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Influence of water on the chirality of camphorsulfonic acid-doped polyaniline

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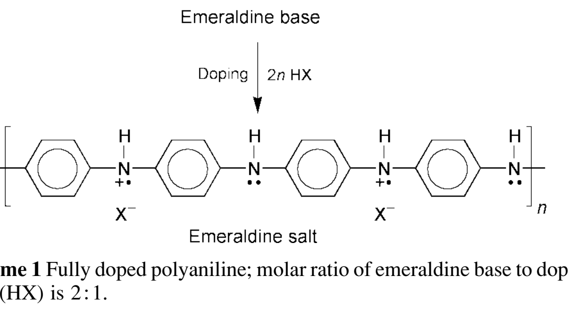
Polyaniline doped with *R*-(−)- or *S*-(+)-camphorsulfonic acid produces an inexpensive chiral substrate; the presence or absence of water can be used to invert the dopant-induced circular dichroism (CD) absorbance at 450 nm, shedding light on conflicting literature reports.

Chiral polyaniline has potential applications in molecular recognition and enantiomeric separations.[1–3] In searching the literature of chiral camphorsulfonic acid-doped polyaniline, we discovered that alternating directions have been reported for the main dopant-induced circular dichroism (CD) absorbance peak centered at 450 nm. For example, when doped with *S*-(+)-camphorsulfonic acid, the CD absorbance at 450 nm is sometimes reported to be in the positive direction,[3–6] whereas at other times it is reported to be in the negative direction.[1,5–9] If chiral polyaniline is to be useful as an active material in sensors and separations[1,2] this phenomenon needs to be understood. Here, we demonstrate that the chirality of polyaniline is critically dependent upon the water content of the polymer before exposure to the chiral acid dopant.

Polyaniline is a simple conjugated polymer, which can be polymerized *via* either chemical[10] or electrochemical oxidation of aniline.[11] Aniline is an inexpensive achiral molecule heavily used in the dye industry.[12] The half-oxidized emeraldine base form of polyaniline can be readily doped to the conducting emeraldine salt form when mixed with a strong acid (Scheme 1).

Emeraldine base doped with either enantiomer of camphorsulfonic acid produces a chiral form of polyaniline.[1,4,6] Since camphorsulfonic acid is only optically active below 300 nm, the doping-induced peak at 450 nm can be attributed exclusively to chiral polyaniline, and therefore, this absorbance can be used to monitor chirality in the polymer. Here, the emeraldine base form of polyaniline was chemically synthesized according to a literature procedure[10,13] and camphorsulfonic acid doping in *N*-methylpyrrolidinone was carried out using a 2:1 mass (5:1 molar) ratio of emeraldine base to camphorsulfonic acid.†

To study the effects of water upon chiral polyaniline, one sample of emeraldine base was placed in a 60 °C oven for four days and allowed to dry thoroughly, while a second sample from the same batch was soaked in deionized water for four days followed by brief vacuum filtration. The dry (3–5% water content determined by thermogravimetric analysis) and wet (> 50% water content determined by thermogravimetric analysis) emeraldine base samples were then doped with either *S*-(+)- or *R*-(−)-camphorsulfonic acid in *N*-methylpyrrolidinone and CD spectra obtained. Surprisingly, a CD peak at 450 nm could be induced to give either a positive or a negative signal simply by thoroughly wetting or drying the emeraldine base polyaniline prior to doping with *S*-(+)-camphorsulfonic acid in *N*-methylpyrrolidinone (see Fig. 1): the dry sample doped with *S*-(+)-camphorsulfonic acid results in the positive CD peak; the wet sample doped with *S*-(+)-camphorsulfonic acid gives the negative CD peak. Tests performed on different batches of wet and dry emeraldine base all exhibited the same trends in CD direction at 450 nm. Therefore, the water content of the emeraldine base prior to doping with camphorsulfonic acid has a dramatic affect upon the chirality of the doped polyaniline.



Scheme 1 Fully doped polyaniline; molar ratio of emeraldine base to dopant acid (HX) is 2:1.

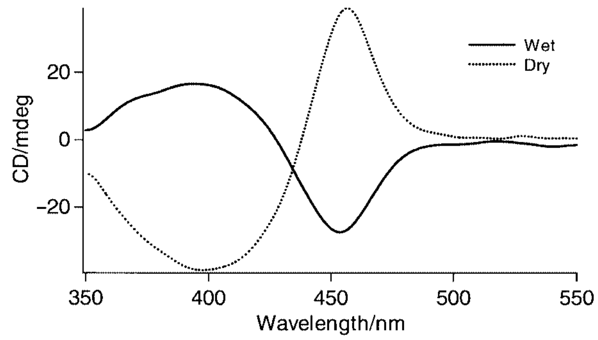


Fig. 1 Resulting CD spectra of polyaniline dried prior to doping with *S*-(+)-camphorsulfonic acid in *N*-methylpyrrolidinone (Dry) and wetted prior to doping with *S*-(+)-camphorsulfonic acid in *N*-methylpyrrolidinone (Wet).

Wet and dry emeraldine base samples doped with *R*-(−)-camphorsulfonic acid in *N*-methylpyrrolidinone gave exactly analogous, but inverted, CD results (see Fig. 2). Note that the direction of the CD peak at 450 nm induced with *R*-

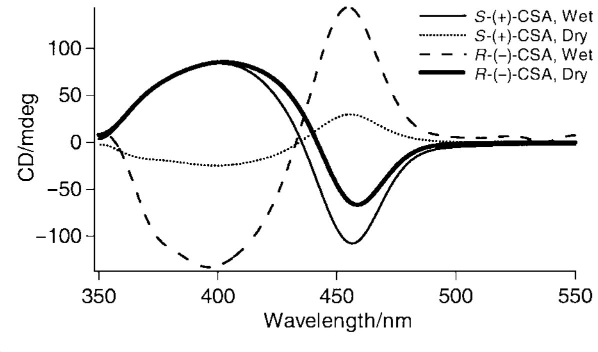


Fig. 2 Resulting CD spectra of polyaniline doped with *R*-(−)- or *S*-(+)-camphorsulfonic acid after exposure to either drying or wetting conditions prior to doping in *N*-methylpyrrolidinone.

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Table 1 Effects of water on the chirality of camphorsulfonic acid-doped polyaniline in *N*-methylpyrrolidinone

Condition of emeraldine base prior to doping with camphorsulfonic acid	CD direction at 450 nm	
	S-(+)-Camphorsulfonic acid	*R*-(−)-Camphorsulfonic acid
Wet	−	+
Dry (60 °C)	+	−
Dry (60 °C) → Wet	−	+
Wet → Dry (60 °C)	+	−
Wet → vacuum dried, room temperature	+	−

(−)-camphorsulfonic acid for wet polyaniline is now in the positive direction, whereas the dry sample is now in the negative direction. Therefore, polyaniline can be readily manipulated to produce the same form of optically active polyaniline when doped with opposite enantiomers. The direction of the CD signal is dependent upon both the condition of the emeraldine base prior to doping, and upon which enantiomer is used for doping. Additionally, all of the solutions were cast as thin, doped emeraldine films onto quartz plates and CD spectra obtained. All the samples gave the same CD peak direction at 450 nm as when in solution. Therefore, this phenomenom exists regardless of whether the sample is in solution or in the solid state.

In order to rule out that the drying temperature caused a chemical change to the emeraldine base structure, a sample of polyaniline dried at 60 °C for a four-day period was subsequently soaked in deionized water to produce the wet form of emeraldine base. The sample was then doped with *S*-(+)-camphorsulfonic acid in *N*-methylpyrrolidinone overnight and analyzed by CD. The resulting CD peak at 450 nm was negative which is the same CD direction observed for unheated, wet polyaniline doped with *S*-(+)-camphorsulfonic acid (see Table 1). To further rule out heating at 60 °C as the cause for the reversal in chirality, water elimination *via* vacuum drying at room temperature was substituted for oven drying. A sample of wet emeraldine base was dried for seven days under vacuum at room temperature and then doped with *S*-(+)-camphorsulfonic acid in *N*-methylpyrrolidinone. The resulting CD direction–positive at 450 nm–was the same as for emeraldine base dried at 60 °C. When the inverse experiment was performed, *i.e.* using wet emeraldine base dried in a 60 °C oven for several days, a positive CD signal at 450 nm was obtained after doping with *S*-(+)-camphorsulfonic acid. This is the same direction as observed for emeraldine base dried at 60 °C as summarized in Table 1. Thus, polyaniline behaves according to the last environment that it is exposed to. This indicates that water is the causal factor rather than a chemical reaction (*e.g.* cross-linking) of the polyaniline itself or involving some impurity. This also demonstrates that the process is fully reversible prior to doping.

The above temperature experiments were also performed with *R*-(−)-camphorsulfonic acid instead of the *S*-(+)-form. A sample of emeraldine base polyaniline dried at 60 °C for a four-day period was subsequently soaked in deionized water and doped with *R*-(−)-camphorsulfonic acid in *N*-methylpyrrolidinone overnight. A second emeraldine base sample was first soaked in water and then dried in a 60 °C oven before doping with *R*-(−)-camphorsulfonic acid. Additionally, wet emeraldine base polyaniline that was dried at room temperature under vacuum was also doped with *R*-(−)-camphorsulfonic acid. All samples were analyzed with CD and the results are summarized in Table 1. The *R*-(−)-camphorsulfonic acid-doped polyaniline behaves analogously to *S*-(+)-camphorsulfonic acid doped polyaniline except that all CD directions at 450 nm are now inverted.

The discovery that water can cause a reversal in chirality, and its ability to make polyaniline doped with opposite enantiomers appear to have the same chiral configuration based on CD is significant because it could explain the observed inversion of expected chiralities reported in the literature.[3,7,14] For example, Wallace and coworkers have shown that chiral polyaniline doped with the same enantiomer of camphorsulfonic acid prepared electrochemically produces an inverted CD peak at 450 nm to that produced chemically.[3,5,7] Their electrochemically prepared chiral polyaniline when doped with *S*-(+)-camphorsulfonic acid produces a negative 450 nm peak, whereas their chemically generated polyaniline doped with *S*-(+)-camphorsulfonic acid in *N*-methylpyrrolidinone produces a positive CD peak at this wavelength. The authors conclude that there must be different configurations for the electrochemically and chemically prepared chiral polyanilines.[5] However, since the electrochemically prepared chiral polyaniline was electropolymerized in an aqueous solution and its CD is similar in direction to the wet polyaniline described here, it is likely that the water used in the electrochemical process contributes to the chiral configuration of the polyaniline.

Thus, the CD spectra of *S*-(+)- and *R*-(−)-camphorsulfonic acid doped polyanilines in *N*-methylpyrrolidinone can appear identical depending upon the water content of the emeraldine base prior to doping. This process is fully reversible before doping and is simply a function of the water content and is not related to the drying temperature.

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Notes and references

† All samples were made with 60 mg of polyaniline and 30 mg (1.3×10^{-4} mole) of camphorsulfonic acid in 4 mL of *N*-methylpyrrolidinone. The mixtures were shaken and allowed to dope for at least four hours and then filtered through cotton. Each sample for CD analysis consisted of 40 μL of a stock solution that was diluted with 150 μL of *N*-methylpyrrolidinone. Films were prepared by placing a few drops of solution onto quartz plates that were dried at 60 °C for two hours. All CD analyses were carried out using a Jasco J715 CD Spectropolarimeter and a Fast Fourier Transform to filter out high frequency noise. Owing to the difficulty of completely dissolving polyaniline in *N*-methylpyrrolidinone, the concentrations, and therefore the CD intensities, vary from sample to sample. The CD spectra presented in Fig. 2 for *S*-(+)- and *R*-(−)-camphorsulfonic acid-doped polyaniline used polymer powder from the same synthesis, whereas the analogous spectra for *S*-(+)-camphorsulfonic acid- doped polyaniline in Fig. 1 used polymer powder from a different synthetic batch.

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