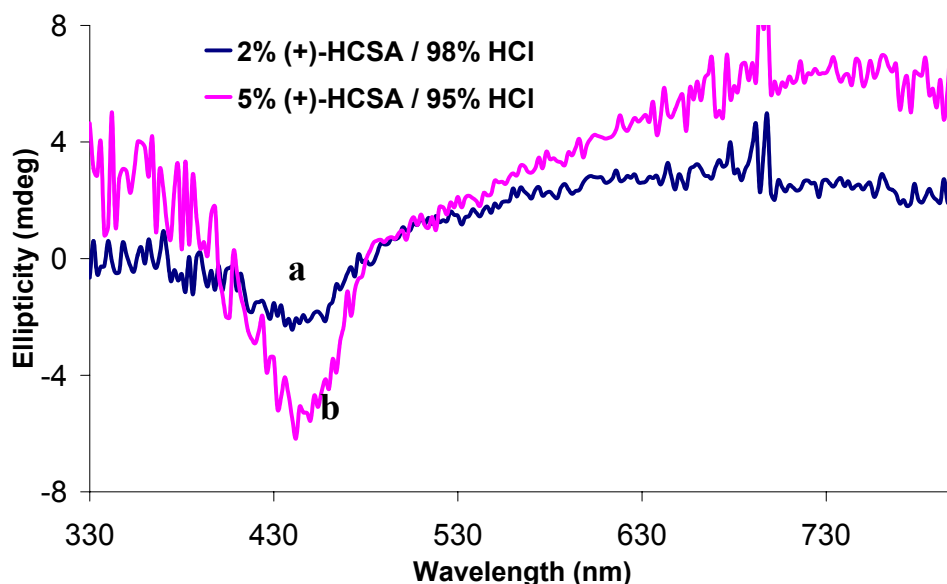


Figure 4.10 CD spectra of emeraldine salt films electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 120 mC/cm^2) from: (a) 0.2 M aniline/1.0 M HA (2% (+)-HCSA, 98% HCl); and (b) 0.2 M aniline/1.0 M HA (5% (+)-HCSA, 95% HCl).

4.3.5 Optimum Thickness of the Initial PAn.(+)-HCSA Film

The optically active polyaniline films produced in the above asymmetric syntheses may be considered as block co-polymers in which an initial short length of polyaniline is composed of PAn.(+)-HCSA, while the second longer block is the chiral PAn.HA species.

It was of interest to determine the minimum thickness of the initial PAn.(+)-HCSA film that could be used as the chiral electrode for subsequent asymmetric polymerizations (step 2 in Scheme 4.1). For this purpose, thin films of PAn.(+)-HCSA were electrodeposited while passing only 5 and 10 mC/cm² of charge (step 1 in Scheme 4.1). Unfortunately, these very thin PAn.(+)-HCSA films came off the ITO-Pt-coated glass electrode during removal from the polymerization solution and methanol washing. Their use as substrates for further electrodeposition was therefore not possible. Initial PAn.(+)-HCSA films of *ca.* 100 nm thickness (25 mC/cm² of charge passed) were therefore used in all subsequent studies.

4.3.6 Influence of Deposition Charge Passed on the Chiroptical Properties of PAn.HA Films Formed Via Macromolecular Asymmetric Proliferation

In all of the above studies the charge passed during the second polymerization step in Scheme 4.1 was 100 mC/cm². Figures 4.11 and 4.12 show the effect of employing a range of deposition charges between 50 and 300 mC/cm² during the stage 2 deposition of PAn.HCl from aqueous 1.0 M HCl.

As expected, increasing the charge passed caused thicker PAn.HCl films to be deposited onto the thin initial PAn.(+)-HCSA substrates, as evidenced by the increase in intensity

of the UV-visible spectra of the final products (Figure 4.11). The PAn.HCl film grown by passing 300 mC/cm^2 of charge in step 2 onto the PAn.(+)-HCSA substrate (25 mC/cm^2 charge) gave a UV-visible spectrum (curve 7) only slightly less intense than that shown in curve 8 for a PAn.(+)-HCSA film electrodeposited directly onto ITO-Pt-coated glass from 1.0 M (+)-HCSA . The thickness of the former film is estimated to be *ca.* 700 nm using the method described by Stejskal *et al.*^{8,9} However, their equation may be inapplicable for such thick films. Films deposited using greater than 300 mC/cm^2 charge passed in step 2 could not be examined quantitatively by UV-visible or CD spectroscopy due to their very strong absorbance.

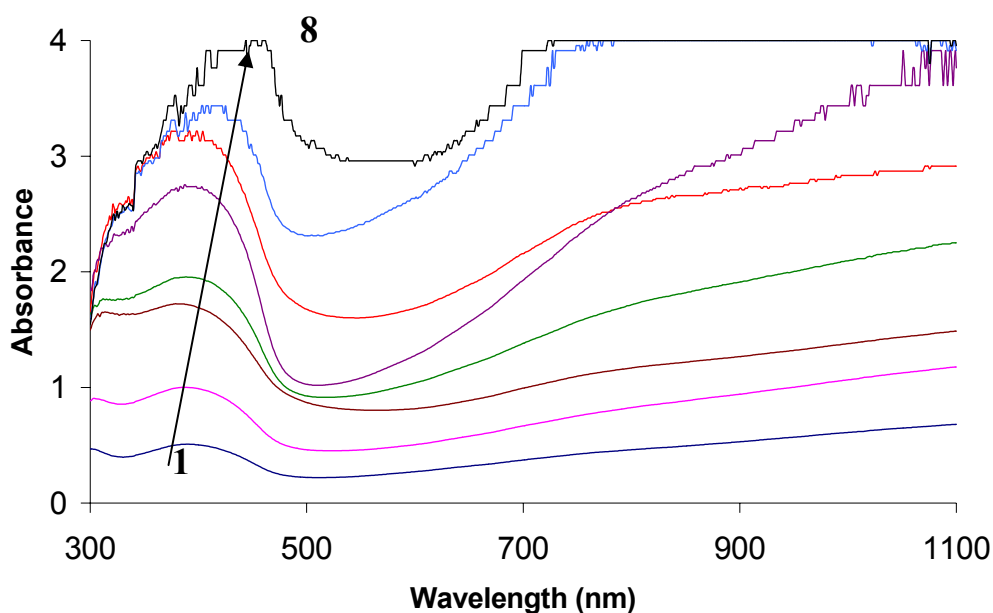


Figure 4.11 UV-visible spectra of emeraldine salt films prepared by deposition of an initial thin film (25 mC/cm^2 passed) of PAn.(+)-HCSA (curve 1), then further depositing PAn.HCl ($50, 70, 100, 150, 200$ and 300 mC/cm^2 passed) (curves 2-7). For comparison, curve 8 is for a PAn.(+)-HCSA film deposited directly onto ITO-Pt-coated glass from 1.0 M (+)-HCSA while passing 325 mC/cm^2 of charge.

The optical activity of the above films also increased markedly with increasing charge passed in the second deposition step, as shown by the CD spectra in Figure 4.12.

Significantly, the ellipticity of the 440 nm CD band of the deposited emeraldine salts increased linearly with the charged passed (Figure 4.13). Chiral induction by the thin initial PAn.(+)-HCSA film therefore extends undiminished for the deposition of PAn.HCl of at least 700 nm thickness. Significantly, the ellipticity of emeraldine salt film grown by passing 300 mC/cm² charge during the second deposition from 1.0 M HCl is seen to be very similar quantitatively to that of a PAn.(+)-HCSA film grown directly onto ITO-Pt-coated glass from 1.0 M (+)-HCSA, despite the fact that > 90% of the dopant acid used in the former case is achiral HCl.

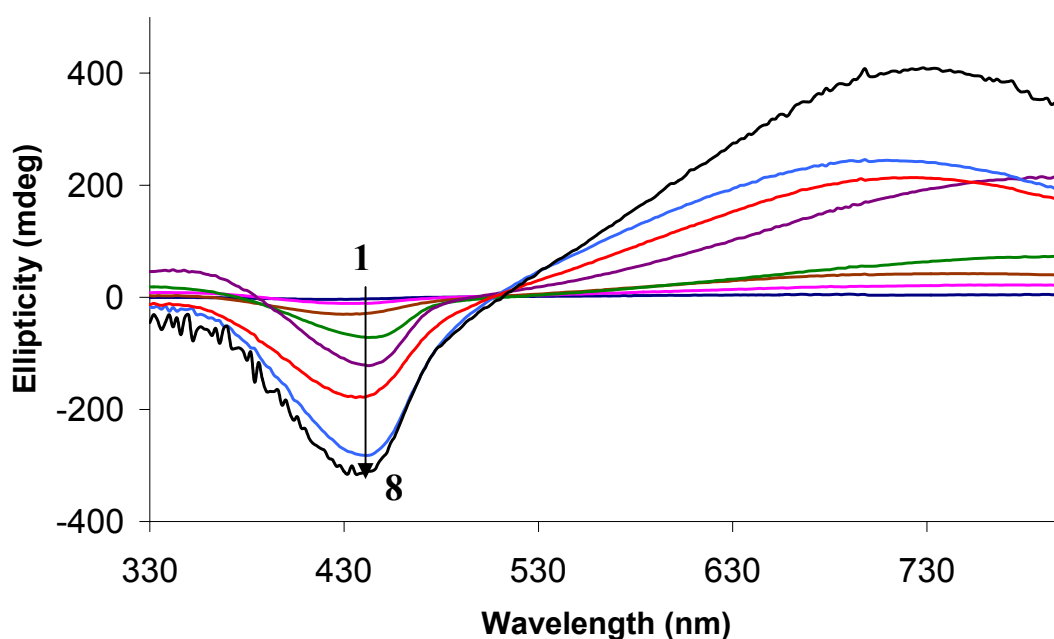


Figure 4.12 CD spectra of emeraldine salt films prepared by deposition of an initial thin film (25 mC/cm² passed) of PAn.(+)-HCSA (curve 1), then further depositing PAn.HCl (50, 70, 100, 150, 200 and 300 mC/cm² passed) (curves 2-7). For comparison, curve 8 is for a PAn.(+)-HCSA film deposited directly onto ITO-Pt-coated glass from 1.0 M (+)-HCSA while passing 325 mC/cm² of charge.

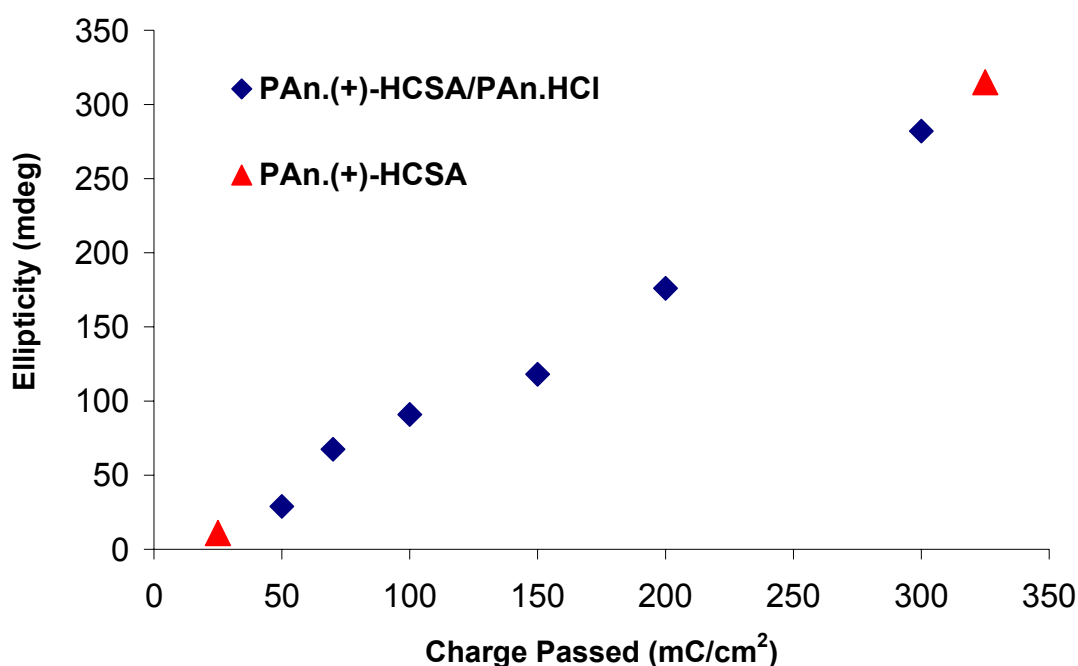


Figure 4.13 Dependence of the optical activity of emeraldine salt films on the deposition charge employed. Each point is the average of duplicate measurements.

4.3.7 Chiroptical Stability of Optically Active PAn.(+)-HCSA/HCl Block Co-polymers During pH and Redox Switching

The effect of pH and redox switching on the chiroptical properties of the optically active block co-polymers produced via the above macromolecular asymmetric proliferation was then investigated. All experiments were performed on emeraldine salt films prepared by deposition of an initial thin film (25 mC/cm² passed) of PAn.(+)-HCSA and then further depositing PAn.HCl (another 100 mC/cm² passed).

4.3.7.1 pH Switching

Treatment of the co-polymer emeraldine salt film with 1.0 M NH₄OH led to rapid dedoping to generate a blue emeraldine base (EB) film. As seen in Figure 4.14a (curve 2), this EB film exhibited characteristic absorption bands at *ca.* 350 and 630 nm. The emeraldine base was optically active, as shown by its CD spectrum in Figure 4.14b

(curve 2). This exhibited two sets of bisignate CD bands at *ca.* 330 and 390 associated with the 350 nm absorption band, and at 500 and 760 nm associated with the 630 nm absorption peak.

Re-doping the EB film with 1.0 M HCl regenerated the emeraldine salt form, as shown by the characteristic UV-visible spectrum in Figure 4.14a (curve 3, λ_{max} *ca.* 390 and 800 nm). The corresponding CD spectrum of the polyaniline re-doped film, showed CD bands at *ca.* 340, 435 and 685 nm (Figure 4.14b – curve 3), similar to those of the film prior to alkaline de-doping. The intensity of the various UV-visible spectra and the ellipticity of the CD bands in Figure 4.14 cannot be quantitatively compared because part of the film came off during the base/acid treatments. However, the CD spectra confirm that the optical activity of the polyaniline is at least largely retained during the de-doping/re-doping cycle. The retention of optical activity presumably arises from constraints in the solid state preventing rearrangement of the polyaniline chains.

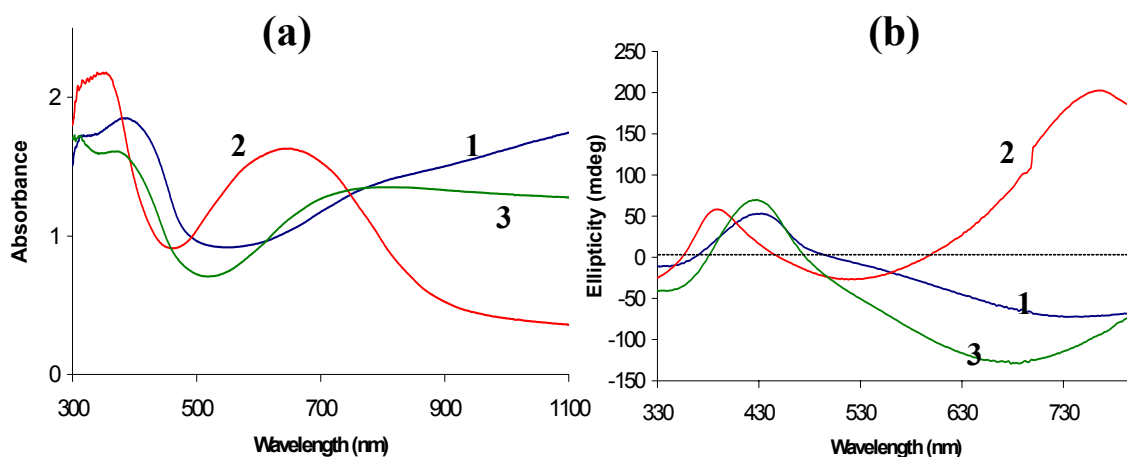


Figure 4.14 UV-vis spectra (a) and CD spectra (b) of an optically active PAN.(+)-HCSA/HCl film : (1) as prepared, (2) after de-doping in 1.0 M NH_4OH for 30 min, and (3) after then re-doping in 1.0 M HCl for 30 min.

4.3.7.2 Redox Switching

As described in Chapter 1 (see Figure 1.4), two main redox couples are usually observed in cyclic voltammograms of polyaniline in aqueous acid. The first redox pair is associated with interconversion between the fully reduced (leucoemeraldine) and semiquinone (emeraldine) forms of polyaniline, while the second redox couple is attributed to interconversion between the emeraldine and fully oxidized (pernigraniline) forms of polyaniline.²²⁻²⁴ It has been reported²⁵⁻²⁷ that anions from the electrolyte are incorporated into the polyaniline films to compensate the positive charges generated during oxidation from leucoemeraldine base to emeraldine salt and then expelled during subsequent reduction, as shown in Scheme 4.2 below.

Scheme 4.2

Therefore, repeated potential scanning in 1.0 M H₂SO₄ of a PAn.HCl film electrodeposited onto a thin PAn.(+)-HCSA film should cause the Cl⁻ and CSA⁻ ions incorporated in the block co-polymer to be replaced by HSO₄⁻ ions.

To avoid oxidative degradation of polyaniline, the potential scanning was performed from -0.3 V to a maximum positive potential of 0.9 V. Thus, the more anodic of the two expected oxidations was not fully observed in the cyclic voltammogram shown in Figure 4.15a. Upon repeated potential cycling the two initial redox peaks gradually decreased in current intensity and a new redox peak or “middle peak” appeared with $E_{1/2}$ *ca.* 0.55 V. This “middle peak” in the CVs of polyanilines is believed to be the redox couple of benzoquinone/hydroquinone, the main product of polyaniline oxidative degradation in aqueous acid at high positive potentials.^{27, 28}

The decrease in the intensity of the UV-visible (Figure 4.15b) and CD spectral bands (Figure 4.15c) of the polyaniline film after the potential cycling may be caused by dissolution of degradation products from the polyaniline film into aqueous solution. However, the decrease in ellipticity of the 440 nm CD band was similar to that observed for the corresponding absorption bands. This suggests that the optical activity of the remaining polyaniline was preserved when the initial (+)-CSA⁻ and Cl⁻ dopant anions were replaced by achiral HSO₄⁻ anions during the repeated potential scanning.

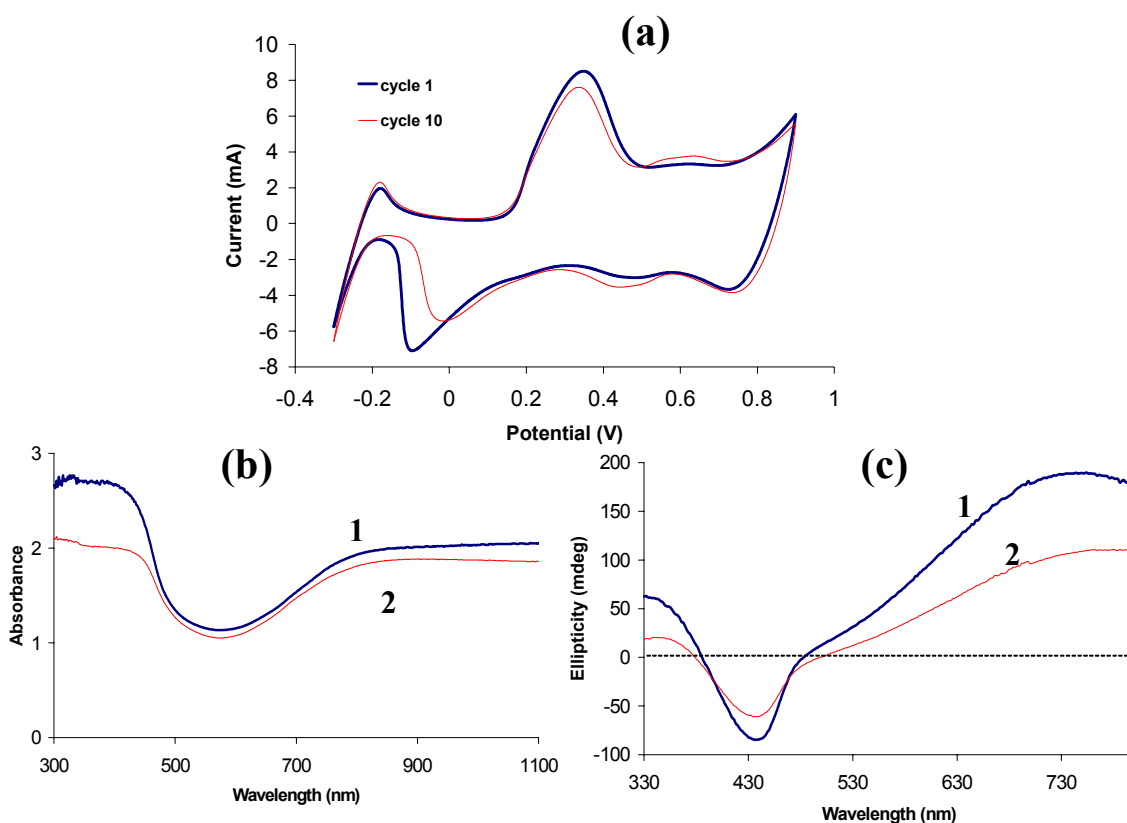


Figure 4.15 (a) CVs of a PAN.(+)-HCSA/PAN.HCl co-polymer film in 1.0 M H₂SO₄, scan rate 50 mV/s; (b) UV-vis spectra and (c) CD spectra measured before (1) and after (2) the cyclic voltammetry.

4.3.8 Role of the (+)-CSA⁻ Dopant Anion of Thin PAN.(+)-HCSA Films in Inducing Chirality into Subsequently Deposited Emeraldine Salts

The origin of the chiral induction in the above asymmetric syntheses of optically active emeraldine salts is uncertain. Induction may be associated with the one-handed helicity of the polyaniline chains in the initial thin PAN.(+)-HCSA film. Alternatively, chiral induction in the subsequently deposited PAN.HA films may be exerted by the CSA⁻ dopant in the thin film. Previous work on chiral PAN.(+)-HCSA films²⁹ indicated that the optical activity of polyanilines in the solid state was not lost after the chiral (+)-CSA⁻ dopant was removed by alkaline de-doping and replaced by achiral Cl⁻ ions via re-doping with HCl, as shown in Scheme 4.3.

Scheme 4.3

In order to explore the possible influence of the (+)-CSA⁻ dopant anion of the initial thin PAn.(+)-HCSA film in the induction of optical activity in PAn.HA emeraldine salts electrodeposited on this substrate, an analogous polymerization study was therefore carried out where the (+)-CSA⁻ dopant anion in the thin film was replaced by Cl⁻ via Scheme 4.3. However, this de-doping/re-doping cycle caused the polymer film to crack and come off the ITO-Pt-coated glass electrode.

An alternative anion exchange procedure was therefore carried out by performing cyclic voltammetry on the initial PAn.(+)-HCSA film in 1.0 M HCl solution. To avoid degradation of the polyaniline at high potential, cycling from -0.2 V to only +0.65 V was employed (scan rate 50 mV/s, 200 cycles). Stable cyclic voltammograms were recorded, indicating no polymer degradation. This was also confirmed by UV-visible and circular dichroism spectra recorded before and after the potential scanning, which showed only relatively small changes (Figure 4.16).

This thin optically active PAn.HCl film was then tested as a potential chiral inducer for the subsequent electrodeposition of a thick PAn.HCl film by potentiostatic

polymerization at 0.9 V of aqueous 0.2 M aniline/1.0 M HCl (100 mC/cm² charge passed). Unfortunately, only poor quality films could be obtained preventing reliable assessment of the chiroptical properties of the final emeraldine salt product. The potential role of the (+)-CSA⁻ dopant in initial PAn.(+)-HCSA in the chiral induction observed during macromolecular asymmetric proliferation therefore remains uncertain at present.

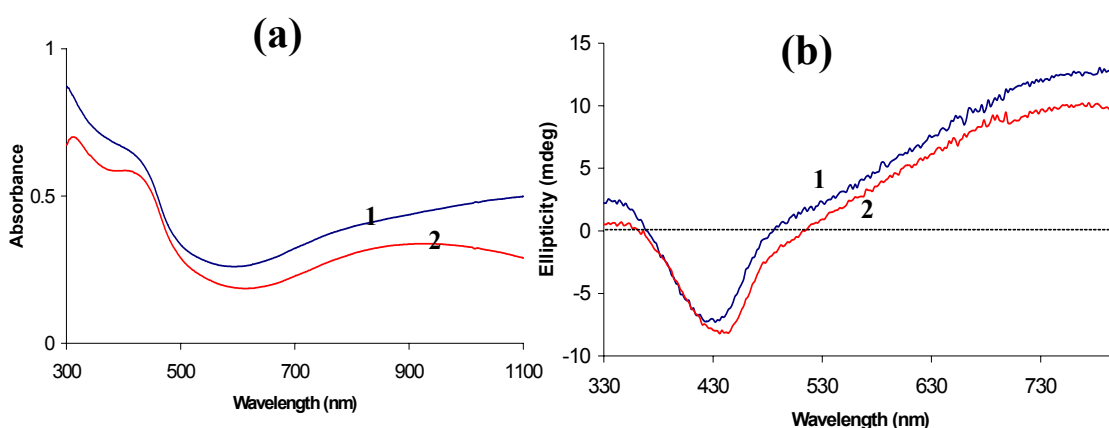


Figure 4.16 (a) UV-visible and (b) CD spectra of: (1) a PAn.(+)-HCSA film electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 25 mC/cm²), and (2) after potential scanning in 1.0 M HCl between -0.2 and +0.65 V (scan rate 50 mV/s, 200 cycles).

4.3.9 Electrochemical Study

Further understanding of the process of chiral induction in aniline polymerizations using thin PAn.(+)-HCSA films as chiral working electrodes has come from electrochemical characterisation of the films during and after growth of the polymers.

4.3.9.1 Cyclic Voltammetry

(i) PAn.(+)-HCSA and PAn.HCl Films

Previous studies on the electrochemical preparation of polyanilines have indicated that the type of acid dopant employed during growth is one of the main factors leading to

different electrochemical properties for the polyaniline products.³⁰⁻³² This has been confirmed in the present study for PAn.(+)-HCSA and PAn.HCl films electrodeposited onto glassy carbon electrodes at 0.9 V (125 mC/cm² charge passed) from aqueous 0.2 M aniline containing 1.0 M (+)-HCSA and 1.0 M HCl, respectively. Cyclic voltammograms for the two modified electrodes recorded in 1.0 M HCl (Figure 4.17) reveal that the redox couples for PAn.HCl appear at potentials more positive than those observed for PAn.(+)-HCSA.

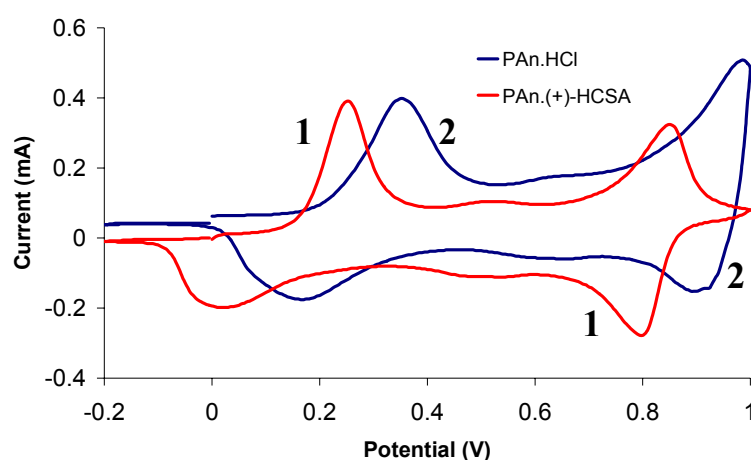


Figure 4.17 Cyclic voltammograms for (1) PAn.(+)-HCSA and (2) PAn.HCl films deposited on GC-disc (0.07 cm²) in 1.0 M HCl (scan rate = 50 mV/s). The polymer films were prepared by electrodeposition at 0.9 V (125 mC/cm² of charge passed) in 0.2 M aniline containing 1.0 M (+)-HCSA and 1.0 M HCl, respectively.

(ii) *PAn.HCl Film Deposited Upon a Thin PAn.(+)-HCSA Film*

Figure 4.18 illustrates the cyclic voltammograms measured in 1.0 M HCl (glassy carbon electrode) for a thin PAn.(+)-HCSA film grown for 25 mC/cm², and after further deposition of PAn.HCl for 100 mC/cm² (1st and 5th cycles shown). Interestingly, double redox peaks appeared in the low and high potential regions of the cyclic voltammogram recorded after depositing the PAn.HCl layer. This may arise from the different electrochemical behaviour of the two polymers, PAn.(+)-HCSA and PAn.HCl, in the final block co-polymer.

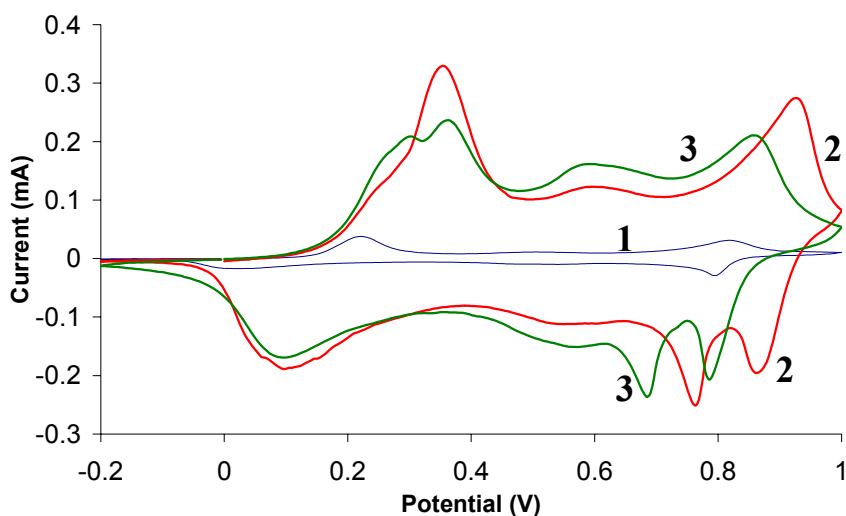


Figure 4.18 Cyclic voltammograms measured in 1.0 M HCl (scan rate of 50 mV/s) for: (1) a thin PAn.(+)-HCSA film on glassy carbon electrode (0.07 cm^2); (2) and (3), the 1st and 5th cycles after further deposition of PAn.HCl on top.

4.3.9.2 Chronoamperometry during Growth

Typical chronoamperograms obtained during potentiostatic deposition of PAn.(+)-HCSA and PAn.HCl onto ITO-Pt-coated glass electrodes (constant potential of +0.9 V, 125 mC/cm^2 charge passed) are shown in Figure 4.19. These indicate that for both polyanilines the polymer growth occurs in two stages. The first stage corresponds to a decrease in current, which can be explained by the creation of nuclei on the surface of bare electrode under diffusion control. The increase in current with time during the second stage is associated with the rapid deposition of the polymer on the polyaniline-covered electrode, similar to the autoaccelerative growth of polyaniline that has been observed previously.³³

Interestingly, the polymerization rates seem to be anion dependent. Polymerization in 1.0 M (+)-HCSA was faster than in 1.0 M HCl. For 125 mC/cm^2 of charge passed, the electrodeposition time for PAn.(+)-HCSA was usually less than 60 sec (Figure 4.19a), while the time for depositing PAn.HCl was *ca.* 90 sec (Figure 4.19b).

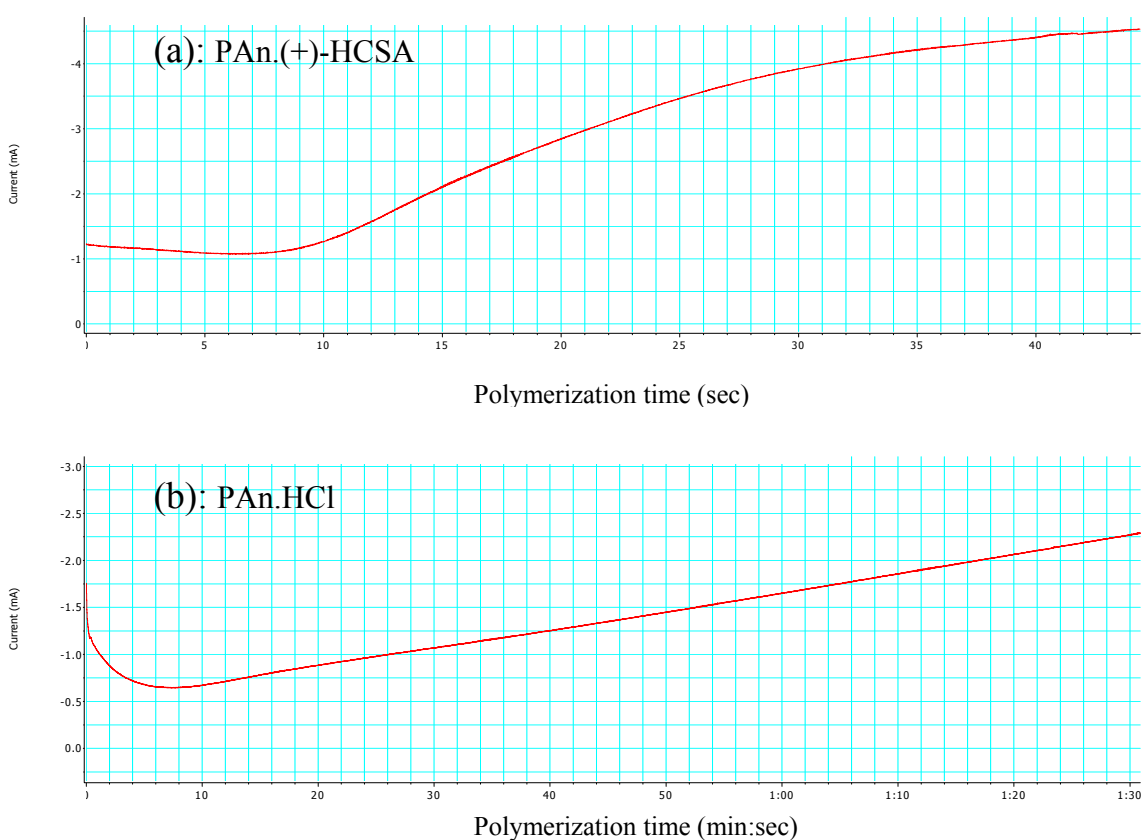


Figure 4.19 Chronoamperograms obtained during deposition of: (a) PAn.(+)-HCSA, and (b) PAn.HCl onto ITO-Pt-coated glass (*ca.* 1 cm²), using + 0.9 V and 125 mC/cm² charge passed.

Duić *et al.*³⁴ have reported the influence of anions on the electrochemical polymerization of polyaniline. They found that the polymerization rate varied in the order $\text{HSO}_4^- > \text{NO}_3^- > \text{Cl}^- > \text{ClO}_4^-$. Differences in the specific adsorption of the anions on the electrode surface were proposed to explain the results.

The influence of the anions present in the polymerization solution on the rate of electrodeposition of polyaniline was also observed in the 1st and 2nd steps of the asymmetric preparation of chiral polyanilines via the novel method in Scheme 4.1 presented here. The deposition time of PAn.HCl during the 2nd step (100 mC/cm²

charge passed) was 85 sec (Figure 4.20b). This indicates that Cl^- might be incorporated into the polyaniline chain during polymerization rather than $(+)\text{-CSA}^-$, where the deposition time was 40 sec for 100 mC/cm^2 charge passed. This suggests that the $(+)\text{-CSA}^-$ bound in the initial thin $\text{PAn.}(+)\text{-HCSA}$ film is not involved in the electrodeposition of PAn.HCl .

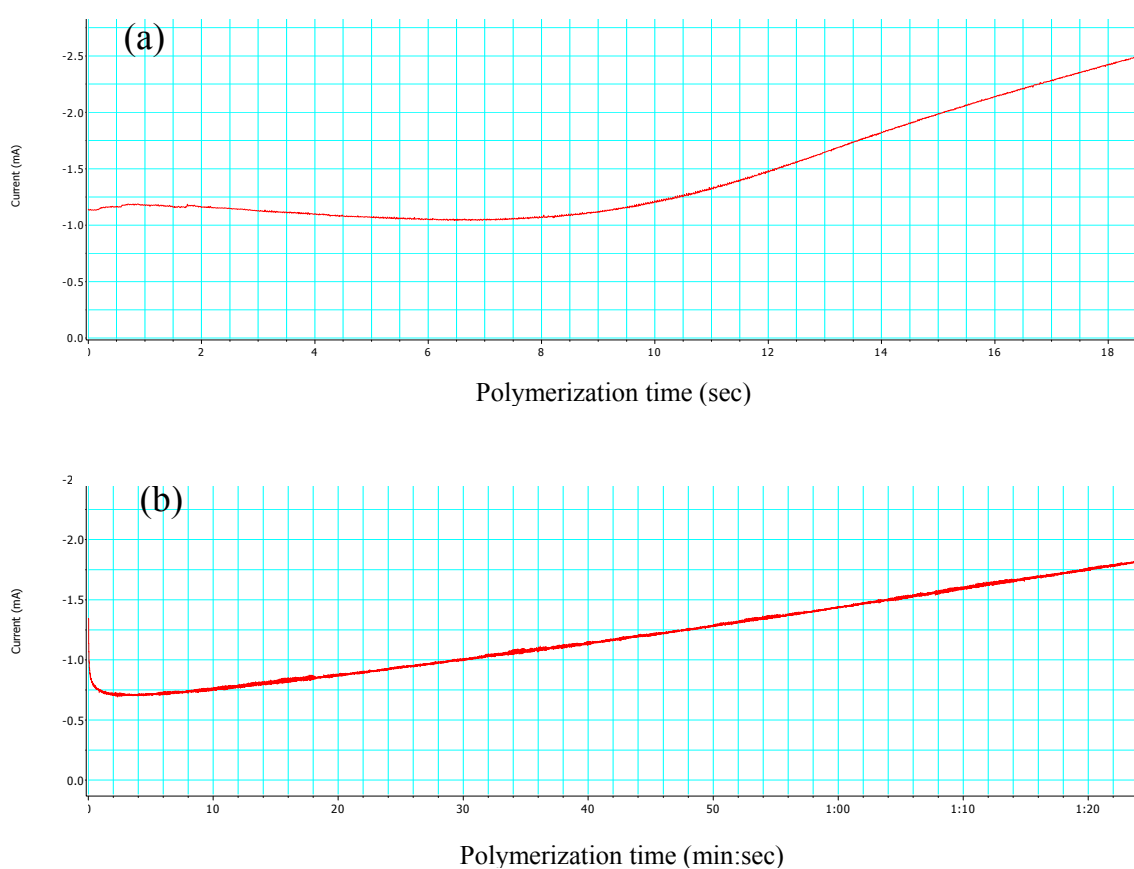


Figure 4.20 Chronoamperograms obtained during deposition of: (a) $\text{PAn.}(+)\text{-HCSA}$ onto ITO-Pt-coated glass (*ca.* 1 cm^2), and (b) PAn.HCl on top of (a) for 100 mC/cm^2 , at $+0.9\text{V}$.

4.3.10 Attempted Asymmetric Electrochemical Synthesis of Optically Active Polypyrrole Induced by Chiral PAn.(+)-HCSA

It was of interest to determine whether thin PAn.(+)-HCSA films could be similarly used as chiral inducers for the asymmetric synthesis of other optically active conducting polymers. A preliminary study was therefore undertaken to explore the asymmetric synthesis of chiral polypyrrole (PPy).

A thin film of PAn.(+)-HCSA was prepared as previously described (electrodeposition charge = 25 mC/cm²), washed with methanol and its chiroptical properties measured. PPy.(±)-CSA was then potentiostatically deposited on top of this chiral polyaniline electrode using an applied potential of 0.9 V and 100 mC/cm² charge passed, employing aqueous 0.2 M pyrrole (monomer)/1.0 M racemic (±)-HCSA as the polymerization solution.

The UV-visible and CD spectra of the thin, initial PAn.(+)-HCSA film are shown in Figures 4.21 (curve 1) and 4.21(curve 2), respectively. After electrodepositing a PPy.(±)-CSA film onto this chiral electrode, the UV-visible spectrum became much more intense (Figure 4.21 - curve 2), with a strong peak at 470 nm and an intense free carrier tail into the near-infrared. These bands may be attributed to the presence of bipolarons, and are indicative of the deposition of a conducting polypyrrole. The spectrum was not significantly modified by washing the film with methanol (Figure 4.21 - curve 3).

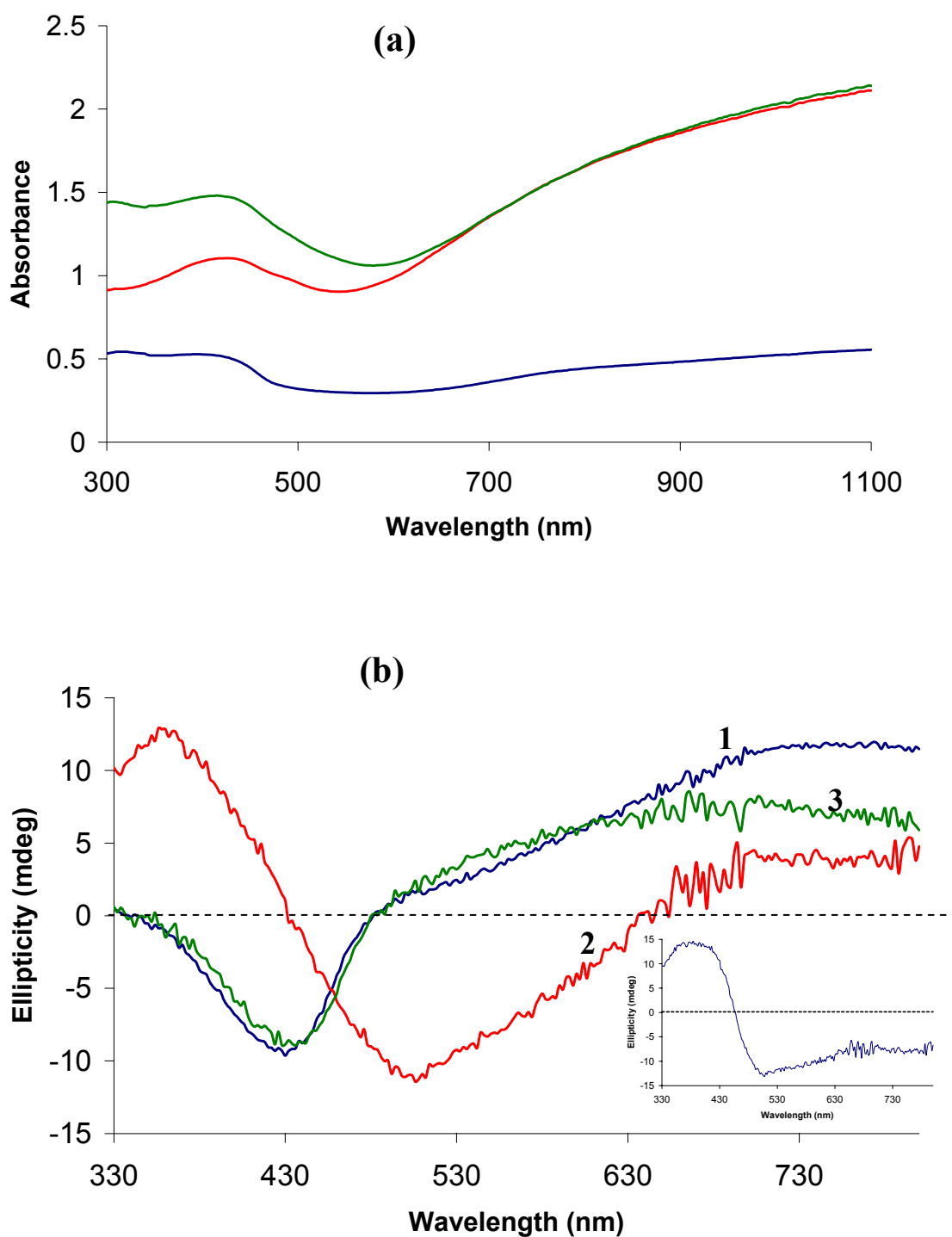


Figure 4.21 (a) UV-visible and (b) CD spectra of: (1) a PAn.(+)-HCSA film electrodeposited on ITO-Pt-coated glass at 0.9 V (deposition charge = 25 mC/cm^2); (2) after depositing a PPy.(±)-CSA film on top of (1) for 100 mC/cm^2 passed, as grown, and (3) after washing with MeOH. Inset: curve 2 after subtracting the spectrum of the PAn.(+)-HCSA under-layer (*i.e.* subtracting curve 1).

Interestingly, before washing with methanol, the CD spectrum of the final composite PAn.(+)-HCSA/ PPy.(±)-CSA film after subtracting that of the thin PAn under-layer, exhibited a pair of bisignate CD bands at *ca.* 370 and 500 nm, which could be associated with the absorption band of the thicker PPy.(±)-CSA over-layer at 470 nm. This suggests the formation of a weakly optically active polypyrrole via induction by the PAn initiator. However, after methanol washing, while not much change in the UV-visible spectrum was observed, the CD spectrum reverted to that recorded for the initial thin chiral PAn.(+)-HCSA film. Further studies will therefore be required to establish whether the asymmetric synthesis of polypyrroles can be achieved using a thin chiral PAn.(+)-HCSA film for chiral induction.

4.4 Conclusions

It is possible to induce optical activity into PAn.HA emeraldine salt chains via electrochemical polymerization of aniline in aqueous racemic or achiral acids (HA) at ITO-Pt-coated glass electrodes coated with a thin film of either PAn.(+)-HCSA or PAn.(-)-HCSA. Strongly optically active polyaniline with the same chiroptical properties as the chiral inducer employed are produced, with PAn.HA films grown on PAn.(+)-HCSA and PAn.(-)-HCSA electrodes having mirror imaged CD spectra. Remarkably, optical activity of the same hand as the chiral inducer (PAn.(+)-HCSA) is also produced when the enantiomeric (-)-HCSA is used as the dopant acid in the second polymerization step.

The preparation of the initial chiral PAn.HCSA electrode requires a minimum of 25 mC/cm² electrodeposition charge, giving a thickness of *ca.* 100 nm for the film. Optically active polyanilines doped with racemic or achiral acids, with film thicknesses

of *ca.* 400 nm are deposited onto this thin film after a further 100 mC/cm² of charge is passed. The ellipticity of the deposited emeraldine salt films increases linearly as the deposition charge is increased from 50-300 mC/cm², indicating that chiral induction by the thin initial polyaniline layer extends undiminished for films of at least 700 nm in thickness.

The optical activity of emeraldine salt films produced by this novel method is retained upon de-doping to emeraldine base and then re-doping to emeraldine salt, or upon redox switching to leucoemeraldine or pernigraniline during potential cycling between -0.3 and +0.9 V in aqueous acid different from the acid used in the polymer growth.

Electrochemical cyclic voltammetric studies both during and after the deposition steps have thrown some light on the mechanism of this macromolecular asymmetric induction. However, the detailed mechanism remains uncertain at the moment. This novel asymmetric synthesis method presents potential applications such as using thin chiral polyaniline films as inducers for the asymmetric synthesis of other conducting polymers.

4.5 References

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