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Chemical generation of optically active polyaniline via the doping of emeraldine base with (+)- or (−)-camphorsulfonic acid

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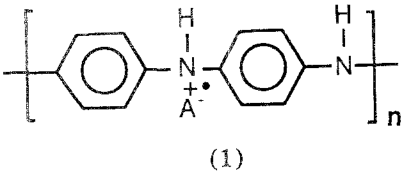
Optically active polyaniline salts can be readily generated in solution via the enantioselective acid doping of the neutral emeraldine base form of aniline with either (+)- or (−)-camphorsulfonic acid in a variety of organic solvents (1-methyl-2-pyrrolidinone (NMP), dimethylformamide, dimethylsulfoxide, $CHCl_3$). Strong mirror-imaged circular dichroism (CD) spectra were observed for the deep green polymer solutions obtained with (+)- and (−)-camphorsulfonic acid (HCSA), respectively, suggesting that the acid doping is enantioselective, with one helical screw of the polymer chain being preferentially produced depending on which hand of the CSA^- anion is incorporated. In contrast, no CD bands were observed for related polytoluidine salts in NMP, consistent with a model proposed for the above enantioselectivity. Films of the optically active polyaniline salts were also obtained by casting from the acid-doped solutions onto glass plates, and showed similar CD spectra.

(Keywords: polyaniline; optical activity; doping)

Introduction

We recently achieved[1,2] the first synthesis of optically active polyaniline via the enantioselective electropolymerization of the achiral monomer, aniline, in water in the presence of either (+)- or (−)-camphorsulfonic acid (HCSA). The polyaniline was deposited on indium-tin-oxide-coated glass electrodes as a film of the dark green, conducting emeraldine salt (**1**), where A^- is either (+)- or (−)-CSA^-. Polymers grown in the presence, respectively, of 1 mol dm^{-3} (+)-HCSA and 1 mol dm^{-3} (−)-HCSA were found to have intense and mirror-imaged circular dichroism (CD) spectra (CD maxima at 780, 445 and 340 nm). This suggested that the electropolymerization was highly enantioselective, with one helical screw of the polymer being predominantly produced when the (+)-CSA^- anion is incorporated, while the opposite helical screw arises in the presence of (−)-CSA^-.



(1)

We now report that optically active polymeric emeraldine salts of type **1** may also be readily generated chemically in solution by reacting the neutral emeraldine base (EB) form of polyaniline with either (+)- or (−)-HCSA. Protonation and doping of EB with protonic acids (e.g. HCl, $HClO_4$, HOAc, HPTSA, etc.) has been studied previously by others[3–8] as a route to related achiral polyaniline salts.

Experimental

All reagents were purchased from Aldrich and were used as supplied.

Neutral EB of intermediate molecular weight[8] was synthesized as previously described[9]. Conversion of this polymer to the optically active emeraldine salt (**1**) *in situ* was achieved by shaking a few milligrams of solid EB with a 0.1 mol dm^{-3} solution (15 dm^3) of (+)-HCSA in various organic solvents (1-methyl-2-pyrrolidinone, (NMP), dimethylformamide (DMF), dimethylsulfoxide (DMSO), $CHCl_3$) and filtering. The CD and u.v.–visible spectra of the deep green solutions thus produced were then recorded using a Jasco-500 C spectropolarimeter and a Shimadzu UV-265 spectrophotometer, respectively.

Films of the green emeraldine salt (**1**) were obtained by casting onto glass plates from such doped solutions, and their CD and u.v.–visible spectra were recorded. In these latter cases the solid neutral EB and (+)- or (−)-HCSA were first ground together in a 2 : 1 molar ratio, dissolved with stirring for 4 h in the appropriate solvent, and filtered. A small amount of the filtrate was then placed on a glass slide. Drying for 6 h in an oven at 60°C (NMP, DMSO) or in air at room temperature ($CHCl_3$, DMF) gave thin green films of salt (**1**).

Results and discussion

Neutral EB was slightly soluble in NMP containing 0.1 mol dm^{-3} (+)-HCSA, generating a deep green solution characteristic of protonation/doping of the EB. The u.v.–visible spectrum of the solution (λ_{max} at 790, 440, 350 nm, *Figure 1*) was very similar to that previously reported[7] for the HCl salt of polyaniline in NMP, confirming formation of an emeraldine salt of type **1** (A^- = (+)-CSA^-). Most significantly, distinctive

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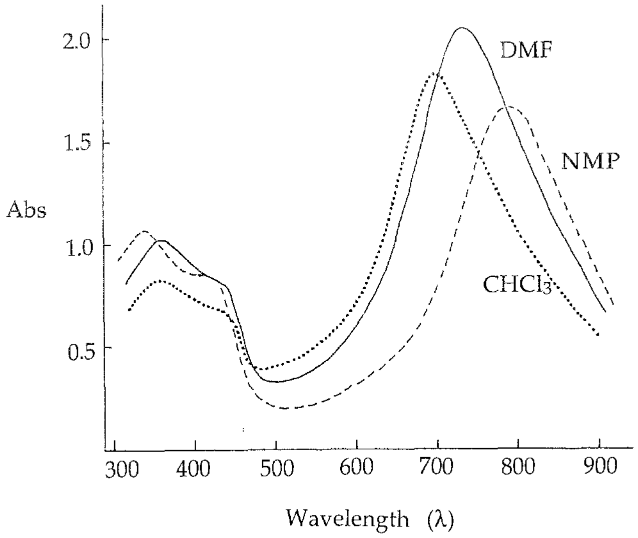


Figure 1 U.v.–visible spectra of polyaniline salts (**1**) generated from emeraldine base (EB) in 0.10 mol dm^{-3} (+)-HCSA in $CHCl_3$ (· · ·), DMF (——) or NMP (– – –) solvents

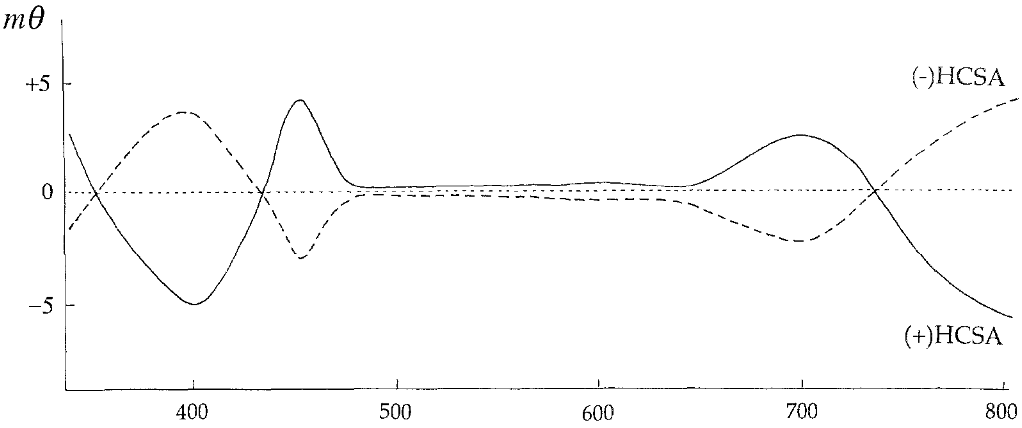


Figure 2 Circular dichroism spectra of polyaniline salts (**1**) generated from EB dissolved in NMP containing 0.10 mol dm^{-3} (+)-HCSA (——) or (−)-HCSA (– – –)

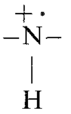
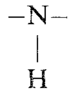
CD bands were observed at *c.* 800, 700, 450 and 390 nm, associated with these visible absorption bands (*Figure 2*). The visible CD bands do not arise from the (+)-CSA$^-$ anion itself, which has an absorption peak at 295 nm. In contrast, a solution of EB in NMP containing 0.1 mol dm^{-3} (−)-HCSA produced a mirror image CD spectrum (*Figure 2*). This indicates that the protonation/doping of EB is enantioselective, with one or other helical screw of the polymer chain being adopted, depending on which hand of the CSA$^-$ anion is incorporated.

The CD and u.v.–visible spectra obtained soon after dissolving EB in NMP/(+)-HCSA or NMP/(−)-HCSA solutions were relatively insensitive to the concentration of acid employed over the range [HCSA] = 0.01–1.00 mol dm^{-3}. This suggests that protonation/doping has reached its maximum extent within a few minutes at an acid concentration of 0.01 mol dm^{-3}. Similar CD and u.v.–visible spectra were also generated with [HCSA] = 0.001 mol dm^{-3}; however, in this latter case protonation/doping was slower, occurring over a period of *c.* 30 min.

Acid doping of EB with (+)- and (−)-HCSA to give optically active polyanilines of type **1** also occurs in a range of other solvents. For example, the CD spectra obtained with 0.10 mol dm^{-3} (+)- and (−)-HCSA in DMF are shown in *Figure 3*. These CD spectra are somewhat different and more intense than those in NMP solvent, especially at longer wavelengths. This is consistent with the differences observed in the respective u.v.–visible absorption spectra in DMF and NMP solvents (*Figure 1*). Earlier spectroscopic studies[6,7,10] revealed similar solvent effects upon the u.v.–visible spectra of chemically generated polyaniline HCl salts.

Very similar CD spectra to those in *Figure 3* were obtained upon dissolving EB in DMSO solutions containing 0.1 mol dm^{-3} (+)- or (−)-HCSA, confirming comparable protonation/doping in DMF and DMSO. Similar CD spectra were also generated using $CHCl_3$ as the solvent for protonation/doping. Shifts in the CD bands with solvent were again associated with differences in the u.v.–visible spectra (*Figure 1*).

Films of the optically active emeraldine salt (**1**) could also be readily obtained by casting from the above acid-doped solutions onto glass plates. The u.v.–visible and CD spectra of these films were similar in each case to the parent solutions, but showed a general red shift and changes in peak intensities.

Protonation/doping of the EB forms of poly(*o*-toluidine) and poly(*m*-toluidine) to give type **1** salts also occurs readily with 0.10 mol dm^{-3} (+)-HCSA in NMP, as confirmed by u.v.–visible spectral changes. Most significantly, with the polytoluidines no CD bands were observed in the 800–300 nm region after (+)-HCSA doping in NMP solvent, indicating the absence of one-screw-sense helicity. This observation supports our earlier hypothesis[1,2] that a fixed helical arrangement (*Figure 4*) of polyaniline salts of type **1** is maintained by chiral CSA$^-$ anions linking  $\begin{array}{c}+\cdot\\-\text{N}-\\|\\\text{H}\end{array}$ and  $\begin{array}{c}-\text{N}-\\|\\\text{H}\end{array}$ centres three dimeric repeating units apart along the chain. The presence of methyl groups *ortho* or *meta* to the N centres would not

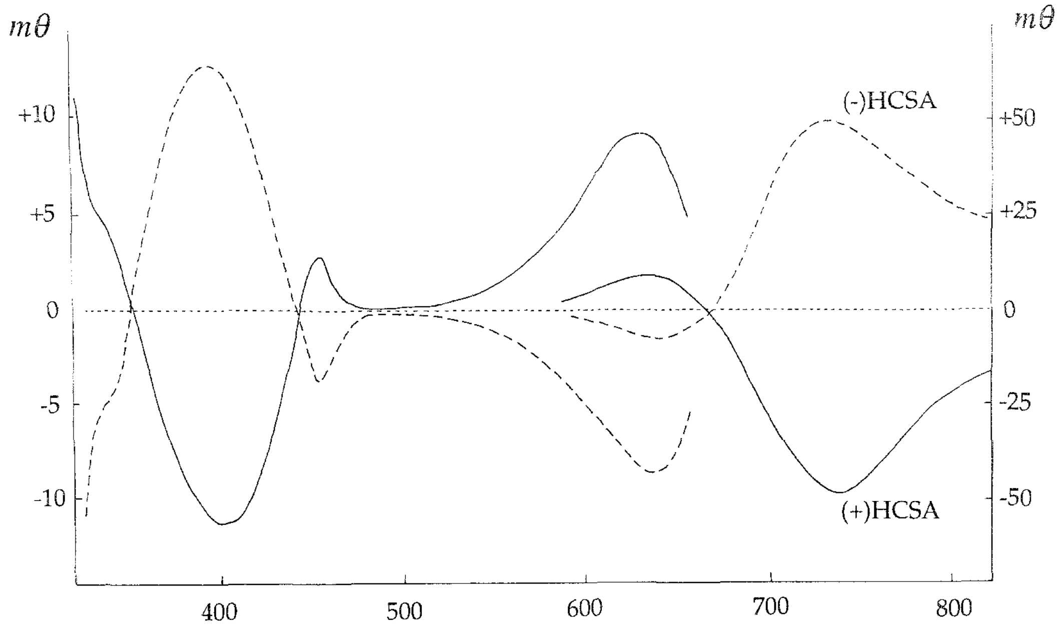


Figure 3 Circular dichroism spectra of polyaniline salts (**1**) generated from EB dissolved in DMF containing 0.10 mol dm^{-3} (+)-HCSA (——) or (−)-HCSA (– – –)

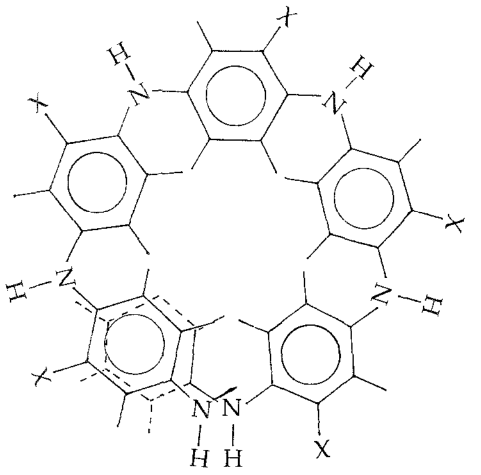


Figure 4 Vertical view of helical polyaniline (X = H) or polytoluidine (X = Me) showing three dimeric repeating units (Dreiding model)

appear from *Figure 4* to hinder the formation of helical polyaniline chains. However, the attachment of chiral CSA$^-$ anions to the $\overset{+}{\mathrm{N}}\mathrm{H}$ and NH centres, essential for one-screw-sense helicity, is clearly sterically blocked by such methyl groups.

This facile new route to chiral polyanilines should assist the study of their chiroptical and other physical properties, together with the exploration of their potential in areas such as electrochemical asymmetric synthesis and chiral chromatography. We are currently examining analogous protonation/doping using emeraldine bases of varying molecular weights, as well as studying the conditions for casting films of chiral polyanilines from such solutions. It will be of particular interest to determine whether polyanilines containing single-handed helical chains have enhanced electrical conductivities. Preliminary studies[11] suggest that other chiral anions of suitable geometry and functionality, such as (1S)-(+)-3-bromocamphor-10-sulfonic acid, may also be used to generate optically active polyaniline salts with helical chirality.

Acknowledgements

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