polymer communications

Enantioselective electropolymerization of aniline in the presence of (+)- or (−)-camphorsulfonate ion: a facile route to conducting polymers with preferred one-screw-sense helicity

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The first and remarkably facile synthesis of optically active polyaniline has been achieved via the enantioselective electropolymerization of aniline on indium-tin-oxide-coated glass electrodes in aqueous solution containing (1S)-(+)- or (1R)-(−)-10-camphorsulfonic acid (HCSA). The dark green films of conducting polyemeraldine salt formed under electrostatic conditions (+1.1 V *versus* Ag/AgCl) exhibited strong circular dichroism (c.d.) spectra typical of polymers possessing helical chirality. The quantitative reversal of the c.d. spectrum of the salt grown in (+)-HCSA as opposed to (−)-HCSA suggests that electropolymerization is highly enantioselective, with one helical screw of the polymer chain being preferentially produced depending on the hand of the CSA$^-$ anion incorporated. The ready electrosynthesis of optically active polyanilines should facilitate studies of their use in asymmetric synthesis and in chiral chromatography.

(Keywords: chiral polyaniline; optical activity; electropolymerization)

Introduction

As a result of its high conductivity, processability, and ability to be switched reversibly and rapidly between several differently coloured oxidation states, polyaniline has attracted considerable recent interest[1–6]. It is a versatile material with potential applications as diverse as rechargeable batteries[7–9], electrochromic devices[10,11], catalysis[12,13] and chromatography[14]. We wish to report now the first and remarkably facile synthesis of optically active polyaniline via the enantioselective electropolymerization of the achiral monomer, aniline, in the presence of either (+)- or (−)-camphorsulfonic acid.

There has been considerable recent interest in the development of chiral conducting polymers, largely because of their potential as electrodes in asymmetric electrochemical synthesis. Studies to date, however, have concentrated on polypyrroles[15–18] and polythiophenes[19,20], and have generally involved the polymerization of monomers in which a chiral substituent has been attached to either the 3-position of the heterocyclic ring or to the pyrrole N-atom. For example, for polypyrroles substituted in the 3-position with chiral amino acid groups, circular dichroism studies indicated[15] the generation of a helical polymer possessing a preponderance of one screw sense. Macromolecular asymmetry of the polymer backbone has also been suggested[17] for a polypyrrole N-substituted with a β-D-glucose derivative. Interestingly, no main-chain chirality was evident in a related pyrrole N-substituted with an optically active camphorsulfonate group[16].

Such routes, requiring the presence of an optically active substituent covalently bound to the monomer substrate, are generally synthetically tedious and/or expensive, and can have a deleterious effect upon the polymer's conductivity and electroactivity. The route we report below for optically active polyaniline has the advantage that it requires no synthetic steps prior to the polymerization of the achiral aniline, and appears to rely instead on the preferential formation of one helical screw of the polymer backbone under the influence of (+)- or (−)-camphorsulfonate ions present in the medium.

Experimental

All reagents were purchased from Aldrich and were used as supplied. The electropolymerization of the aniline was carried out potentiostatically on indium-tin-oxide (ITO)-coated glass electrodes in aqueous solutions containing 0.2 mol dm^{-3} aniline and 1 mol dm^{-3} (1S)-(+)- or (1R)-(−)-10-camphorsulfonic acid (HCSA), at an applied potential of +1.1 or +1.2 V *versus* Ag/AgCl. Subsequent reduction of polyemeraldine salt film thus produced was carried out at an applied potential of −0.5 V *versus* Ag/AgCl in 1 mol dm^{-3} (+)- or (−)-HCSA.

The circular dichroism (c.d.) spectra of the chiral polymers on ITO-coated glass were recorded on a Jasco-500C spectropolarimeter. Cyclic voltammetric characterization of the polyanilines was carried out either during polymer growth or on the deposited polymer films using ITO-coated glass as the working electrode (1 cm^2 surface area), Ag/AgCl reference electrode and a scan rate of 10 mV s^{-1}.

Results and discussion

Under the electropolymerization conditions outlined above (+1.1 V *versus* Ag/AgCl, 1 mol dm^{-3} (+)- or (−)-HCSA), aniline is oxidized to the dark green, conducting polyemeraldine salt, which is believed[2] to have the polysemiquinone radical cation repeating unit **1** (where A$^-$ is either (+)- or (−)−CSA$^-$). The total

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charge applied was varied between 75 and 140 mC cm^{-2}, giving polyemeraldine salt films of varying thickness. Transmission of visible light through these films on ITO-coated glass was sufficient to permit the recording of both c.d. and u.v.–visible spectra between 800 and 300 nm.

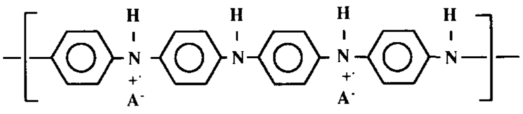

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Figure 1 shows the c.d. spectrum of polyemeraldine salt polymers, **1a** and **1b**, grown on ITO-coated glass (at 140 mC cm^{-2}) in the presence of 1 M (+)-HCSA and 1 M (−)-HCSA, respectively. The polymers **1a** and **1b** are seen to have mirror image c.d. spectra, each possessing two strong c.d. bands in the visible region at ~780 and 445 nm. These c.d. bands correspond to two strong visible absorption bands at ~800 and 410 nm observed for the same films. The visible c.d. spectra of polymers **1a** and **1b** do not arise from the associated (+)-CSA$^-$ and (−)-CSA$^-$ ions, since the optically active anion has been independently shown to have a c.d. band at 290 nm and to be transparent in the visible region.

The absolute magnitude of the c.d. bands for polymers **1a** and **1b** could be estimated approximately from the mass of polymer deposited in the films. The $\Delta\varepsilon_{L\text{-}R}$ values are quite large (e.g. 16 mol^{-1} dm^2 for the 445 nm band of **1b**), as expected for a polymer possessing helical chirality. The quantitative reversal of the c.d. spectrum of the polyemeraldine salt grown in (−)-HCSA as opposed to (+)-HCSA strongly suggests that the electropolymerization is highly enantioselective, with one helical screw of the polymer chain being predominantly produced when the (+)-CSA$^-$ anion is incorporated, while the opposite helical screw arises in the presence of (−)-CSA$^-$. Molecular models suggest that the helical arrangement of the polyemeraldine salts may be maintained by CSA$^-$ anions linking $-\overset{+\cdot}{\underset{|\atop \text{H}}{\text{N}}}-$ and $-\underset{|\atop \text{H}}{\text{N}}-$ centres three repeating units apart along the chain (via ionic and H-bonds).

The conductive and electroactive nature of the polymers **1a** and **1b** is evident from cyclic voltammetry either during polymer growth (*Figure 2*) or on the deposited polymer films. The well defined oxidation and reduction processes observed are typical of those described previously[1,21] for polyaniline materials.

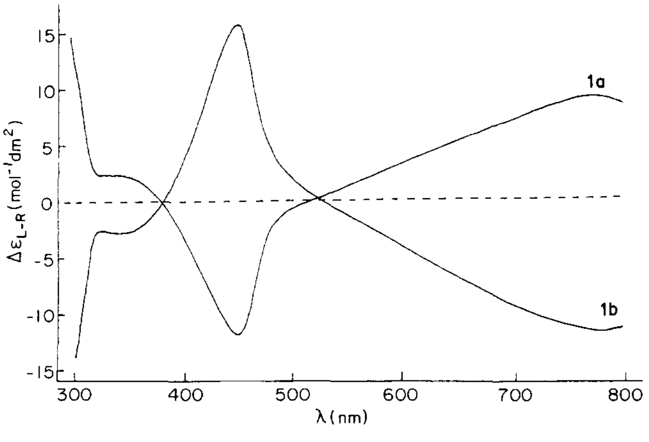


Figure 1 Circular dichroism spectra of films of the polyemeraldine salts **1a** and **1b** grown on ITO-coated glass (at 140 mC cm^{-2})

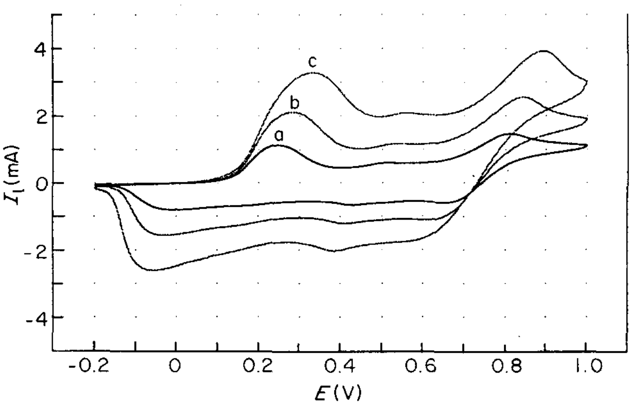
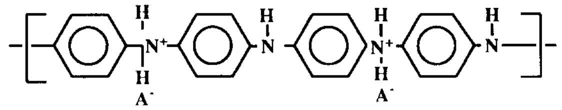


Figure 2 Electrodeposition of **1a** by potentiodynamic methods using ITO-coated glass as working electrode (1 cm^2 surface area), Ag/AgCl reference electrode and 10 mV s^{-1} scan rate: (a) scan no. 7, (b) scan no. 10, (c) scan no. 13

Electrochemical reduction of the polyemeraldine salt film **1a** was subsequently carried out at an applied potential of −0.5 V *versus* Ag/AgCl (in 1 M (+)-HCSA). The colour of the film changed to pale yellow-green, as expected for the formation of reduced polyleucoemeraldine salt **2**, reported[1,2] to be formed under these conditions. This colour change arises from the disappearance of the long-wavelength absorption band at 800 nm. The c.d. spectrum of this reduced polyemeraldine film was recorded and, as anticipated, the long-wavelength c.d. band at 780 nm was markedly decreased in intensity. However, a relatively strong c.d. band (of unchanged sign) was present at 440 nm, corresponding to the absorption band at 440 nm found for this yellow-green reduced polymer. These results suggest that the same helical structure and screw sense is retained during the electrochemical reduction of **1a** to **2a**. This is not unexpected as the (+)-CSA$^-$ anion is retained in the polymer during the reduction in 1M HCSA.



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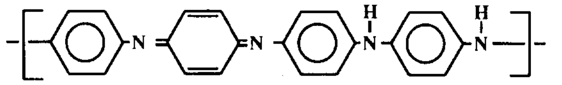
The essential role of the (+)-CSA$^-$ group in maintaining the helical structure of polyaniline was demonstrated by dissolving the dark green polyemeraldine salt **1a** in neat pyrrolidine. A deep blue solution of the neutral base form of polyemeraldine **3** was produced via this rapid deprotonation. The concomitant loss of CSA$^-$ anion from the polymer was accompanied by the disappearance of all c.d. signals in the visible region.



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The generation from achiral monomers of optically active polymers, in which the activity arises solely from macromolecular asymmetry, has attracted considerable recent attention in the area of non-conducting polymers[22–31]. In these cases, which may be regarded as examples of atropisomerism, bulky substituents on the polymer chain stabilize one helical screw arrangement via steric hindrance to rotation about single carbon–carbon bonds. Examples include polyisocyanides[25,26], polyisocyanates[27], poly(triarylmethyl methacrylates)[28,29] and polychlorals[30,31]. Our synthesis, above, of optically active polyaniline represents the first preparation of a chiral conducting polymer from an achiral monomer, and uses a different mechanism for achieving one-screw-sense helicity.

The facile electrosynthesis of optically active polyaniline in either helical hand will greatly facilitate exploration of the utility of such chiral conducting polymers in asymmetric electrosynthesis. We are also interested in examining these new chiral polymers as novel, voltage-sensitive chiral stationary phases for the chromatographic separation of racemates. Related studies have also commenced to determine whether similar enantioselective electropolymerization of aniline can be carried out in the presence of other optically active anions.

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