Articles

Influence of Electrochemical Polymerization Temperature on the Chiroptical Properties of (+)-Camphorsulfonic Acid-Doped Polyaniline

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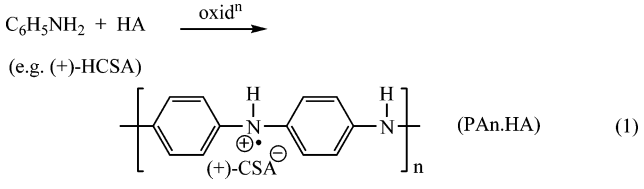
ABSTRACT: The chiroptical properties of electrochemically deposited emeraldine salt PAn·(+)-HCSA (HCSA = 10-camphorsulfonic acid) films have been found to vary markedly with the temperature employed during polymerization. The circular dichroism spectra of such films grown at >40 °C are inverted compared to the spectra of analogous films deposited at temperatures ≤25 °C, indicating an inversion of conformation for the polyaniline chains. These observations are rationalized in terms of a temperature-induced interconversion between the two diastereomeric emeraldine salt products from the doping of the growing polyaniline chains by the chiral (+)-CSA^- anion. The marked temperature dependence of the diastereoselectivity highlights the importance of employing a fixed temperature during the electrosynthesis of optically active polyanilines.

Introduction

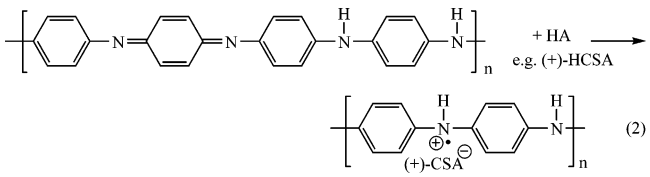
There has been considerable recent interest in optically active polyanilines (PAn's) because of their potential applications in areas such as chiral sensors, electrochemical asymmetric synthesis, and chiral separations.[1] Apart from one example[2] involving the covalent attachment of a chiral substituent to amine nitrogen centers on aniline repeat units, optical activity has been generally induced into polyaniline emeraldine salts (PAn·HA) via the incorporation of chiral dopant anions (A^-) at radical cation nitrogen sites along the polymer chains.[3−6] Two distinct routes have been employed:

(i) Incorporation of the chiral dopant anion during the oxidative polymerization of aniline and substituted anilines in the presence of a chiral acid HA (eq 1). A range of polymerization methods have been successfully employed, ranging from electrochemical[3] or chemical[4] (e.g., $S_2O_8^{2-}$) oxidation in aqueous solutions or emulsions to the use recently[5] 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.



(1)

(ii) Acid-doping of preformed emeraldine base with a chiral acid in an organic solvent (eq 2).[6] The most commonly used acid to date has been (1*S*)-(+)- or (1*R*)-(−)-10-camphorsulfonic acid (HCSA), leading to optically active solutions of the PAn·HCSA salts from which chiral polymer films can be readily cast.



(2)

It has been suggested[3,5,6b] 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,[7] 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 PAn chains into a chiral superstructure.

Circular dichroism (CD) spectroscopy has proved a valuable tool for probing the three-dimensional structures adopted by polyanilines in optically active emeraldine salts. It was used, for example, to show[8] unequivocally that PAn·(+)-HCSA films produced via electrochemical polymerization have different structures to those obtained by acid-doping of preformed emeraldine base. The CD spectra for the two types of films were markedly different (but not mirror-imaged) and were attributed to "extended coil" and "compact coil" conformations, respectively. The sensitivity of polyaniline structures to their synthesis conditions has been further demonstrated by the very

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different CD spectra observed for PAn·(+)-HCSA salts (and ring-substituted analogues) prepared using the electron acceptor DDQ[5] for polymerization compared to the spectra of related electrochemically grown[3a,b,f] emeraldine salts. Other recent CD studies[9,10] have shown that the chiroptical properties, and hence polymer chain structures, of optically active PAn·(+)-HCSA salts prepared by acid-doping emeraldine base in organic solvents are also critically dependent on the water content of the EB solution prior to adding the (+)-HCSA dopant.

Our ability to manipulate and exploit the properties of conducting polymers such as polyaniline at the nanodimension will increasingly depend on our ability to generate them in predetermined and predictable three-dimensional configurations/conformations. Central to achieving these goals will be acquiring a detailed understanding of the influence of polymer synthesis conditions upon the structural and electronic properties of the polymeric products. As part of a program addressing this question, the present paper provides the first study of the influence of polymerization temperature on the chiroptical properties of electrochemically produced polyaniline emeraldine salts.

The circular dichroism spectra of electrochemically deposited PAn·(+)-HCSA films are found to be remarkably dependent on the temperature employed during polymerization. Films grown at 40−65 °C exhibit mirror-imaged CD spectra compared to those deposited at 0−25 °C, indicating inversion of molecular or supermolecular conformation/configuration for the polyanilines growing at the higher temperatures. A possible origin for this remarkable inversion is proposed. It clearly has significant implications for the electrosynthesis of optically active polyanilines to be used in applications such as electrochemical asymmetric synthesis and chiral sensors.

Experimental Section

Materials. Aniline (Aldrich) was distilled and stored under nitrogen prior to use. (1*S*)-(+)-10-Camphorsulfonic acid (HCSA) was purchased in the purest form available from Aldrich Chemical Co. and used as supplied. Milli-Q water was employed for the preparation of all aqueous solutions. Indium tin oxide (ITO)-coated glass was purchased from Delta Technology. It was sputter-coated with platinum at 30 mA for 5 s in order to obtain uniform and strongly adhering polyaniline emeraldine salt films in the subsequent aniline electropolymerizations.

Preparation of PAn·(+)-HCSA Films. Electrochemical polymerizations were carried out in a one-compartment cell using a three-electrode configuration and a BAS CV-27 potentiostat. ITO-coated glass, sputter-coated with Pt, was employed as the working electrode (3 cm^2), while Pt-mesh and $Ag/AgCl_{(3M\ NaCl)}$ were used as auxiliary and reference electrodes, respectively. The PAn·(+)-HCSA films were potentiostatically deposited from aqueous 0.20 M aniline containing 1.0 M (+)-HCSA using an applied potential of +0.9 V and passing 120 mC/cm^2 of charge. The polymerization temperature was maintained (±0.5 °C) using a thermostated water bath.

UV−Vis and CD Spectra of Films. After electrodeposition, the PAn·(+)-HCSA films were washed with methanol to remove oligomers, excess monomer, and unincorporated (+)-HCSA. Their UV−vis (300−1100 nm) and UV−vis-NIR (300−3000 nm) spectra were then recorded using a Shimadzu UV-1601 and a Cary 500 spectrophotometer, respectively. CD spectra (330−800 nm) spectra were measured with a Jobin-Yvon Dichrograph 6.

Scanning Electron Microscopy. The surface morphology of the PAn·(+)-HCSA films electrodeposited at temperatures between 0 and 65 °C was assessed with a Leica Cambridge 440 scanning electron microscope. The polymer films were washed with methanol and coated with a thin layer of gold to improve resolution.

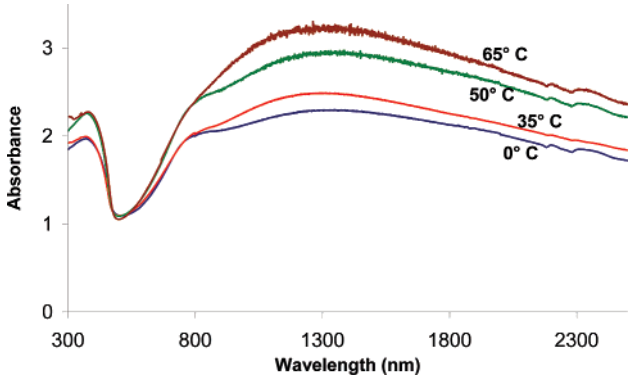


Figure 1. UV−vis-near-IR spectra of PAn·(+)-HCSA films electrochemically deposited at 0, 35, 50, and 65 °C.

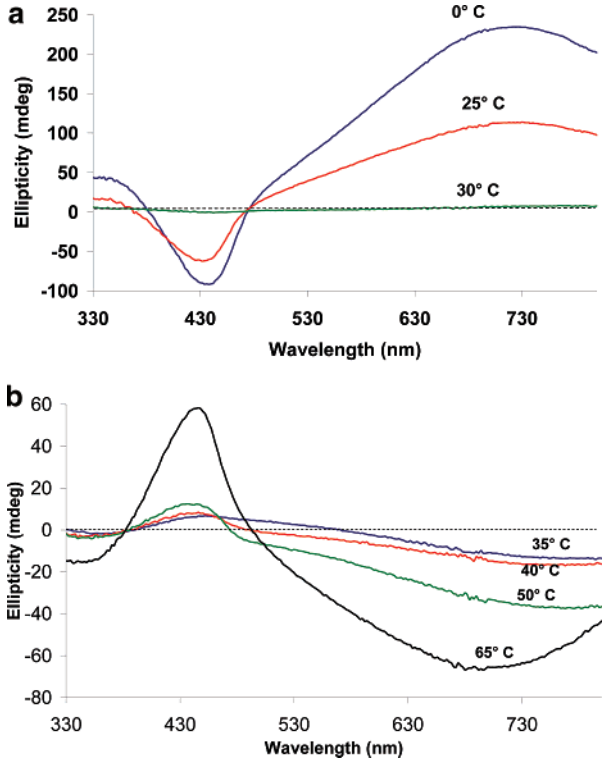


Figure 2. CD spectra of PAn·(+)-HCSA films electrochemically deposited at (a) 0, 25, and 30 °C and at (b) 35, 40, 50, and 65 °C.

Postpolymerization Heat Treatment of a PAn·(+)-HCSA Film. A PAn·(+)-HCSA film grown at room temperature (20−25 °C) was heated at 45 °C in 1.0 M (+)-HSCA for $1^1/_2$ h, and its UV−vis and CD spectra were recorded again. Another PAn·(+)-HCSA film was heated for successive 30 min periods in an air oven at 70 °C and then 100 °C. The UV−vis and CD spectra were recorded at each stage after cooling to room temperature.

pH Switching of a PAn·(+)-HCSA Film. A PAn·(+)-HCSA film deposited at 65 °C was dedoped to the emeraldine base (EB) form by immersing in aqueous 1.0 M NH_4OH for 1 h. After recording its UV−vis and CD spectra, it was redoped to PAn·HCl by treatment with 1.0 M HCl for 1 h. This dedoping/redoping cycle was then repeated. The UV−vis and CD spectra of the polyaniline film were recorded at each stage of the base/acid treatments.

Results and Discussion

Influence of Polymerization Temperature on Chiroptical Properties of PAn·(+)-HCSA Salts. Previous temperature dependence studies on aniline polymerization have mostly concerned chemical polymerization, where ammonium persulfate was typically employed as oxidant in the presence of an

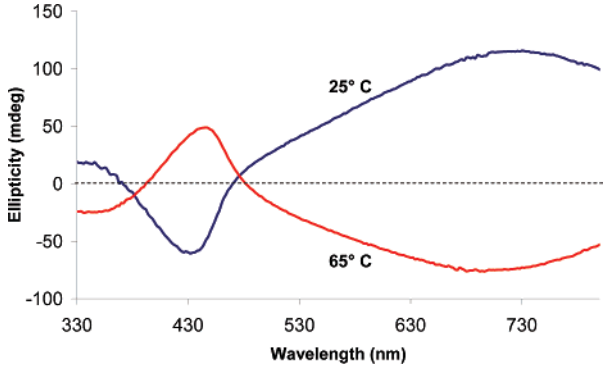


Figure 3. Comparison of the CD spectra for PAn·(+)-HCSA films electrochemically grown at 25 and 65 °C.

acid such as HCl. The use of low temperatures (≤0°C) during such chemical polymerizations was found[11−13] to favor the formation of high molecular weight emeraldine (PAn·HA) salts. However, the products were obtained as powders, and consequently no direct UV−vis spectroscopic evidence was obtained concerning the conformation adopted by the polyaniline chains.

Limited studies into the effect of temperature on the electropolymerization of aniline have been carried out.[14] In these studies it has been shown that the molecular weight does not change significantly over the temperature range of interest here.

In contrast, the electrochemical polymerization of aniline in aqueous acid (HA) leads to the deposition of thin PAn·HA films on the working electrode. Using ITO-coated glass as the electrode, UV−vis spectra can be readily obtained for the electrodeposited emeraldine salt films, providing useful information concerning the polymer chain arrangements. In one of the few studies to date on the influence of polymerization temperature on the properties of electrodeposited polyanilines, Wan reported[15] that the UV−vis spectra of galvanostatically generated emeraldine salt films was independent of the temperature employed, suggesting little influence on the polymer chain conformation.

Circular dichroism (CD) spectroscopy has been recently shown to provide a powerful probe for polyaniline chain (or supermolecular) structures.[3b,5b,8] The present paper exploits this technique in combination with UV−vis-NIR studies to explore for the first time the influence of polymerization temperature on the chiroptical properties (and hence chain conformations) of electrochemically deposited polyaniline emeraldine salts. Optically active PAn·(+)-HCSA films were grown at different temperatures using an applied potential of 0.9 V (vs Ag/AgCl), while passing 120 mC/cm^2 charge in order to obtain films of constant thickness. As expected, the rate of electrochemical deposition of the PAn·(+)-HCSA films increased with increasing polymerization temperature. For example, to achieve 120 mC/cm^2 deposition charge, polymerization times at 0, 25, and 65 °C were ca. 5, 2, and 1 min, respectively.

The UV−vis-NIR spectra of the electrochemically deposited PAn·(+)-HCSA films showed little dependence on the temper-

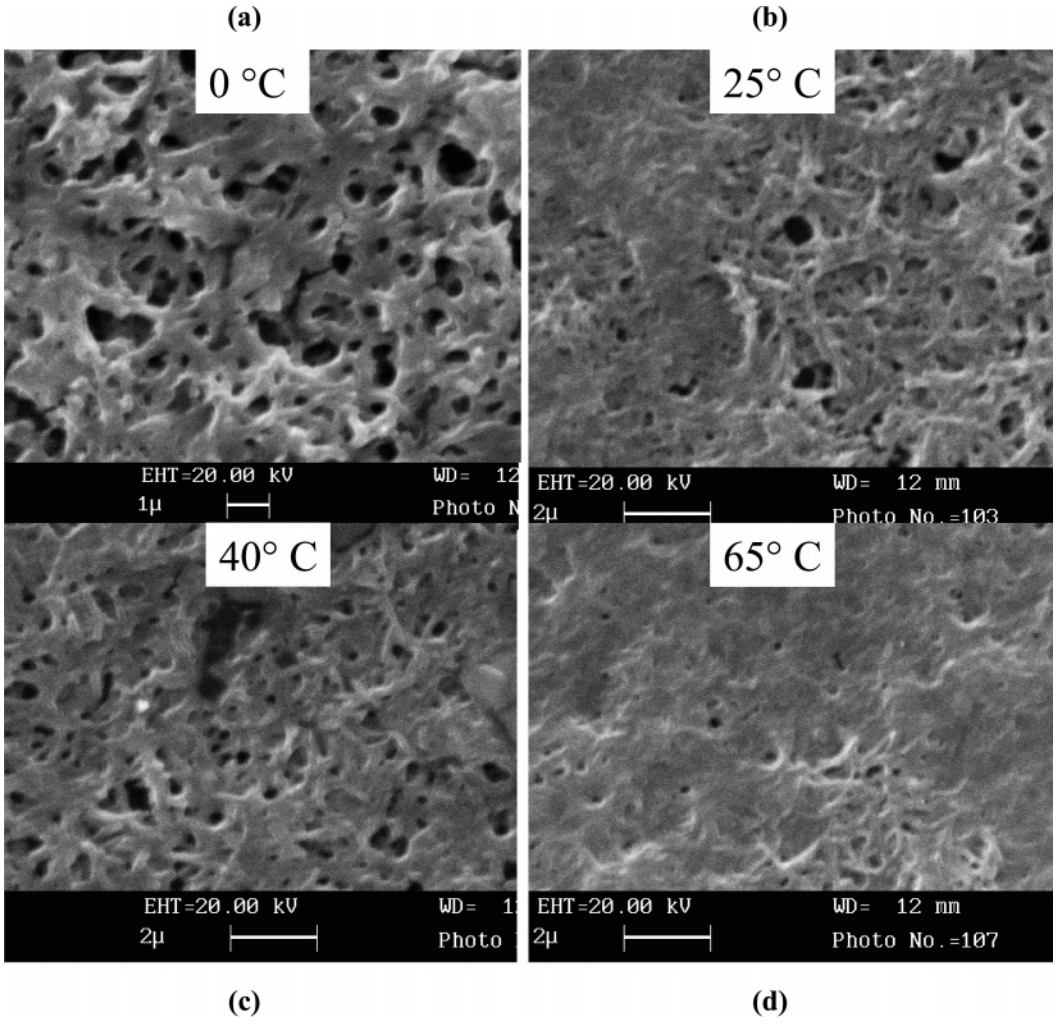


Figure 4. Scanning electron micrographs of PAn·(+)-HCSA films electrosynthesized at (a) 0, (b) 25, (c) 40, and (d) 65 °C.

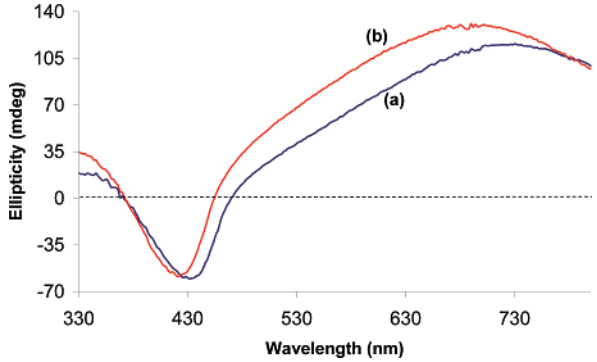


Figure 5. CD spectra of (a) an electrochemically deposited PAn·(+)-HCSA film at room temperature (25 °C) and (b) after heat treatment at 45 °C in 1.0 M (+)-HCSA for 1.5 h.

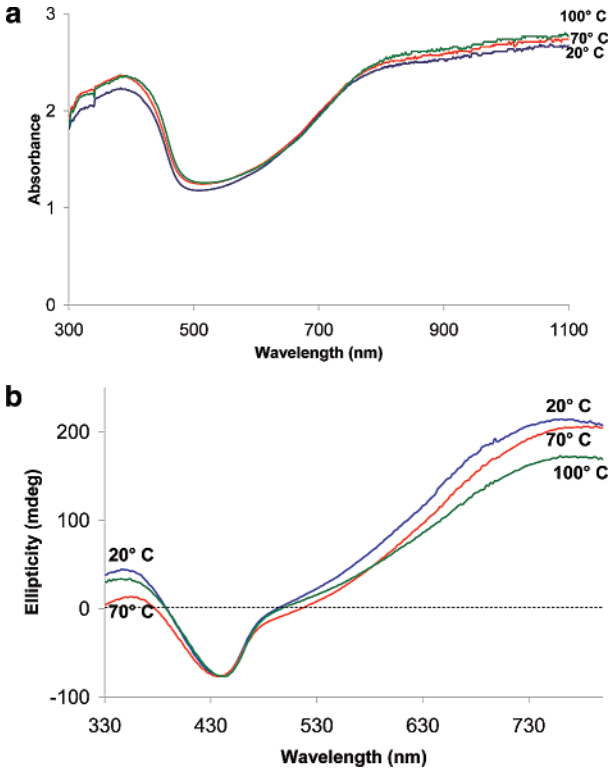
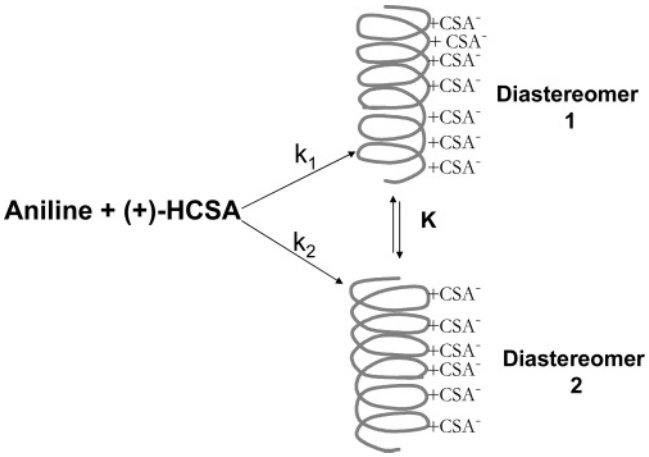


Figure 6. (a) UV−vis and (b) CD spectra of a PAn·(+)-HCSA film: (i) as electrochemically deposited at 20 °C, (ii) after heating at 70 °C for 30 min, and (iii) after further heating at 100 °C for 30 min.

ature employed during the electropolymerization. For example, Figure 1 shows the absorption spectra for the chiral emeraldine salts grown at 0, 35, 50, and 65 °C. Each film exhibited a strong band at ca. 390 nm, a weak shoulder at ca. 800 nm, and an intense broad band in the near-infrared (with λ_{max} ca. 1300 nm). These spectroscopic features are characteristic of emeraldine salts in which the polyaniline chains adopt a largely "extended coil" conformation.[16] The only changes caused by increasing the electropolymerization temperature from 0 to 65 °C were a decrease in the intensity of the weak shoulder at 800 nm and an increase in the relative intensity of the 1300 nm peak compared to the 390 nm band. These changes are consistent with further enhancement of the "extended coil" conformation for the polyaniline chains with increasing temperature.

In contrast to the UV−vis spectra, the corresponding CD spectra of the PAn·(+)-HCSA films revealed marked differences with polymerization temperature. In Figure 2a, the emeraldine salt films grown at 0 and 25 °C are seen to exhibit a bisignate CD band (positive and negative signals at ca. 350 and 440 nm)

Scheme 1



associated with the absorption band centered at 390 nm as well as a broad CD band at ca. 700 nm. This latter CD band is believed to be the low wavelength component of the expected bisignate CD signals associated with the very broad absorption band centered at ca. 1300 nm. These CD spectra were qualitatively similar to that previously reported[3a,b] for PAn·(+)-HCSA electrodeposited at room temperature. However, the CD bands for the PAn·(+)-HCSA film deposited at 0 °C were considerably more intense than those for the film grown at 25 °C (Figure 2a), indicating higher diastereoselectivity during electrodeposition at the lower temperature. (This may also be partly attributed to more regular head-to-tail coupling of the polyaniline chains during electropolymerization at 0 °C, with fewer faults such as ortho-coupling interfering with the adoption of regular predominantly one-handed helical chains.)

Remarkable changes occurred for the CD spectra of the PAn·(+)-HCSA films electrochemically deposited at higher temperatures. The CD bands for the 30 °C sample were very weak in intensity (Figure 2a and inset), although qualitatively still similar to the films grown at 0−25 °C. Weak CD signals were again observed for a PAn·(+)-HCSA film grown at 40 °C, but they were inverted in sign (Figure 2b). The intensity of these inverted CD signals increased progressively for emeraldine salts deposited at 50 and 65 °C (Figure 2b). Comparison of the CD spectra for the 25 and 65 °C films (Figure 3) shows them to be mirror-imaged. Assuming, as suggested previously,[3a,b,6b] that the visible region optical activity observed for these emeraldine salts arises from the presence of predominantly one-handed helical PAn chains, this inversion of their CD spectra with change in polymerization temperature indicates an inversion of the favored helical conformation.

As far as we are aware, these observations represent the first example of temperature-induced helix inversion *during* the synthesis of a conducting organic polymer. However, inversion of polymer CD spectra via *postsynthesis* heating or cooling has recently been reported[7a,b] for some chiral polythiophenes, where the optical activity was believed to arise from helical superstructures of aggregated polythiophene chains. Similar temperature-induced helix reversal has also been recently reported for synthetic DNA,[17] poly(L-aspartic acid ester)s,[18] poly(isocyanate)s,[19] polyacetylenes,[20] and polysilanes[21] where the energy barrier to helix−helix interconversion is relatively low. These temperature-sensitive, chiral polymers have generated considerable recent interest because of their potential applications as molecular switches or for data storage.

The helix reversal during the electrochemical growth of PAn·(+)-HCSA films at temperatures ≥35 °C does not affect their

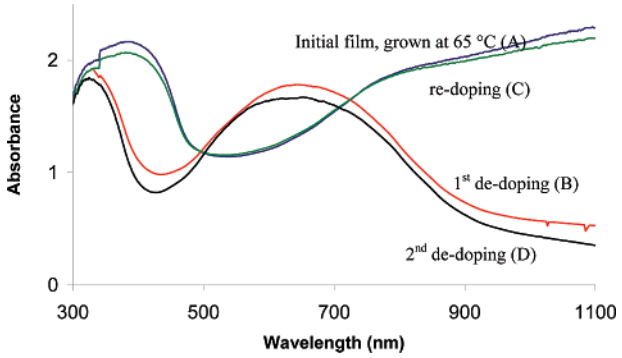


Figure 7. UV−vis spectra of (A) a PAn·(+)-HCSA film electrochemically deposited at 65 °C, (B) after dedoping with 1.0 M NH_4OH, (C) after redoping with 1.0 M HCl, and (D) after again dedoping with 1.0 M NH_4OH.

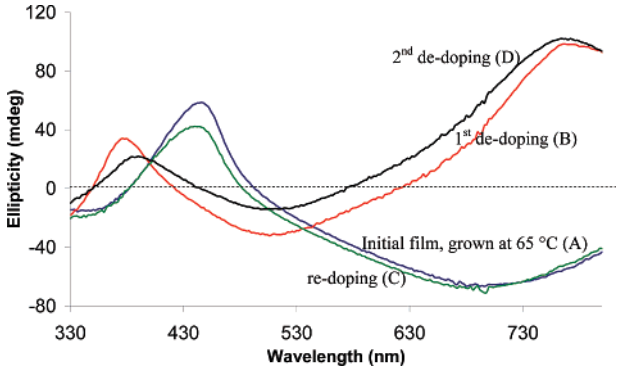


Figure 8. CD spectra of (A) a PAn·(+)-HCSA film electrochemically deposited at 65 °C, (B) after dedoping with 1.0 M NH_4OH, (C) after redoping with 1.0 M HCl, and (D) after again dedoping with 1.0 M NH_4OH.

morphology. As seen in Figure 4a−d, scanning electron micrographs for the PAn·(+)-HCSA films grown over the temperature range 0−65 °C revealed similar fibrous morphologies in each case. They also exhibit similar chemical reactivities, as revealed by studies (vide infra) of their behavior toward pH switching.

The remarkable temperature effects on the conformation of electrochemically grown PAn·(+)-HCSA emeraldine salts have important implications for researchers wishing to synthesize optically active polyanilines for use in applications such as chiral separations and electrochemical asymmetric synthesis. The different room temperatures experienced in laboratories around the world would lead to such PAn·(+)-HCSA emeraldine salts grown in tropical/subtropical areas having the opposite visible region chiroptical properties to those grown in temperate regions (temperature ≤ 25 °C). Should the laboratory temperature be 33 °C, the researcher would obtain an apparently racemic polyaniline product, as we have confirmed by carrying out the electropolymerization at this temperature.

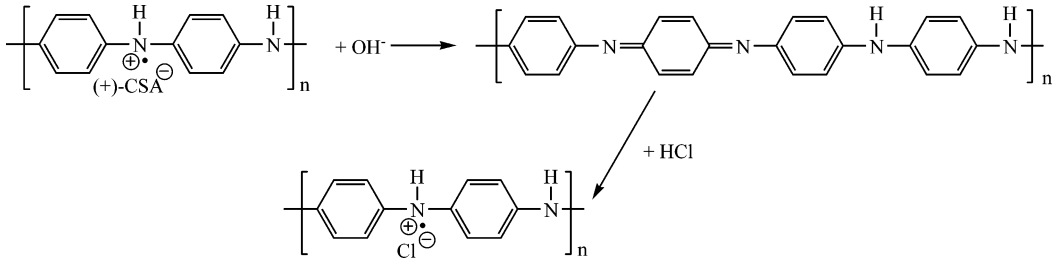
Origin of the Temperature-Dependent Chiral Discrimination. A priori, the preferred hand of the chiral emeraldine salt product from electropolymerization may be determined either prior or after deposition upon the ITO-glass working electrode. To distinguish between these two possibilities, a film of optically active PAn·(+)-HCSA that had been electrochemically deposited at 25 °C was subsequently heated at 45 °C in aqueous 1.0 M (+)-HCSA for 1.5 h. No significant changes were observed in its UV−vis or CD spectra after this heat treatment (e.g., Figure 5). In a further experiment, a film of PAn·(+)-HCSA electrochemically deposited at 20 °C was heated in an oven to 70 °C for 30 min. This caused no change to either its UV−vis or CD spectra, which remained constant even after further heating to 100 °C for 30 min (Figure 6). These observations establish that the conformation of the polyaniline chains in PAn·(+)-HCSA emeraldine salts cannot be inverted by heat treatment after electrodeposition. The chiral discrimination in the electrosynthesis giving rise to the observed optically active emeraldine salt products must therefore occur during the polymer growth prior to deposition on the working electrode.

The inverted CD spectra obtained here for chiral PAn·(+)-HCSA films grown at different temperatures may be explained in terms of the formation and interconversion of the two diastereomeric emeraldine salt products **1** and **2** shown in Scheme 1. These diastereomers possess inverted helices (P and M, respectively) for their polyaniline chains, while sharing a common *S*-configuration for the dopant (+)-CSA^- anions that are electrostatically bound to radical cation nitrogen sites along the polymer backbone. Their CD spectra in the visible region recorded (330−800 nm) should therefore appear mirror-imaged (as observed) due to their enantiomeric helical chains, since the chiral (+)-CSA^- dopant anions only exhibit CD bands in the UV region (at 193 and 290 nm).

Kinetic discrimination in the attachment of the (+)-CSA^- anions to the growing polyaniline chains would lead to an initial preponderance of one of the diastereomers, depending on the relative magnitudes of the two rate constants k_1 and k_2 in Scheme 1. However, a relatively low energy barrier to helix−helix (P−M) interconversion is expected for the flexible chains of unsubstituted polyanilines (vide infra), leading to facile interconversion of diastereomers **1** and **2** via equilibrium *K* in Scheme 1. Thus, the observed diastereoselection in aniline electropolymerization may be thermodynamically controlled, with the ratio of diastereomeric products **1** and **2** being determined by the magnitude of the equilibrium constant *K*. A strong temperature dependence for the position of equilibrium *K* would consequently provide a likely rationale for the remarkable temperature effects observed here for electrosynthesis of chiral PAn·(+)-HCSA salts.

The above rationale assumes a molecular origin for the optical activity observed in chiral polyanilines (arising from a one-handed helicity of individual polyaniline chains). Alternatively, as has been elegantly demonstrated for chiral polythiophenes,[7] the optical activity may have a supermolecular basis involving a predominantly one-handed packing of essentially planar polyaniline chains. Should the latter be the case, a similar

Scheme 2



explanation for the observed temperature effects could be envisaged in which the two diastereomeric emeraldine salt products **1** and **2** are supermolecular helices of opposite hand.

The possibility that the inverted CD spectra found for the PAn·(+)-HCSA films grown at low (0−20 °C) and high (40−65 °C) temperatures may arise from polyanilines of different MWt being deposited is considered extremely unlikely. Mattoso et al.[14] have shown that varying the polymerization temperature over the range studied here has only a small effect on the MWt of electrodesposited emeraldine salts. In addition, we have found that PAn·(+)-HCSA salts formed by doping emeraldine bases of widely different MWts all exhibit CD spectra of the same sign.[22]

pH Switching of PAn·(+)-HCSA Salts Electrosynthesized at High Temperature. It has been recently shown[3b,23] that chiral PAn·(+)-HCSA salts prepared at room temperature undergo pH switching cycles with retention of conformation/configuration for their polyaniline chains. Similar pH switching experiments have now been carried out on PAn·(+)-HCSA films electrochemically grown at 65 or 70 °C to determine whether the chemical reactivity of such chiral emeraldine salts is affected by the higher temperature employed in their electrodeposition.

Alkaline (1.0 M aqueous NH_4OH) dedoping of a PAn·(+)-HCSA film electrochemically deposited at 65 °C generated a blue film exhibiting absorption bands at ca. 330 and 640 nm characteristic[24] of the anticipated emeraldine base (EB) (Figure 7b). The film was strongly optically active, showing CD bands at ca. 380, 510, and 760 nm (Figure 8b). The two higher wavelength CD bands are assigned as a bisignate pair associated with the absorption band at 640 nm, while the CD band at 380 nm is believed to be the high-wavelength component of a bisignate signal associated with the UV−vis band at 330 nm. The CD bands in Figure 8b are opposite in sign to those previously reported[3b,21] for EB films generated by dedoping PAn·(+)-HCSA grown at room temperature. This again supports the helix reversal proposed above for PAn·(+)-HCSA emeraldine salts electrochemically grown at elevated temperatures (≥35 °C).

Redoping the EB film with aqueous 1.0 M HCl regenerated the emeraldine salt form (as PAn·HCl), as shown by the characteristic UV−vis spectrum in Figure 7c (λ_{max} ca. 390 nm, 800 w sh, >1100 nm). The corresponding CD spectrum of the redoped film (CD bands at ca. 340, 445, and 695 nm; Figure 8c) was quantitatively almost identical to that of the PAn·(+)-HCSA film prior to alkaline dedoping. This confirmed retention of the polyaniline chain conformation/configuration during the dedoping/redoping cycle shown in Scheme 2. Further alkaline (1.0 M NH_4OH) dedoping of the regenerated PAn·HCl film produced an emeraldine base film with effectively identical UV−vis and CD spectra (Figure 7d and Figure 8d, respectively) to the EB formed in the initial alkaline dedoping.

The retention of optical activity and polyaniline chain conformation during the repeated release (alkaline dedoping) and reattachment (acid redoping) of the chiral (+)-CSA^- dopant anion presumably arises from constraints in the solid state, preventing rearrangement of the polymer chains. However, dissolution of an optically active emeraldine base film in an organic solvent such as *N*-methylpyrrolidinone resulted in rapid racemization, as evidenced by the loss of all CD signals. This is consistent with the relatively facile helix−helix (P to M) interconversion expected for unsubstituted polyaniline chains, as proposed in the above temperature dependence studies.

Conclusion

The chiroptical properties of electrochemically deposited PAn·(+)-HCSA emeraldine salts are markedly dependent on the temperature employed during polymerization. Films grown at elevated temperatures (35−65 °C) have inverted CD spectra compared to analogous films grown at 0−25 °C, indicating inversion of the molecular or supermolecular conformation/structure of the polyaniline. These observations may be rationalized in terms of a temperature-induced interconversion between the two diastereomeric emeraldine salts formed during the doping of the growing polyaniline chains with the chiral (+)-CSA^- anion. This is facilitated by the relatively low-energy barrier to helix inversion in the unsubstituted polyaniline chains. The marked temperature dependence of the diastereoselectivity highlights the importance of employing a fixed temperature during the electrosynthesis of optically active polyanilines.

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