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Asymmetric proliferation with optically active polyanilines†

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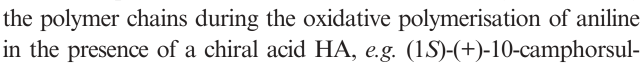
Thin optically active polyaniline layers have been shown to function as platforms to induce optical activity in polyanilines (containing achiral dopants) that are formed by subsequent electrodeposition.

There has been considerable recent interest in optically active polyanilines (PAn's) because of their potential applications in areas such as chiral sensors, electrochemical asymmetric synthesis and chiral separations.[1] Optical activity has been most commonly induced into polyaniline emeraldine salts (PAn·HA) *via* the incorporation (eqn (1))



(1)

of chiral dopant anions (A^-) at radical cation nitrogen sites along the polymer chains during the oxidative polymerisation of aniline in the presence of a chiral acid HA, *e.g.* (1*S*)-(+)-10-camphorsulfonic acid, (+)-HCSA. A range of polymerisation methods had been successfully employed, ranging from electrochemical[2] or chemical[3] (*e.g.* $S_2O_8^{2-}$) oxidation in aqueous solutions or emulsions, to the use recently[4] of the strong electron acceptor 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in an organic solvent. The chiral emeraldine salt products can be obtained as either films or nanodispersions.

It has been suggested[2a,b,3b,4b] that the optical activity of the chiral PAn·HCSA materials arises from individual polyaniline chains preferentially adopting a one-handed helical screw (depending on the hand of CSA^- employed), with chiral induction being due to specific electrostatic and hydrogen bonding between the PAn chains and the enantiomeric dopant CSA^- anions. Alternatively, as has been elegantly shown for chiral polythiophenes,[5] the observed optical activity may arise from the formation of aggregates in which the chiral dopant anion induces a predominantly one-handed helical packing of essentially planar polyaniline chains into a chiral superstructure.

We wish now to report a novel and potentially widely applicable route to optically active polyanilines generated *via* polymerisation from achiral reagents, using a chiral emeraldine salt as platform. This discovery arose during a wider program exploring the factors controlling the electrochemical synthesis of chiral polyanilines, in which we speculated whether an initially deposited thin film of optically active PAn·(+)-HCSA may exert asymmetric induction during the subsequent electrochemical polymerisation of aniline in the presence of racemic (±)-HCSA. This was indeed found to be the case. A thin film of PAn·(+)-HCSA was electrochemically deposited at room temperature onto an ITO-glass electrode from aqueous aniline (0.20 M) in 1.0 M (+)-HCSA, using an applied potential of 0.9 V (*vs* Ag/AgCl) and passing 25 mC cm^{-2} charge. Using the approach previously described by Stejskal *et al.*[6] this corresponds to a film thickness of *ca.* 100 nm. After washing with methanol to remove unreacted reagents, its CD spectrum (Fig. 1b) exhibited weak bands at *ca.* 440 and 700 nm associated with absorption bands seen in this region (Fig. 1a). The film was then placed in fresh aqueous aniline in the presence of racemic (±)-HCSA (1.0 M) and the electropolymerisation continued while passing a further 100 mC cm^{-2} charge. The emeraldine salt film grew considerably thicker, as shown by the increase in intensity of the absorption bands in Fig. 1a. Remarkably, the CD bands for the film were also observed to increase strongly in intensity (Fig. 1b), despite the fact that the dopant acid present during the second aniline polymerisation was racemic HCSA.

Related studies were subsequently carried out in which the second electropolymerisation was performed in a range of achiral acids such as HCl and *p*-toluenesulfonic acid (PTSA). As illustrated in Figs. 2 and 3, similar marked induction of optical activity was observed for the PAn·HCl and PAn·PTSA films grown respectively on top of the thin initial PAn·(+)-HCSA film. Replacement of both the (+)-CSA^- and chloride dopant anions in such a composite PAn·(+)-HCSA/HCl film by HSO_4^- *via* subsequent redox cycling (between potentials of −0.3 and +0.9 V) gave a PAn·HSO_4 film with similar optical activity. The initial chiral PAn·(+)-HCSA therefore appears to behave as a macromolecular asymmetric platform, inducing new polyaniline chains growing from it to preferentially adopt the same helical hand (molecular or supermolecular) as itself, irrespective of the nature of the dopant anion (A^-) being incorporated.

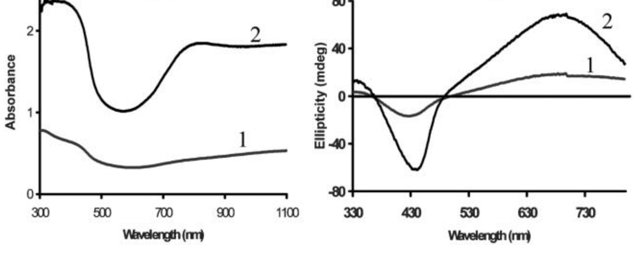


Fig. 1 UV-vis (a) and CD spectra (b) of: (1) a PAn·(+)HCSA film deposited on ITO-glass at 0.9 V (25 mC cm^{-2} passed), and (2) after depositing a further PAn·(±)-HCSA film (another 100 mC cm^{-2} passed).

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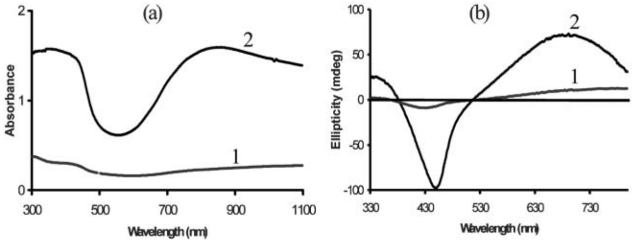

Fig. 2 UV-vis (a) and CD spectra (b) of: (1) a PAn·(+)HCSA film deposited on ITO-glass at 0.9 V (25 mC cm^{-2} passed), and (2) after depositing a further PAn·HCl film (another 100 mC cm^{-2} passed).

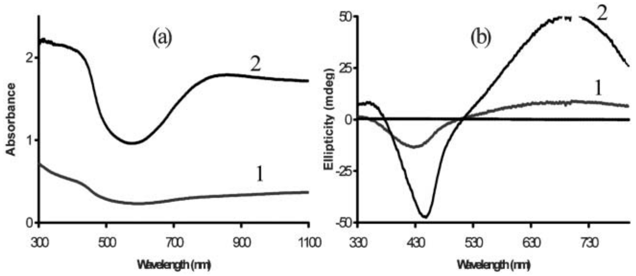

Fig. 3 UV-vis (a) and CD spectra (b) of: (1) a PAn·(+)HCSA film deposited on ITO-glass at 0.9 V (25 mC cm^{-2} passed), and (2) after depositing a further PAn·PTSA film (another 100 mC cm^{-2} passed).

This hypothesis was further tested by performing similar experiments in which the opposite hand of camphorsulfonic acid, namely (1*R*)-(−)-HCSA, was employed to grow initial thin films of PAn·(−)-HCSA (25 mC cm^{-2} charge passed). PAn·(±)-HCSA and PAn·HCl films subsequently electrodeposited (100 mC cm^{-2} charge passed) upon these thin PAn·(−)-HCSA films exhibited mirror imaged CD spectra (*e.g.* Fig. 4) to those grown on PAn·(+)-HCSA surfaces.

A series of other experiments was performed in which PAn·HCl films of increasing thickness were grown upon a thin PAn·(+)-HCSA film by carrying out subsequent electropolymerisation in 1.0 M HCl using deposition charges varying between 50 and 300 mC cm^{-2}. The optical activity of the final emeraldine salts (estimated from the intensity of their 440 nm CD bands) was found to increase linearly with increasing film deposition charge, as seen from the plot in Fig. 5. This indicates that chiral induction by the initial PAn·(+)-HCSA extends undiminished for deposition of PAn·HA films varying in thickness between *ca.* 100 and 800 nm (based[6] on the intensity of their 400 nm absorption bands). It is also significant to note that the CD spectrum of the thickest composite PAn·(+)-HCSA/PAn·HCl film was very similar in intensity to that of a PAn·(+)-HCSA film deposited by electropolymerising aniline in 1.0 M (+)-HCSA while passing 325 mC cm^{-2} charge (Fig. 5). Both films exhibited ellipticities of *ca.* 300 mdeg for their 440 nm CD band, despite the fact that the dopant anion in the composite film was predominantly (>90%) achiral Cl^- ions.

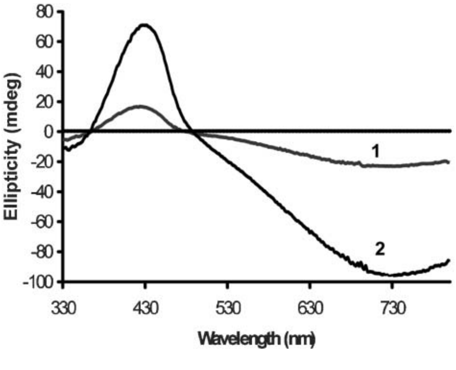

Fig. 4 CD spectra of: (1) a PAn·(−)-HCSA film deposited on ITO-glass at 0.9 V (25 mC cm^{-2} passed), and (2) after depositing a further PAn·HCl film (another 100 mC cm^{-2} passed).

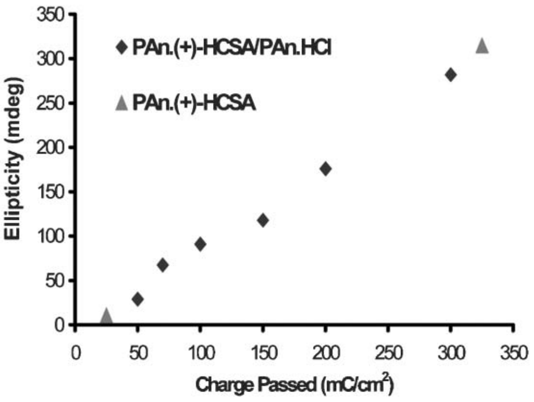

Fig. 5 Dependence of the optical activity of emeraldine salt films on the deposition charge employed. Each point is the average of duplicate experiments.

The origin of this remarkable macromolecular asymmetric induction is presently uncertain. Interestingly, Samuelson *et al.*[7] have recently 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[2] and chemical[3] polymerisation 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. Our observations may also be compared to the asymmetric polymerisation of achiral alkylisocyanate monomers to give optically active polyalkylisocyanates (-[OCNR]$_n$-), using optically active anionic metal complexes as catalysts.[8] The presence of the chiral initiator on a chain terminus was believed to induce a single-screw sense on the growing poly(alkylisocyante) chains.

We have also considered the possibility that the (+)-CSA^- anion in the thin initial PAn·(+)-HCSA films could reversibly exchange on the polyaniline surface during further polymerisation 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[9] and poly(alkylthiophene)s.[10] This latter mechanism appears highly unlikely on two counts: (i) the maximum possible concentration of (+)-CSA^- in the second-stage polymerisation medium is extremely low compared to the racemic CSA^- or achiral anion (1.0 M); (ii) in recent studies[11] we have observed only a small degree of chiral amplification in the electrochemical synthesis of PAn·HCSA salts (*e.g.* the observed optical activity of emeraldine salt films grown in the presence of 2% (+)-HCSA/ 98% w/v (±)-HCSA was *ca.* 1/50 the intensity of an analogous film grown in 100% (+)-HCSA).

Further studies are underway to further elucidate the mechanism of this unprecedented asymmetric proliferation process and to extend its potential applications. This discovery should enable the electrosynthesis of a wide range of optically active polyanilines without the requirement for optically active active CSA^- in the outer layers. One can imagine, for example, electrocatalytic centres such as ferrocenes or porphyrins being incorporated as the dopant in a chiral polymer environment.

Notes and references

1 J. Huang, V. M. Egan, H. Guo, J.-Y. Yoon, A. L. Briseno, I. E. Rauda, R. L. Garrell, C. M. Knobler, F. Zhou and B. Kaner, *Adv. Mater.*, 2003, **15**, 1158–1161 and references therein.

2 (*a*) M. R. Majidi, L. A. P. Kane-Maguire and G. G. Wallace, *Polymer*, 1994, **35**, 3113–3116; (*b*) M. R. Majidi, L. A. P. Kane-Maguire and G. G. Wallace, *Aust. J. Chem.*, 1998, **51**, 23–30; (*c*) P. C. Innis, I. D. Norris, L. A. P. Kane-Maguire and G. G. Wallace, *Macromolecules*, 1998, **31**, 6521–6528; (*d*) I. D. Norris, L. A. P. Kane-Maguire and G. G. Wallace, *Macromolecules*, 2000, **33**, 3237–3243.

3 (*a*) L. A. P. Kane-Maguire, A. G. MacDiarmid, I. D. Norris, G. G. Wallace and W. Zheng, *Synth. Met.*, 1999, **106**, 171–176; (*b*) G.-L. Yuan and N. Kuramoto, *Macromolecules*, 2002, **35**, 9773–9779; (*c*) W. Li, P. A. McCarthy, D. Liu, J. Huang, S.-C. Yang and H.-L. Wang, *Macromolecules*, 2002, **35**, 9975–9982; (*d*) P. A. McCarthy, J. Huang, S.-C. Yang and H.-L. Wang, *Langmuir*, 2002, **18**, 259–263; (*e*) Y. Yang and M. Wan, *J. Mater. Chem.*, 2002, **12**, 897–901; W. Li, D. E. Hooks, P. Chiarelli, Y. Jiang, H. Xu and H.-L. Wang, *Langmuir*, 2003, **19**, 4639–4644.

4 (*a*) S.-J. Su and N. Kuramoto, *Macromolecules*, 2001, **34**, 7249–7256; (*b*) S.-J. Su and N. Kuramoto, *Chem. Mater.*, 2001, **13**, 4787; (*c*) S.-J. Su, M. Takeishi and N. Kuramoto, *Macromolecules*, 2002, **35**, 5752–5757.

5 (*a*) M. M. Bouman, E. E. Havinga, R. A. J. Janssen and E. W. Meijer, *Mol. Cryst. Liq. Cryst.*, 1994, **256**, 439–448; (*b*) M. M. Bouman and E. W. Meijer, *Adv. Mater.*, 1995, **7**, 385–387; (*c*) B. M. W. Langeveld-Voss, E. Peters, R. A. J. Janssen and E. W. Meijer, *Synth. Met.*, 1997, **84**, 611–614; (*d*) B. M. W. Langeveld-Voss, R. A. J. Janssen and E. W. Meijer, *J. Mol. Struct.*, 2000, **521**, 285–301.

6 J. Stejskal, I. Sapurina, J. Prokes and J. Zemek, *Synth. Met.*, 1999, **105**, 195–202.

7 M. Thiyagarajan, L. A. Samuelson, J. Kumar and A. L. Cholli, *J. Am. Chem. Soc.*, 2003, **125**, 11502–11503.

8 (*a*) K. Maeda, M. Matsuda, T. Nakano and Y. Okamoto, *Polym. J.*, 1995, **2**, 141–146; (*b*) K. Maeda and Y. Okamoto, *Polym. J.*, 1998, **30**, 100.

9 S. K. Jha, K. Cheon, M. M. Green and J. V. Selinger, *J. Am. Chem. Soc.*, 1999, **121**, 1665–1673; M. M. Green, J.-W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger and J. V. Selinger, *Angew. Chem. Int. Ed.*, 1999, **38**, 3138–3154 and references therein.

10 B. M. W. Langeveld-Voss, R. J. M. Waterval, R. A. J. Janssen and E. W. Meijer, *Macromolecules*, 1999, **32**, 227–230.

11 Y. Pornputtkul, L. A. P. Kane-Maguire and G. G. Wallace, unpublished results.