Thermochromism in Optically Active Polyaniline Salts

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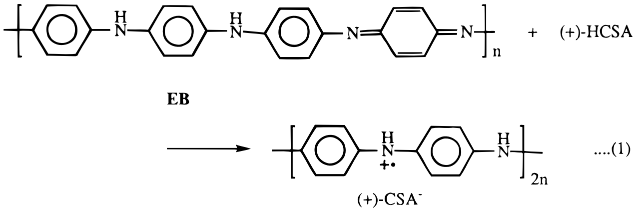
ABSTRACT: Optically active polyaniline salts PAn.(+)-HCSA (HCSA = 10-camphorsulfonic acid) have been shown to have different conformations for their polyaniline chains depending on whether they are synthesized chemically or electrochemically. These conformations are assigned as "compact coil" and partial "expanded coil", respectively. An "expanded" to "compact" coil transformation is induced by heating to 140 °C for 10 min, as evidenced by UV−visible and circular dichroism spectral studies. At temperatures greater than 180 °C, progressive dedoping of the PAn.(+)-HCSA salt films occurs, with the formation of racemic emeraldine base.

Introduction

Thermochromism has been extensively studied in substituted polythiophenes, where heating of films or solutions leads to a marked blue shift of the highest wavelength absorption band.[1−6] These color changes were attributed to a twisting of the polymer backbone from a planar to a less ordered nonplanar conformation. The temperature-dependent circular dichroism (CD) spectra of related chiral polythiophenes have provided[7,8] further insights into the nature of the thermochromism in such systems.

In contrast, there has been little investigation of thermochromism in polyanilines. Several papers have noted a moderate blue shift of the exciton peak of emeraldine base (EB)[9−11] and ring-substituted EB[12] films or solutions upon heating. However, there have been no reports to date of thermochromism in polyaniline salts, PAn.HA (HA = acid). In preliminary studies we observed only minor changes in the color of PAn.HA (HA = sulfonic acids) salts over the temperature range 50−150 °C.[13]

However, the high sensitivity of circular dichroism spectroscopy to molecular conformation changes suggested to us that recently reported[14−17] optically active polyanilines may provide promising substrates for observing and characterizing thermochromism in polyaniline salts. Two facile methods have been described for the production of the optically active salt PAn.(+)-HCSA (HCSA = 10-camphorsulfonic acid) **1**: (i) enantioselective electropolymerization of aniline in the presence of aqueous (+)-HCSA,[14] and (ii) enantioselective doping of EB with (+)-HCSA in a range of organic solvents (eq 1).[15−17] We describe here the temperature dependence (20−240 °C) of the circular dichroism (CD) and UV−visible spectra of films of both the electrochemically and chemically prepared salts **1**. These studies, supported by thermogravimetric analysis measurements, reveal (i) that electrochemically and chemically derived PAn.(+)-HCSA **1** possess different room temperature conformations; (ii) the presence of a thermochromic effect, wherein the conformation of electrochemically deposited **1** is converted at 140 °C to that of the chemically prepared film.



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To our knowledge, this is the first time that different conformations have been unequivocally demonstrated for the polymer chains of electrochemically and chemically prepared polyanilines. The facile thermal interconversion of the polyaniline backbone conformation described here will also have implications in other studies where the physical properties of PAn.HA salts are examined at moderately elevated temperatures (>140 °C).

Experimental Section

Materials. Aniline was purchased from Aldrich Chemical Co. and distilled under dinitrogen prior to use. (1*S*)-(+)-10-camphorsulfonic acid (HCSA) and dimethyl sulfoxide (DMSO) were purchased in the purest grades available from Aldrich Chemical Co. and used as supplied. Indium−tin oxide (ITO) coated glass was obtained from Delta Technology Ltd.

Emeraldine base (EB) was synthesized as previously described.[18]

Electrochemically deposited films of PAn.(+)-HCSA **1a** were obtained on ITO-coated glass using the previously described[14] procedure (applied potential of 1.1 V vs Ag/AgCl; 120 mC cm^{-2} charge passed). Analogous powder samples of **1a** for thermogravimetric and conductivity studies were similarly prepared via electrodeposition on a Pt working electrode using a potential of +0.8 V vs Ag/AgCl. After scraping from the Pt electrode, the powders were dried for several days in a desiccator prior to physical measurements.

A film of chemically derived PAn.(+)-HCSA **1b** was obtained on a glass slide by evaporatively casting from a concentrated solution of the EB and (+)-HCSA in DMSO, as reported previously.[16]

After their room temperature CD and UV−visible spectra were recorded, the above films were exposed for 10 min periods to successively higher temperatures from 50 to 240 °C in an oven under atmospheric conditions. After each 10 min treatment, the films were cooled to room temperature before measuring their CD and UV−visible spectra.

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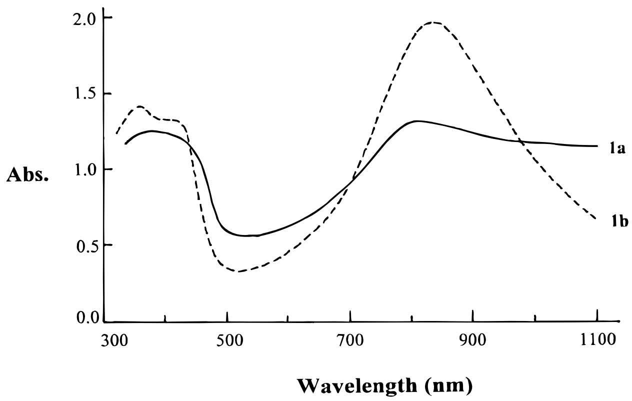

Figure 1. Room-temperature UV−visible spectra of PAn.(+)-HCSA films **1** prepared (a) electrochemically and (b) chemically.

Spectroscopic Studies. CD spectra were recorded between 300 and 700 nm using a Jobin-Yvon Dichrograph 6. UV−visible spectra were measured between 300 and 1100 nm using a Shimadzu UV 1601 spectrophotometer.

Thermogravimetric Studies. Thermogravimetric analyses (TGA's) were carried out on electrochemically prepared powders of **1a** (5−10 mg samples) using a Perkin-Elmer Model TGA7 thermogravimetric analyzer. A temperature range from 20−800 °C was examined using a heating rate of 40 °C min^{-1}, under either dinitrogen or air.

Conductivity Studies. A powder sample of electrochemically prepared PAn.(+)-HCSA **1a** was pressed into a pellet (thickness 0.806 nm) and the conductivity measured both at room temperature and after heating at 140 °C for 30 min. The method of van der Pauw[19] was employed. Current was applied using a PAR 363 and the resulting potential measured with a HP34401A multimeter.

Results and Discussion

Conformations of Electrochemically and Chemically Prepared PAn.(+)-HCSA Films. The room temperature UV−visible spectra of the electrochemically and chemically prepared PAn.(+)-HCSA films (**1a** and **1b**, respectively) are compared in Figure 1. The absorption spectra of **1a** and **1b** were significantly different, indicating different conformations for the polyaniline chains in the two salt films. The spectrum of the chemically produced PAn.(+)-HCSA **1b** was very similar to that reported previously by us[17] and others[20,21] for PAn.HCSA films cast from DMSO and solvents such as $CHCl_3$, DMF, and NMP. The presence of an intense, well-defined localized polaron band at ca. 825 nm is characteristic of a "compact coil" conformation for the polyaniline chain. In contrast, this polaron band was weaker and broader in the electrochemically produced film **1a**, and a free-carrier tail appeared in the rear infrared. This indicates significant delocalization in the polaron band for **1a**, suggesting a more "expanded coil" type conformation for the polymer chain. However, the near infrared absorption in **1a** was much less dominant than that observed previously[20] for PAn.(+)-HCSA films cast from *m*-cresol or in-situ deposited PAn.HCl films exposed to *m*-cresol.[21] In the latter cases, the very intense near-infrared absorptions (with $\lambda_{max} > 2000$ nm) and the virtual disappearance of the localized polaron band were identified as signatures for the presence of an extreme "expanded coil" conformation.

The different conformations for the polyaniline salts **1a** and **1b** are particularly evident from their respective CD spectra, shown in Figure 2. The more complex low wavelength CD spectrum for **1b** is consistent with the presence (Figure 1) of two UV−visible absorption bands in this region. The CD bands at 405 and 460 nm may be tentatively assigned as the bisignate, exciton-coupled bands associated with the localized polaron absorption band observed for **1b** at ca. 425 nm (Figure 1). Partly overlapping with these is another probable pair of bisignate exciton-coupled CD bands (one of which is evident at 345 nm), associated with the $\pi-\pi^*$ absorption band seen for **1b** at ca. 350 nm.

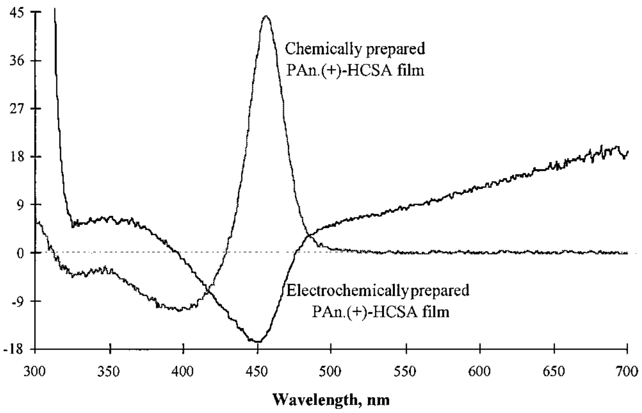

Figure 2. Room-temperature CD spectra of PAn.(+)-HCSA films **1** prepared (a) electrochemically and (b) chemically.

In contrast, the CD spectrum of **1a** (Figure 2) exhibited only one pair of bisignate, exciton-coupled bands at 360 and 450 nm, as anticipated from the presence of only one broad absorption band in this region at ca. 400 nm (Figure 1). Interestingly, unlike **1a**, the chemically prepared **1b** showed only weak CD ellipticity in the region 500−700 nm. Strong absorption by the film at longer wavelengths prevented the identification of the anticipated CD band associated with the localized polaron absorption band at 825 nm.

The above results provide the first evidence that electrochemically and chemically produced polyaniline salts possess different conformations for their polymer chains. It has been previously considered[22] that polyanilines synthesized via these two routes had similar chemical structures, although differences in molecular weights have been reported.[23] The lower molecular weights for electrochemically prepared polyaniline salts may be responsible for their different conformations compared to chemically doped salts. However, an alternative possible explanation for the different chiroptical properties of the electrochemically and chemically prepared PAn.(+)-HCSA salts is the presence of different configurational or regioisomers. In either case, these structural differences will need to be borne in mind when comparisons are made between electrochemically and chemically prepared polyanilines.

Thermochromism in PAn.(+)-HCSA Salts. Chemically produced PAn.(+)-HCSA films **1b** exhibited no thermochromism when heated to 140 °C. No significant changes occurred in their UV−visible and CD spectra, indicating that they retained a "compact coil" conformation over the 20−140 °C temperature range.

Little change was also observed in the chiroptical properties of the electrochemically prepared PAn.(+)-HCSA films **1a** over the temperature range 20−80 °C. However, at temperatures progressively above 80 °C the UV−visible and especially the CD spectra of these films underwent a series of marked changes. These culminated with the appearance at 140 °C of UV−visible and CD spectra (Figure 3) characteristic of the chemically

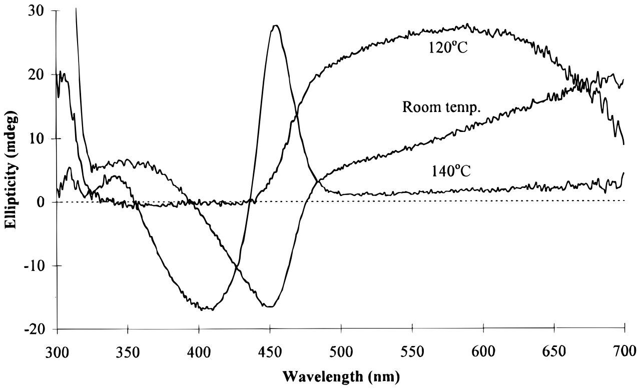

Figure 3. CD spectrum of an electrochemically prepared PAn.(+)-HCSA **1a** film: (i) at room temperature, (ii) after heating at 120 °C for 10 min, (iii) after heating at 140 °C for 10 min.

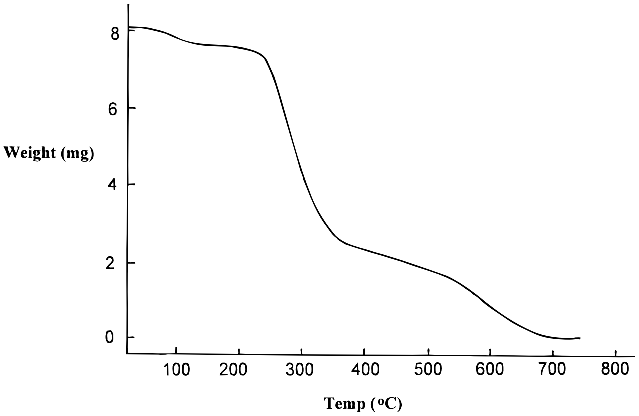

Figure 4. Thermogravimetric analysis (TGA) trace (20−800 °C) for an electrochemically prepared PAn.(+)-HCSA **1a** powder (8.025 mg, under dinitrogen).

produced salt **1b**. That is, unexpectedly, the polyaniline chain had undergone a transition from an "expanded coil" like conformation to a "compact coil" conformation.

This unprecedented temperature-induced structural change in polyanilines above 140 °C suggests that the "compact coil" conformation is the more thermodynamically stable for PAn.(+)-HCSA salts. It is not reversed on cooling, unlike the thermochromic effects previously observed[1−6] in substituted polythiophenes. This behavior may therefore be more strictly defined as a thermal rearrangement rather than thermochromism.

A series of intermediate UV-visible and CD spectra were observed for the electrochemical **1a** films at temperatures between 90 and 130 °C. For example, the CD spectrum obtained after heating at 120 °C for 10 min is shown in Figure 3. Interestingly, upon cooling to room temperature and allowing to stand for 30 min, the CD spectrum reverted to the original room-temperature spectrum. This reversible behavior contrasts with the irreversible changes observed above when **1a** was heated to temperatures ≥140 °C. It may arise from reversible structural changes associated with the thermal loss of water from the polymer film and its subsequent readsorption with time at room temperature.

Thermogravimetric analysis of a powder sample of the electrochemically deposited **1a** (Figure 4) showed a 6% weight loss over the temperature range 50−150 °C, consistent with water loss from the polymer. Similar losses were observed by Monkman et al.[24] for a chemically derived PAn.(+)-HCSA sample obtained from *m*-cresol. Studies[25] have suggested that water molecules are bound to the N atoms of polyanilines via strong H-bonding interactions. Their thermal loss from the polymer should generate increased free volume between the polymer chains, facilitating conformational changes.

Resistance measurements on a pellet of the electrochemically produced PAn.(+)-HCSA powder **1a** (see Experimental Section) showed that the conductivity decreased from 20 to 12 S cm^{-1} after heat treatment for 10 min at 140 °C. The latter conductivity is in the range expected[20] for "compact coil" polyaniline salts. However, the only moderately higher conductivity observed for the untreated (room temperature) PAn.(+)-HCSA **1a** indicated that it does not possess an extreme "expanded coil" conformation, for which conductivity values greater than 100 S cm^{-1} have been reported.[20,26] This conclusion is consistent with the room-temperature UV−visible spectrum of **1a** in Figure 1, which also suggested only partial delocalization of the localized polaron based in this salt and a partially "expanded" polymer chain. It should be noted, however, that the thermally induced changes in the chiroptical properties of the electrochemically produced PAn.(+)-HCSA film may arise from other sources such as changes in the degree of crystallization.

The thermally induced structural changes observed above for electrochemically deposited PAn.(+)-HCSA may have significant implications when other physical and mechanical properties of such salts are examined at temperatures above 130 °C. We have begun a study of other electrochemically derived PAn.HA salts to determine whether this thermochromic effect is general or associated with special characteristics of the HCSA dopant.

It is interesting to note that the presence of secondary dopants[20] may also influence the occurrence of such thermochromic effects. For example, thermal treatment of a poly(methyl methacrylate) blend with an "expanded coil" form of PAn.(+)-HCSA (cast from *m*-cresol), revealed no change to a "compact coil" chain conformation even at 180 °C.[27] Instead, thermal dedoping (loss of HCSA) occurred directly from the "expanded coil" conformation of the PAn.(+)-HCSA to give neutral emeraldine base.

Dedoping at Elevated Temperatures. Monkman et al.[24] tentatively assigned a glass transition temperature, T_g, of 150 °C for their chemically derived PAn.(±)-HCSA salt. We observed no significant further changes in the chiroptical properties of our PAn.(+)-HCSA films when heated to 170 °C that may be associated with this transition.

However, after heat treatment at >180 °C, irreversible changes were progressively observed in the UV−visible and CD spectra. For example, the electrochemically derived film **1a** gradually lost its localized polaron band at 825 nm, while a new peak grew at lower wavelengths (Figure 5). These changes are consistent with the thermally induced dedoping of the PAn. (+)-HCSA to give emeraldine base (EB), i.e. the reverse of eq 1. These UV−visible spectral changes were accompanied by a large mass loss (Figure 4), which we attribute to the loss of the HCSA dopant. The facile loss of HCSA observed at temperatures above 200 °C may be facilitated by the melting of this dopant acid at 198 °C.

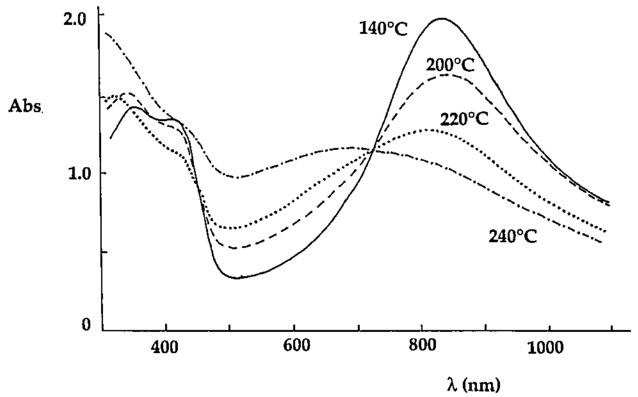

Figure 5. Effect of heat treatment (140−240 °C) on the UV−visible spectrum of an electrochemically prepared PAn.(+)-HCSA **1a** film.

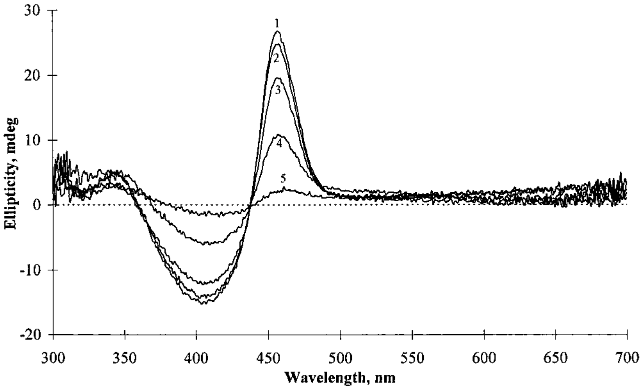

Figure 6. Effect of heat treatment on the CD spectrum of an electrochemically prepared PAn.(+)-HCSA **1a** film: (1) 160 °C, (2) 180 °C, (3) 220 °C, (4) 200 °C, (5) 240 °C.

The associated CD spectra changes shown in Figure 6 are also consistent with the progressive loss of the chiral (+)-HCSA dopant at temperatures $>$180 °C. The strong CD bands for the initial "compact coil" PAn. (+)-HCSA diminish with increasing temperature, until the film is almost optically inactive after 10 min at 240 °C. The observation of an isodichroic point at 440 nm is consistent with the conversion of PAn.(+)-HCSA to racemic emeraldine base (EB). The failure to observe CD bands for the neutral EB product confirms the essential role of the (+)-CSA$^-$ dopant anion in maintaining the macroasymmetry of the polyaniline chain. It is significant to note, however, that the alternative room-temperature dedoping of PAn.(+)-HCSA with NH_4OH has been shown[15,28] to give optically active EB. Presumably at room temperature, unlike the elevated temperatures in the present study (above the polymer glass transition temperature), the EB chain does not have sufficient mobility to undergo the inversions required for racemization.

Very similar UV−visible and CD spectral changes associated with dedoping were observed when the chemically prepared PAn.(+)-HCSA film was heated at temperatures greater than 160 °C. However, the CD spectral results in Figure 7 suggest that this film is more stable to thermal dedoping than the electrochemically derived film.

Conclusions

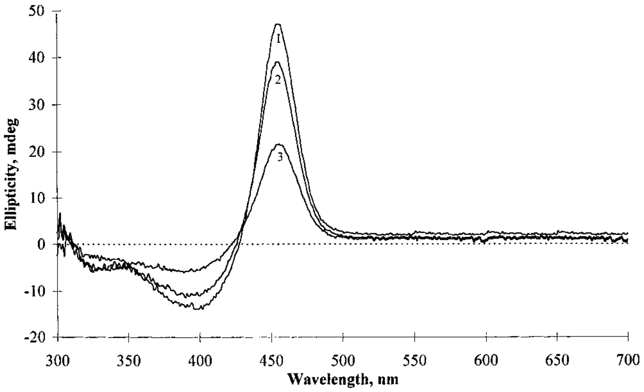

Figure 7. Effect of heat treatment on the CD spectrum of a chemically produced PAn.(+)-HCSA **1b** film: (1) 160 °C, (2) 200 °C, (3) 240 °C.

UV−visible and CD spectroscopic studies show that chemically and electrochemically prepared PAn.(+)-HCSA films have different conformations for their polyaniline chains, assigned as "compact coil" and partial "expanded coil", respectively. These conformations may be transformed in the direction "expanded" to "compact" coil by heating the films to 140 °C for 10 min, providing the first reported instance of thermochromism in polyaniline salts. Heating at temperatures greater than 180 °C results in progressive dedoping of the PAn.(+)-HCSA films, with the formation of racemic emeraldine base.

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