

## Electropolymeric generation of optically active polypyrrole

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The facile synthesis of optically active polypyrrole has been achieved via the enantioselective electropolymerization of pyrrole on indium-tin-oxide-coated glass electrodes in aqueous solution containing D-(+) or L-(-) tartaric acid, (1S)-(+)-10-camphorsulfonic acid and L-lactic acid. The dark films of conducting polypyrroles salt formed under electrostatic conditions (+0.65V vs. Ag/AgCl) exhibited strong circular dichroism (CD) spectra typical of polymers possessing helical chirality. The quantitative reversal of the CD spectrum of the salt grown in (+)-tartaric acid as opposed to (-)-tartaric acid suggests that electropolymerization is highly enantioselective, with one helical screw of the polymer chain being preferentially produced depending on the hand of the tartaric anion incorporated. © 1997 Elsevier Science Ltd.

(Keywords: chiral polypyrrole; optical activity; electropolymerization)

### Introduction

Following the first reports on chiral conducting polymers in 1985<sup>1,2</sup>, a number of these kind of optically active structure have been studied in detail<sup>3–9</sup>. The introduction of chiral side groups at the 3-position of polythiophenes and N-atom of polypyrroles has led to the conjugated polymers featuring high specific rotation up to  $[\alpha]_D = 3000^\circ$ . Furthermore, due to the high regioregularity, the conductivity was enhanced to 1000 s/cm and bandgap was decreased to 1.7 eV<sup>10,11</sup>. However, synthesis of a chiral monomer is generally tedious and expensive. Sometimes this way might have a deleterious effect on the polymers conductivity and electroactivity. Recently, Majidi reports two facile routes to obtain a chiral polyaniline, which do not need the synthetic steps to prepare the expensive chiral monomers, e.g. the enantioselective polymerization of aniline in the presence (+) or (-)-camphorsulfonic acid and the enantioselective acid doping of the neutral emeraldine based form of polyaniline by HCSA<sup>12–14</sup>. The optical activity was attributed to the one-handed helical conformation of the polymer chain. Until now, the use of such routes was only limited to the preparation of polyaniline and polytoluidine. In the present paper, optically active polypyrrole with one-handed helical conformation was synthesized for the first time by the electropolymerization of achiral pyrrole in the presence of four kinds of chiral acid. The influence of chiral acids used on the polymer's optical activity was discussed.

### Experiment

Pyrrole was purified by distillation with CaH<sub>2</sub> under an argon atmosphere and stored in the dark at a low temperature. All chiral acids were commercially available (Aldrich). Twice deionized distilled water was used. All other reagents were analytical grade. A Ag/AgCl electrode (saturated potassium chloride) was used as the reference electrode and all potential were recorded and reported with

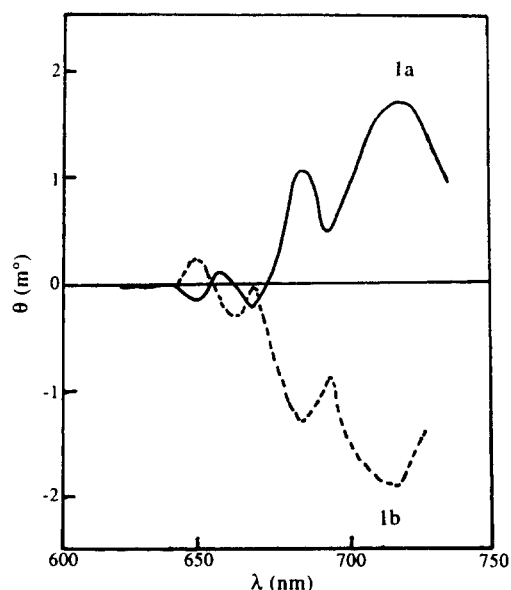
respect to the electrode. The platinum foil was used as a counter electrode. Indium-tin-oxide (ITO)-coated glass electrode (geometric area 1 cm<sup>2</sup>) and disk-shaped Pt shrouded in a Kel-F tube was used as working electrodes (geometric area 0.0078 cm<sup>2</sup>). The electropolymerization of the pyrrole was carried out potentiostatically on the ITO-coated glass electrodes in aqueous solutions containing 0.2 mol/L pyrrole and 1 mol/L D-(+)-tartaric acid or L-(-)-tartaric acid, (1S)-(+)-10-camphorsulfonic acid and L-lactic acid, at an applied potential of +0.65 vs. Ag/AgCl. After 100 mC/cm<sup>2</sup> of charge was passed (the film thickness was about 0.42 μm), subsequent reduction of polypyrrole salt film thus produced was carried out at an applied potential of -0.2V vs. Ag/AgCl in 1 mol/L D-(+)-tartaric acid or L-(-)-tartaric acid, (1S)-(+)-10-camphorsulfonic acid and L-lactic acid. In addition, cyclic voltammetric characterization of the polypyrrole was carried out during polymer growth using Pt as working electrode and a scan rate of 100 mV/s. The circular dichroism (CD) spectra of the chiral polymers in ITO-coated glass electrodes were recorded on a Jasco-500C spectropolarimeter. Electrochemical experiments were carried out using an EG and G Princeton Applied Research Potentiostat/Galvanostat.

### Results and discussion

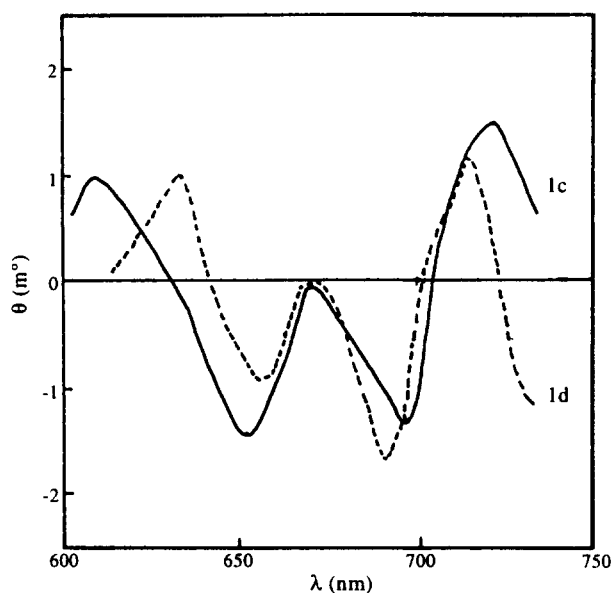
Under the electropolymerization conditions outlined in the experiment section, pyrrole is oxidized to the dark, conducting polypyrrole salt, which is believed<sup>15</sup> to have the propagated oligomeric unit<sup>13</sup>. Transmission of visible light through these films on ITO-coated glass was sufficient to permit the recording of CD spectra between 800 and 300 nm.

Figure 1 shows the CD spectrum of polypyrrole film, 1a and 1b grown on ITO-coated glass (0.42 μm) in the presence of 1 mol/L D-(+)-tartaric acid and L-(-)-tartaric acid, respectively. The polymers 1a and 1b have mirror image CD spectra, each possessing two main CD bands in the visible region at 680, 720 nm. Obviously the visible CD spectra of polymers 1a and 1b should not arise from the associated (+) or (-)-tartaric ions, since the corresponding chiral anions are transparent in the visible region. Thus the

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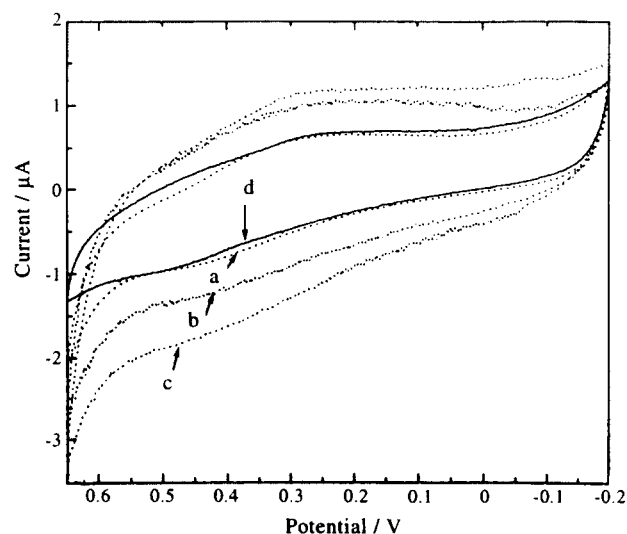
**Figure 1** Circular dichroism spectra of films of the polypyrrole 1a(D-(+)-tartaric acid) and 1b(L-(-)-tartaric acid) grown on ITO-coated glass; the film thickness is  $0.42 \mu\text{m}$



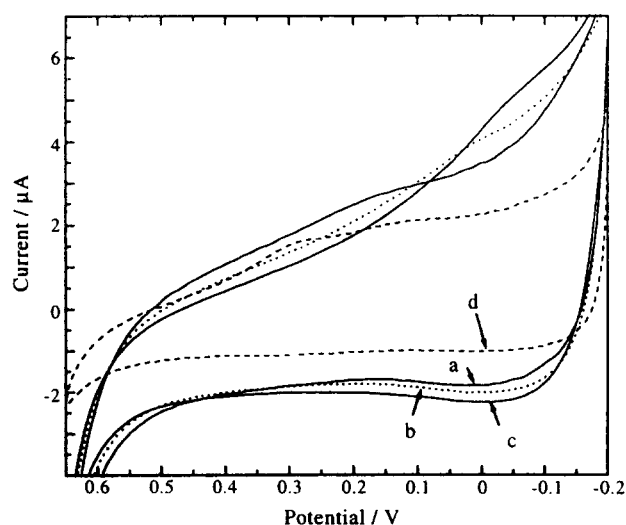
**Figure 2** Circular dichroism spectra of films of the polypyrrole 2((1S)-(+)-10-camphorsulfonic acid) and 3(L-lactic acid) grown on ITO-coated glass; the film thickness is  $0.42 \mu\text{m}$

CD bands must be attributed to chiral conformation of the polymer chains, e.g. the one-handed helical conformation, as the case of polyaniline salts in the presence of chiral camphorsulfonic acid<sup>13</sup>. It is the chirality of tartaric acid that induces the polypyrrole chain to be transformed into the helical conformation with a predominant screw sense (right- or left-handed helix). The one-handed helical conformation are stabilized by the acid-base interaction between polypyrrole and chiral acid used. This kind of interaction was also observed between poly(4-carboxyphenylacetylene) and chiral amines by Okamoto<sup>16</sup>. The mirror images of the CD spectra for polypyrrole salts in the presence of L-tartaric acid and D-tartaric acid strongly suggested that the electropolymerization is equally enantioselective.

The induced circular dichroism (ICD) was also observed when the electropolymerization was carried out in the



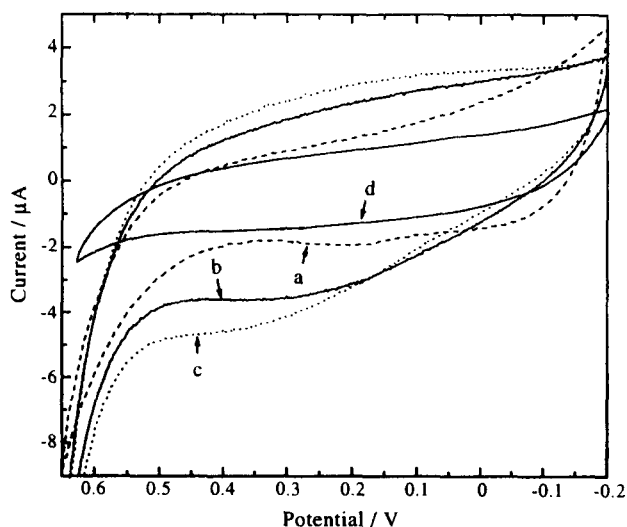
**Figure 3** Electrodeposition of film of the polypyrrole 1a by potentiodynamic methods using Pt as working electrode and  $100 \text{ mV/s}$  scan rate. Curve a: scan no. 20, Curve b: scan no. 70, Curve c: scan no. 100, Curve d: background voltammogram,  $\nu = 20 \text{ mV/s}$



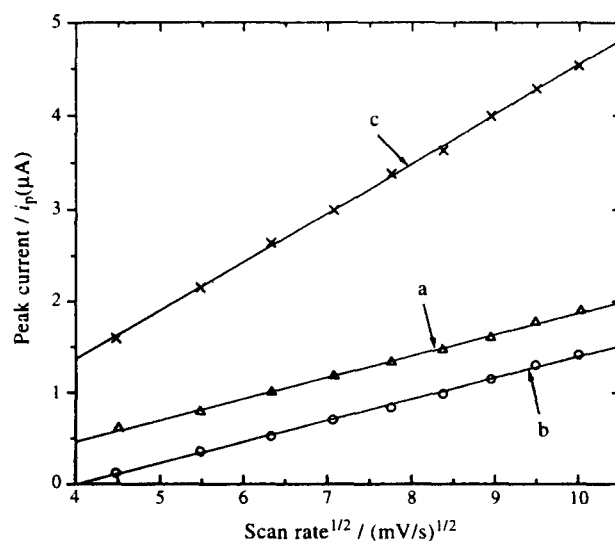
**Figure 4** Electrodeposition of film of the polypyrrole 2 by potentiodynamic methods using Pt as working electrode and  $100 \text{ mV/s}$  scan rate. Curve a: scan no. 15, Curve b: scan no.: 60, Curve c: scan no. 80, Curve d: background voltammogram,  $\nu = 30 \text{ mV/s}$

presence of (+)-camphorsulfonic acid and L-lactic acid, respectively, as shown in Figure 2. The slight difference for these ICD spectra in Figures 1 and 2 might reflect the strength of the acid-base interaction. The difference in the configuration, acidity and bulkiness of the acids would reasonably influence the split type and magnitude of the cotton effects as the case of poly(4-carboxyphenylacetylene) complexed with chiral amines<sup>16</sup>.

The conductive and electroactive nature of the polymers 1a and 1b is evident from cyclic voltammetry either during polymer growth (Figure 3) or on the deposited polymer films. The well defined oxidation and reduction processes observed are typical of those described previously<sup>17</sup> for polypyrrole materials and the shape of curves 1a and 1b is similar. The amount of anion found in each film is governed by the level of oxidation of the polymer and is a characteristic of each film<sup>18</sup>. This polymer-optically active anion compositional balance of the films actually proves to be quite useful, so the properties of the films can



**Figure 5** Electrodeposition of film of the polypyrrole 3 by potentiodynamic methods using Pt as working electrode and 100 mV/s scan rate. Curve a: scan no. 6, Curve b: scan no. 15, Curve c: scan no. 30, Curve d: background voltammogram,  $\nu = 20$  mV/s



**Figure 6** Plot of cyclic peak currents as a function of scan rate. Curve a: the film of the polypyrrole 1a in 1 mol/L D-(+)-tartaric acid solution, Curve b: the film of the polypyrrole 2 in 1 mol/L (1S)-(+)-10-camphorsulfonic acid solution, Curve c: the film of the polypyrrole 3 in 1 mol/L L-lactic acid solution

be conveniently altered by changing the anion. *Figures 4 and 5* are the cyclic voltammogram of polypyrrole film on platinum substrate containing (1S)-(+)-10-camphorsulfonic acid and (+)-L-lactic acid. The slight difference of CV must be arose from the difference of optically active anion used. In addition, a linear relationship between the cathodic peak current and the square root of the scan rate is discovered (*Figure 6*), as expected for a diffusion-limited electrode reaction.

Thus, optically active polypyrrole with one-handed helical conformation can be synthesized by the electropolymerization of achiral pyrrole in the presence of four kinds of chiral acid. Related studies are undergoing to determine whether similar enantioselective electropolymerization of conducting polymer can be carried out in the presence of other optically active anions and the mechanism of the optically active polymer should also be further studied as well.

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