

## Facile synthesis of optically active polyaniline and polytoluidine

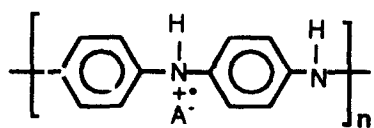
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Films of optically active polyaniline salts (PAN/HCSA) have been obtained by casting from solutions of emeraldine base doped with (1S)-(+)- or (1R)-(-)-10-camphorsulfonic acid (HCSA) in various solvents (NMP, DMF, DMSO or  $\text{CHCl}_3$ ). The mirror-imaged circular dichroism spectra for the salt films derived using (+)- and (-)-HSA, respectively, indicate enantioselectivity in the doping process. The first optically active ring-substituted polyanilines, namely poly(*o*-toluidine)/(+)-HCSA and poly(*o*-toluidine)/(-)HCSA, have also been produced in solution and as films via a similar doping procedure in DMSO.

(Keywords: polyaniline salts; optical activity; synthesis)

### Introduction

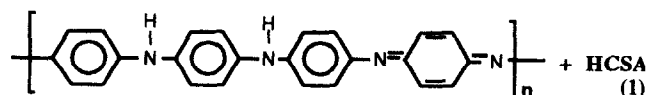
In late 1993<sup>1</sup> and in a subsequent paper<sup>2</sup> we reported the first and remarkably facile synthesis of optically active polyaniline via the enantioselective electropolymerization of the achiral monomer, aniline, in the presence of aqueous (1S)-(+)- or (1R)-(-)-10-camphorsulfonic acid (HCSA). Dark green films of the conducting emeraldine salts (**1a**,  $\text{A}^- = (+)\text{-CSA}^-$ ; and **1b**,  $\text{A}^- = (-)\text{-CSA}^-$ ) were deposited on indium-tin-oxide (ITO)-coated glass electrodes under potentiostatic conditions (+1.1 V vs. Ag/AgCl). The intense and mirror imaged circular dichroism (c.d.) spectra of salts **1a** and **1b** were rationalized<sup>1,2</sup> in terms of enantioselective electropolymerization in which one helical screw sense of the polymer chain is preferentially produced depending on which hand of the chiral  $\text{CSA}^-$  anion is incorporated.



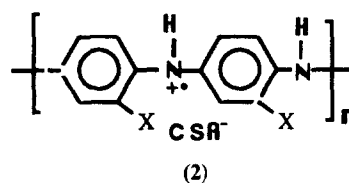
(1)

We have subsequently found<sup>3</sup> that optically active polyaniline salts **1a** and **1b** can also be generated chemically in various organic solvents (NMP, DMF, DMSO,  $\text{CHCl}_3$ ) via the doping of neutral emeraldine base (EB) with  $0.1 \text{ mol dm}^{-3}$  (+)- or (-)-HCSA, respectively (equation (1)). The nature of the solvent can have a marked influence on the chiroptical properties. For example, studies by Havinga *et al.*<sup>4</sup> and in our laboratories<sup>5,6</sup> have shown that solutions of **1a** obtained by analogous doping of EB with (+)-HCSA in *m*-cresol solvent do not exhibit any visible c.d. bands. Nevertheless, Havinga *et al.*<sup>4</sup> reported that

an optically active film of **1a** could be spun-cast onto poly(methyl methacrylate) from such a *m*-cresol solution.



We have similarly found that optically active films of both **1a** and **1b** can be readily cast onto ITO-coated glass following enantioselective doping (equation (1)) in each of the solvents NMP, DMF, DMSO and  $\text{CHCl}_3$ . The c.d. and u.v.–visible spectra and electroactivities of these films are reported below and their solvent dependence examined. Also reported for the first time is the preparation of optically active poly(toluidine) salts (**2**,  $\text{X} = \text{Me}$ ) both in solution and as films, via analogous doping of neutral poly(*o*-toluidine) base with (+)- or (-)-HCSA in DMF or DMSO solvent.



(2)

### Experimental

Emeraldine base (EB) and the corresponding poly(toluidine) base were synthesized via oxidation of aniline or *o*-toluidine with ammonium persulfate in  $1.0 \text{ mol dm}^{-3}$  HCl at  $0^\circ\text{C}$ , followed by de-doping with  $\text{NH}_4\text{OH}$  and washing as previously described<sup>7</sup>.

In order to obtain solutions suitable for casting films of salt **1**, the acid doping of EB was carried out under

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different conditions to those reported<sup>3</sup> in our earlier *in situ* studies. Solid emeraldine base (EB) and (+)- or (-)-HCSA were ground together in a 2:1 molar ratio (dopant anion: EB tetrameric repeating unit) and then dissolved by vigorous stirring for 4 h in the appropriate solvent (NMP, DMF, DMSO or CHCl<sub>3</sub>). A small amount of the filtered solution was then placed on an ITO-coated glass slide with a pipette. Drying for 6 h in an oven at 60°C (NMP, DMSO) or for 24 h at room temperature (DMF, CHCl<sub>3</sub>) gave thin green films of the chiral polymers **1a** and **1b**. A similar procedure was employed for the casting of films of the optically active poly(toluidine) salts **2a** and **2b**.

Circular dichroism spectra of the films were recorded on a Jasco-500C spectropolarimeter or a Jobin-Yvon Dichrograph 6. U.v.-visible spectra were measured with a Shimadzu UV-265 spectrophotometer. Cyclic voltammetric studies of the films were carried out using the ITO-coated glass as the working electrode ( $\sim 1 \text{ cm}^2$  surface area), Ag/AgCl reference electrode and a scan rate of  $10 \text{ mV s}^{-1}$ .

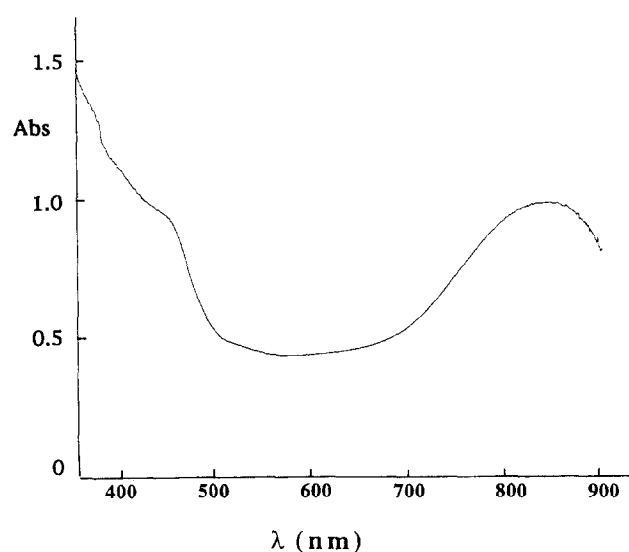
### Results and discussion

The u.v.-visible spectra of the green films cast from each of the doping solutions confirm the formation of the polyaniline salt **1** in each case. This is evidenced by the appearance of the three absorption bands characteristic of **1** (at 825, 420 and 345 nm when cast from DMSO: Table 1, Figure 1), and the absence of the band at  $\sim 630 \text{ nm}$  associated with the initial neutral EB. Unlike

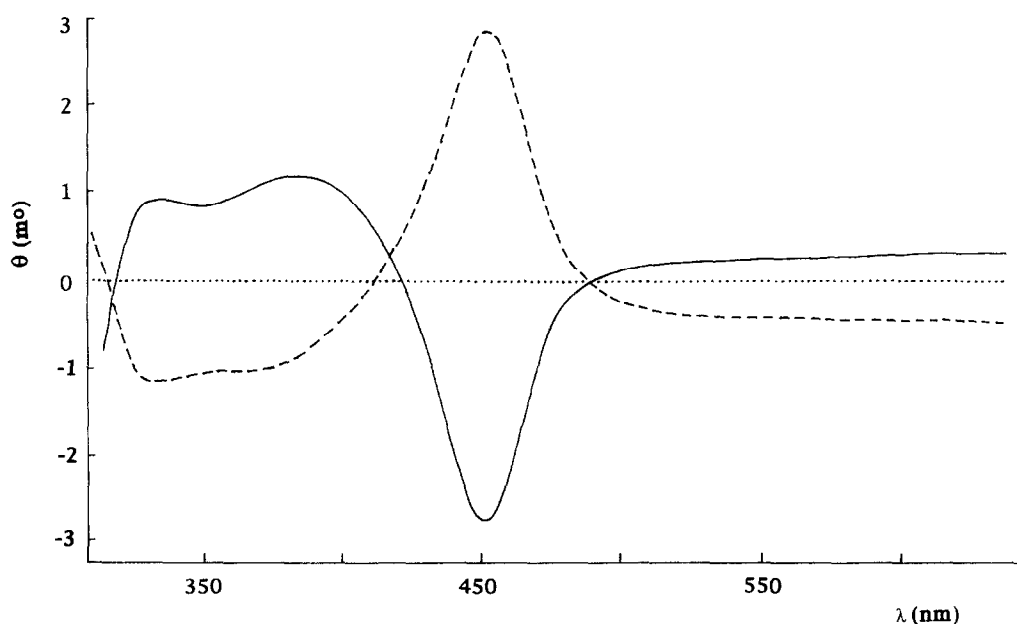
the solutions from which they were cast, the u.v.-visible spectra of the salt **1** films show only small variations with the nature of the solvent (Table 1). The most striking difference between the film and solution spectra is the large red shift (55–130 nm, depending on solvent) experienced by the highest wavelength visible band. This band has been assigned<sup>8</sup> to a localized polaron absorption. The red shift may indicate a change in polymer conformation and a longer conjugation length in the films compared with the solutions. (It may be noted that these u.v.-visible spectra are also unlike those previously reported by MacDiarmid and Epstein<sup>8</sup> for PAN/(\pm)-HCSA films exposed to *m*-cresol, where the high wavelength localized polaron band at  $\sim 800 \text{ nm}$  is replaced by an intense free carrier tail in the near i.r. MacDiarmid and Epstein<sup>8</sup> explained this dramatic effect of *m*-cresol in terms of a conformation change in the

**Table 1** U.v.-visible spectrum of polyaniline/(+)-HCSA salt **1a** in solution and as cast film

Solvent	Solution $\lambda_{\text{max}}$ (nm)	Film $\lambda_{\text{max}}$ (nm)	Redshift ( $\Delta\text{nm}$ ) for high $\lambda$ band
CHCl <sub>3</sub>	700, 440, 365	830, 435, 360	130
DMF	730, 440, 360	825, 425, 355	95
DMSO	745, 438, 352	825, 425, 347	80
NMP	785, 425, 340	840, 430, 355	55



**Figure 1** U.v.-visible spectrum of the polyaniline salt **1a** cast from a 2:1 mixture of (+)-HCSA and EB in DMSO



**Figure 2** Circular dichroism spectra of films of salts **1a** and **1b** cast from NMP solution: (+)-HCSA (—); (–)-HCSA (---)

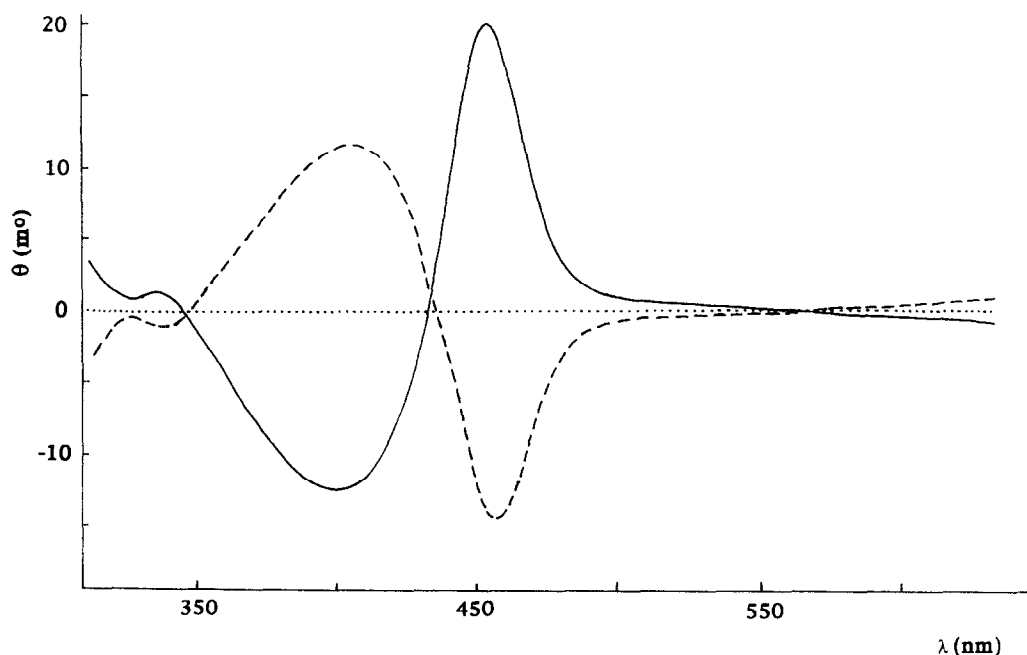


Figure 3 Circular dichroism spectra of salt films **1a** and **1b** cast from DMSO solution: (+)-HCSA (—); (–)-HCSA (---)

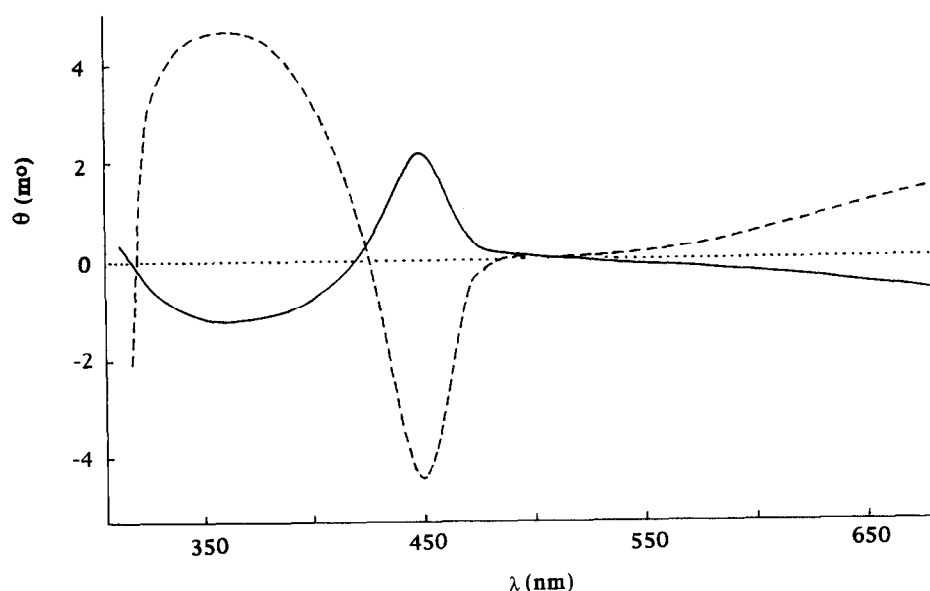


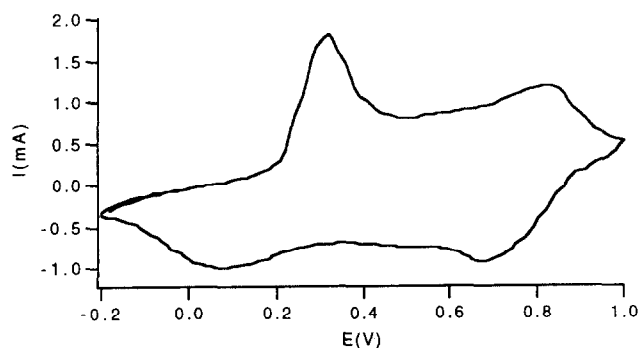
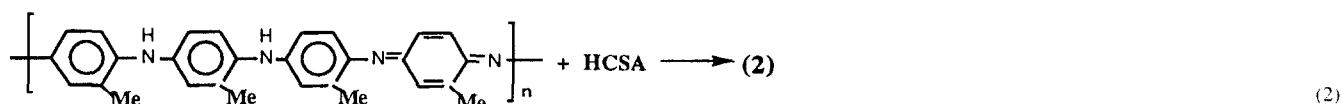
Figure 4 Circular dichroism spectra of salt films **2a** and **2b** cast from a 1:2 mixture in DMSO of poly(*o*-toluidine) and (+)-HCSA (—) or (–)-HCSA (---)

polymer chain from a compact coil to an expanded coil configuration.

The c.d. spectra of the cast films (e.g. Figures 2 and 3) confirm the production of optically active salt **1** from each of the solvents NMP, DMF, DMSO and  $\text{CHCl}_3$ . Particularly significant are the mirror-imaged CD spectra observed for salts **1a** and **1b** cast from solutions containing (+)- and (–)-HCSA, respectively. This reaffirms the enantioselectivity previously observed by us<sup>3</sup> in solution for these doping reactions. The visible region c.d. bands in Figures 2 and 3 correspond with the strong absorption bands observed in the associated u.v.–visible spectra (Figure 1, Table I). They do not arise from the presence of the optically active  $\text{CSA}^-$  ion in the salt, since this anion exhibits only a u.v. c.d. band at 295 nm. The c.d. spectra of the films are more sensitive to the

nature of the solvent employed for doping than are the associated u.v.–visible spectra, but overall show similar features.

Analogous doping of poly(*o*-toluidine) base with (+)- or (–)-HCSA in DMSO (equation (2)) has also provided optically active poly(toluidine) salts **2** for the first time. The solution c.d. spectra for **2a** and **2b**, obtained by doping in DMSO (or DMF) with (+)- and (–)-HCSA, respectively, are mirror-imaged, indicating that the doping process is again enantioselective. Generation of the optical activity, however, is substantially slower than with the parent polyaniline. Dark green films of optically active poly(toluidine) could be cast from these DMSO solutions and exhibit c.d. spectra (Figure 4) similar to the parent polyaniline salts **1a** and **1b** (Figure 3).



**Figure 5** Cyclic voltammogram of salt **1a** (cast from NMP) using ITO-coated glass as working electrode ( $1\text{ cm}^2$  surface area), Ag/AgCl reference electrode and  $10\text{ mV s}^{-1}$  scan rate

The conductive and electroactive nature of the optically active polymers **1** and **2** is confirmed from cyclic voltammetry on the films cast on ITO-coated glass. The well-defined oxidation and reduction processes observed (e.g. *Figure 5*) are typical of those previously described<sup>9</sup> for polyaniline materials. Only relatively small differences are observed for films cast from different solvents. The electrochemical behaviour for the cast polyaniline **1** is also similar to that previously

reported<sup>2</sup> for **1** prepared via enantioselective electro-polymerization.

#### Acknowledgements

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