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Influence of the chiral dopant anion on the generation of induced optical activity in polyanilines

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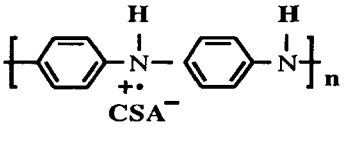
Emeraldine base (EB) is doped with (1S)-(+)-3-bromocamphor-10-sulfonic acid and a novel chiral acrylamidesulfonic acid (**4**) in NMP and DMF solvents to give new optically active polyaniline salts (PAn.HA). The conjugate base anions (A^-) of these chiral dopants (as with the previously studied (+)-camphor-10-sulfonic acid, HCSA) contain SO_3^- and carbonyl (C=O) groups that may maintain the polyaniline chains in a preferred one-sense helical screw via simultaneous electrostatic and H-bonding. Optically active polyaniline salts are also produced via analogous doping of EB (in NMP or DMF) with the chiral dicarboxylic acids (+)- or (−)-tartaric acid and O,O′-dibenzoyl-D-tartaric acid, which possess quite different structural motifs to HCSA. A common feature of all the dopants successful in generating optically active polyaniline salts is their bidental nature, allowing attachment of the dopant to the polymer backbone at two places simultaneously. © 1997 Elsevier Science Ltd.

(Keywords: polyaniline salts; induced optical activity; chiral dopant)

INTRODUCTION

We recently reported[1,2] the first synthesis of optically-active polyaniline salts of type (**1**) via the enantioselective electropolymerization of the achiral monomer, aniline, in the presence of either (+)- or (−)-camphorsulfonic acid (HCSA). Subsequently, we have shown that such optically active polyaniline salts can also be readily generated in solution[3] and as films[4] by the acid doping of emeraldine base (EB) with (+)- or (−)-HCSA in various organic solvents. Havinga *et al.*[5] have also recently produced an optically active polyaniline salt film via the doping of EB with (+)-HCSA in *m*-cresol solvent.



(1)

We postulated[1–4] that the observed macromolecular asymmetry arose from the polyaniline chain adopting, at least partially, a preferred one-sense helical screw which was maintained by the enantiomeric CSA^- anions linking $\overset{+\cdot}{N}H$ and NH centres three dimeric repeating units apart along the polymer chain. Two simultaneous modes of attachment of the chiral anion to the polymer chain were considered essential for enantioselectivity, namely electrostatic bonding of the CSA^- sulphonate ion to polyaniline $\overset{+\cdot}{N}H$ centres and H-bonding of the CSA^- carbonyl group to NH sites (*Scheme 1*).

In order to test this hypothesis and to throw further light on the factors responsible for the generation of induced optical activity in such doping reactions, we have now examined the acid doping reaction (1) of emeraldine base with a series of other chiral dopant acids (**2–6**) incorporating different structural motifs. The chiroptical properties of the new chiral polyaniline salts (**7**) obtained are described.

EXPERIMENTAL

Materials

(1S)-(+)-3-bromocamphor-10-sulfonic acid (**2**), (+)- and (−)-tartaric acid (**5a**, **5b**), (+)-O,O′-dibenzoyl-L-tartaric acid (**6**), N-methylpyrrolidinone (NMP), dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were purchased from Aldrich Co., Australia, and employed as received. The synthesis of the novel sulfonic acids (**3**) and (**4**) has been recently described by some of us[6]. Neutral emeraldine base (EB) was prepared using a previously described procedure[7].

Doping experiments

Doping of this neutral polymer with each of the chiral acids (**2–6**) to generate polyaniline salts of the type (**7**) was carried out *in situ* by vigorously shaking 1 mg of solid EB with a 10 ml solution of the dopant acid in the appropriate solvent for 15 min (dopants

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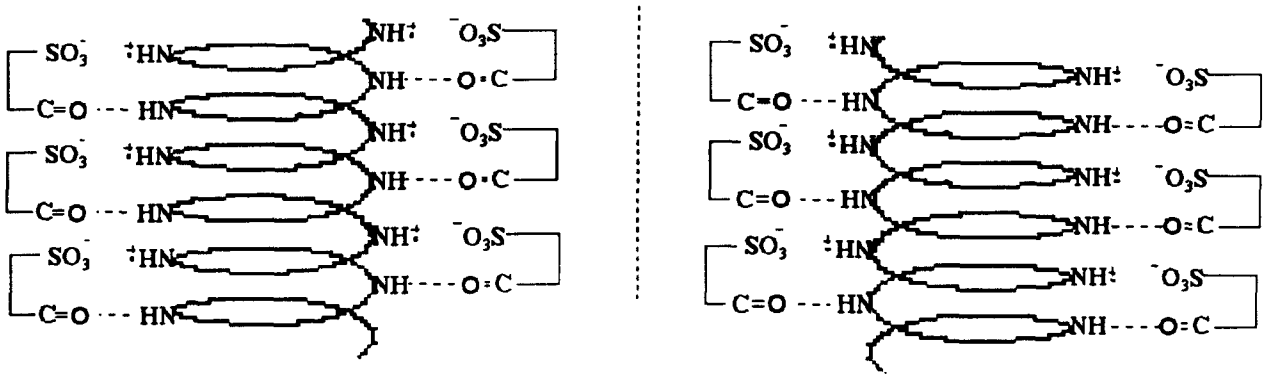
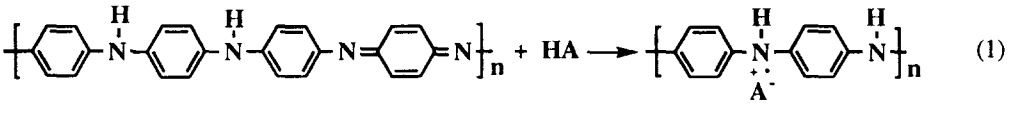
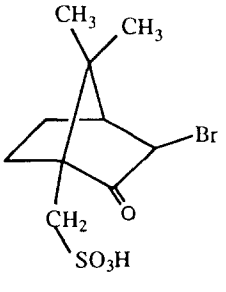


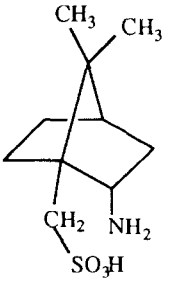
Scheme 1



EB (7) (1)



(2)



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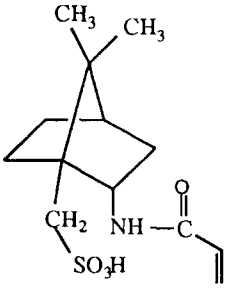

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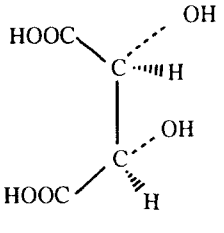
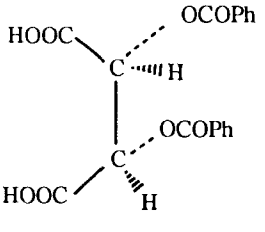


(5a)



(6)

2–4) or 2–24 h (dopants **5** and **6**). Dilute (0.05–0.10 mol dm^{-3}) solutions of the sulfonic acids (**2–4**) were employed, while more concentrated solutions (0.4–0.5 mol dm^{-3}) were used for the less reactive dicarboxylic acids (**5**) and (**6**). After filtering through a 0.5 μ filter, the u.v.-visible and circular dichroism (c.d.) spectra of the deep green solutions of the polyaniline salts (**7**) produced were immediately recorded.

Spectroscopic studies

U.v.-visible spectra of the doped solutions were recorded using a Shimadzu UV-265 spectrophotometer over the range 300–900 nm. Circular dichroism (c.d.) spectra of the same solutions were measured employing a Jobin-Yvon Dichrogram 6.

RESULTS AND DISCUSSION

Doping with the chiral sulfonic acids (2–4)

Doping of emeraldine base (EB) with the optically active (1S)-(+)-3-bromocamphor-10-sulfonic acid (**2**) (0.05 mol dm^{-3}) occurred readily in DMF or NMP solvents, generating within minutes a deep green solution

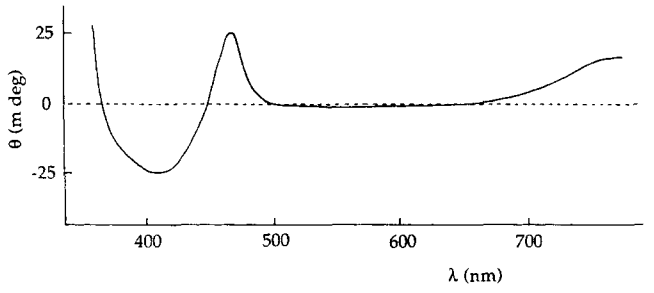
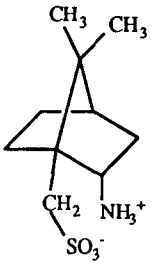


Figure 1 C.d. spectrum of polyaniline salt (**7a**, A^- = (+)-BrCSA$^-$) generated after 20 min from EB dissolved in NMP containing (**2**)



(3a)

characteristic of the expected polyaniline salt (**7a**; A^- = conjugate base of **2**). The u.v.-visible spectrum of the doped solution in NMP (λ_{max} at 800 and 370 nm) was very similar to that previously reported for PAn.HCSA[3] and PAn.HCl[8] salts of polyaniline in NMP. This new polyaniline salt (**7a**) was found to be optically active, as evidenced by its distinctive c.d. spectrum (*Figure 1*). The c.d. bands at *ca.* 400, 455 and $\geq$ 750 nm associated with the above absorption bands are similar to those previously reported[3] for the analogous PAn.(+)-HCSA salt (**1**) in NMP. These visible region c.d. bands do not arise from the incorporated optically active acid (**2**), which exhibits CD bands below 300 nm. This suggests, as found previously[3,4] with (+)- or (−)-HCSA, that either: (i) the protonation/doping of EB with (**2**) is enantioselective giving a preferred one-screw-sense helicity to the polymer chain; or (ii) macromolecular asymmetry arises from some other rearrangement subsequent to the doping reaction itself.

The result with (+)-3-bromocamphor-10-sulfonic acid (**2**) is not surprising in view of the close structural similarity of this dopant to the previously studied (+)-HCSA. However, it is noteworthy that a recent study by Havinga *et al.*[5] reported that a film spun cast from a solution of EB doped with (**2**) in *m*-cresol/chloroform (5 : 1 w/w) was optically inactive. This indicates that the generation of optically active polyanilines is very sensitive to parameters such as the solvent employed (as we have recently observed[4,9] for the generation of optically active polytoluidines).

Interestingly, the optically active aminosulfonic acid (**3**) (isolated[6] as a diastereomerically pure product from the reduction of (+)-HCSA) did not dope emeraldine base (EB). Addition of excess (**3**) to a blue solution of EB in either NMP or DMF solvents caused no significant change to the visible spectrum of EB (λ_{max} *ca.* 630 nm), with no evidence for the formation of a polyaniline salt of type (**7**). This inability to dope EB presumably arises

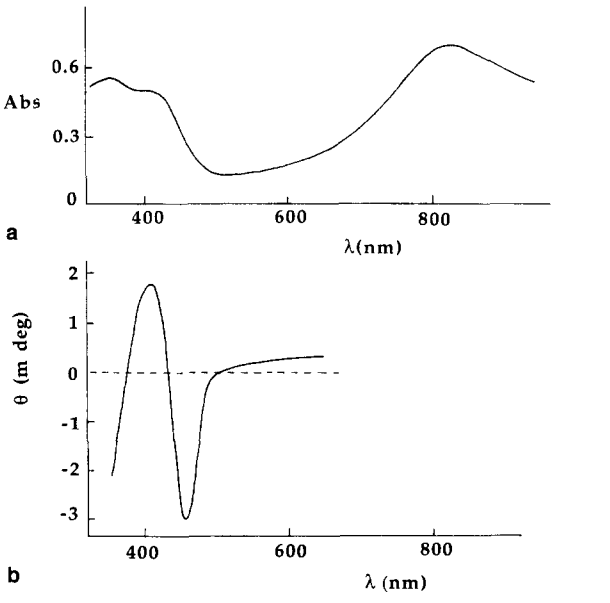


Figure 2 (a) U.v.-visible and (b) c.d. spectra of polyaniline salt (**7b**, A^- = conjugate base of **4**) generated after 20 min from EB dissolved in NMP containing (**4**)

from the aminosulfonic acid adopting the zwitterion form (**3a**) in solution.

However, a 0.05 mol dm^{-3} solution of the related acrylamidesulfonic acid derivative (**4**)[6] was found to dope EB in DMF to give a polyaniline salt (**7b**, A^- = conjugate acid of **4**), as evidenced by the rapid formation of a green solution with absorption bands at 355, 420 and 830 nm (*Figure 2a*). Significantly, this salt was found to be optically active, with visible CD bands (*Figure 2b*) qualitatively similar to those for (**1**) and (**7a**). This observation is consistent with our earlier hypothesis[3,4] for the origin of asymmetric induction in polyaniline salts, since this dopant (like CSA$^-$) contains both an SO_3^- and a carbonyl (CO) site for electrostatic and H-bonding, respectively, to the polyaniline chain.

Doping with the chiral dicarboxylic acids (5) and (6)

The acid doping of emeraldine base (EB) via reaction (1) has generally been carried out in the past with relatively strong acids (HCl, HBF_4, HPTSA, etc.), and the related electropolymerizations of anilines are usually unsuccessful at pH values higher than 3. However, we have now found that EB can be partially doped with the relatively weak (+)- or (−)-tartaric acids (**5a**, **5b**) in DMF or NMP solvents, although it is considerably less facile than with chiral sulfonic acids such as HCSA, (**2**) and (**4**).

For example, stirring a mixture of EB with a 0.5 mol dm^{-3} solution of (+)-tartaric acid (**5a**) in NMP solvent slowly (overnight) generated the green colour anticipated for the associated polyaniline salt (**7**). (This contrasts with the analogous doping of EB with (+)-HCSA in the same solvent, which is complete within a few minutes.) The u.v.-visible spectrum after 24 h confirmed formation of the salt (**7c**; A^- = (+)-tartrate), showing a strong localized polaron band at 780 nm (*Figure 3a*). However, the doping reaction had not proceeded to completion, since a shoulder remained in the absorption spectrum at *ca.* 630 nm characteristic

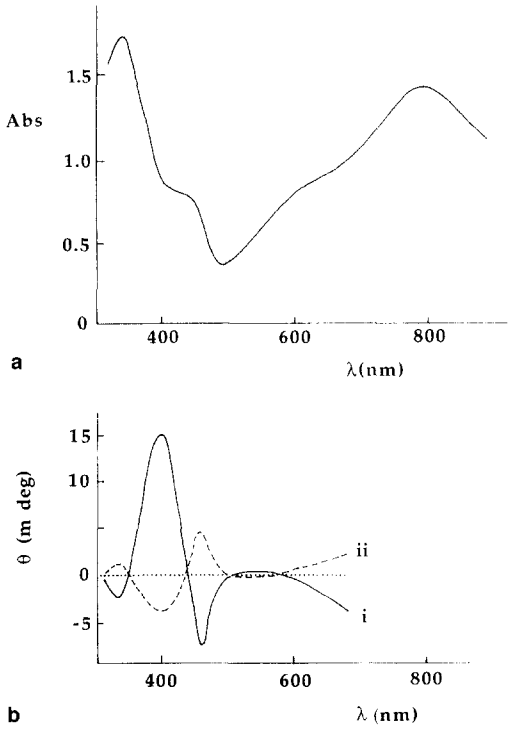


Figure 3 (a) U.v.-visible spectrum of polyaniline salt (**7c**) generated after 24 h from EB dissolved in NMP containing (+)-tartaric acid. (b) Corresponding c.d. spectra of polyaniline salts (**7c**) generated from EB dissolved in NMP containing: (i) (+)-tartaric acid; (ii) (−)-tartaric acid

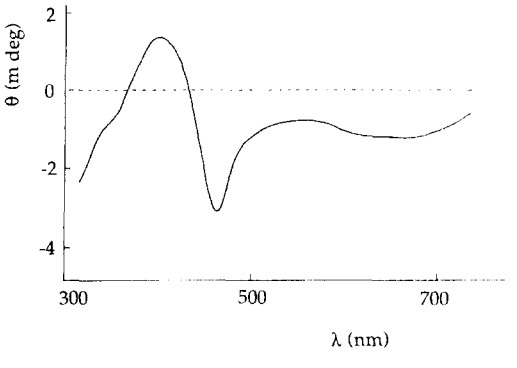
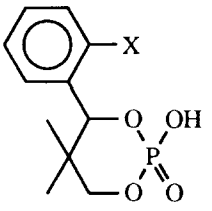


Figure 4 C.d. spectra of polyaniline salt (**7d**) generated after 30 min from EB dissolved in DMSO containing (**6**)

of unreacted EB. A similar, but more rapid (3 h), partial doping reaction occurred in DMF solvent generating a localized polaron band for the salt (**7c**) at *ca.* 810 nm.

Most significantly, the c.d. spectra of the latter partially doped solutions confirmed that optically active polyaniline salt (**7c**; $A^- = (+)$-tartrate) was generated in each solvent (e.g. *Figure 3b* in NMP). The strong visible region c.d. bands observed are not associated with the incorporated (+)-tartrate ions, since these exhibit only an ultraviolet c.d. band. Furthermore, a similar but mirror imaged c.d. spectrum (*Figure 3b*) was generated via the analogous doping of EB with (−)-tartaric acid in NMP solution. This suggests an enantioselective doping process as was previously observed[2] with (+)- and (−)-HCSA.

A similar doping experiment reacting EB with a 0.4 mol dm^{-3} solution of O,O′-dibenzoyl-L-tartaric acid



(8)

(**6**) in DMSO also generated an optically active polyaniline salt (**7d**), exhibiting a broad localized polaron absorption band at *ca.* 800 nm and a c.d. spectrum (*Figure 4*) similar to that of (**7c**). This indicates that the hydroxy substituents in tartaric acid are not critical participants in the processes leading to the generation of optical activity in the resultant polyaniline salts. However, the extent of salt formation and the intensity of the resultant CD spectrum was lower than with (+)-L-tartaric acid.

The success of the above doping experiments with tartaric acids led us to examine the possibility of forming optically active films of these novel PAn.tartaric acid polymers via the enantioselective electropolymerization of aniline in aqueous (+)-tartaric acid. The polymerizations were carried out using the potentiodynamic technique previously employed[1,2] for (+)-HCSA. However, although specks of a dark green material formed in the electrolyte solution, adherence of this material to either Pt or ITO-coated glass working electrodes was poor and films could not be obtained.

The generation of optically active (**7c**) and (**7d**) with the dicarboxylic acids (**5**) and (**6**) as dopants in equation (1) demonstrates that it is not essential for the induction of optical activity in PAn.HA salts that the chiral dopant anion possess the structural features of the CSA^- anion (including SO_3^- and C=O sites for electrostatic and H-bonding). However, it is interesting that all the dopants successful to date in generating optically active polyanilines are bidental, allowing attachment of the dopant to the polymer backbone at two places simultaneously. In contrast, Havinga *et al.*[5] have recently reported no optical activity in polyaniline salts obtained by doping emeraldine base with several chiral phosphoric acids (**8**; X = H, Cl, or OMe). Further studies will therefore be necessary to elucidate the structural motifs and/or electronic properties required in chiral dopant anions in order to induce macromolecular asymmetry in polyaniline salts derived from the doping reactions (1).

ACKNOWLEDGEMENTS

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