

# Preparation of Conducting Fibers via the Electrochemical Polymerization of Pyrrole

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**ABSTRACT:** Cyclic voltammograms of pyrrole monomer and polypyrrole films prepared potentiostatically at 1.0 V versus an Ag/AgCl electrode have been examined. The insulating natural fibers, such as cotton, silk, and wool become electrically conducting when they are subjected to electrical treatment in the polymerizing solution of pyrrole in acetonitrile containing *p*-toluenesulfonic acid as a supporting electrolyte. The weight gain and the electrical conductivity of the fibers increase with the time of electrolysis and impressed current levels. The conductivities are in the range of 0.2 to 15 s/cm and dependent on the nature of the fibers. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1073–1077, 1997

## INTRODUCTION

Electronic conducting polymers and fibers recently received much interest because of their technological importances.<sup>1–7</sup> In spite of many interesting practical aspects of these new generation materials, their industrial applications are limited due to their insolubility in common solvents, infusibility, and desirable stability. We previously described a new methodology for the synthesis of electronic conducting fibers from the insulating fibers via the electrochemically directed polymerization of aniline.<sup>8–9</sup> The electrochemical technique overcomes difficulties of fiber formation from the intractable conducting polymers.

Polypyrrole is one of the conducting polymers that have been intensely studied and highly characterized. Polypyrrole is quite stable and adheres very strongly to substrates.<sup>1,10–12</sup> Its chemical stability is also very high.<sup>13</sup> Thus, we now report the

formation of conducting fibers from natural insulating fibers such as cotton, silk, and wool using the electrochemical polymerization of pyrrole on these fiber substrates. The polypyrrole was found to make the fibers relatively more conductive compared to polyaniline.<sup>8,9</sup> Kuhn<sup>14</sup> reported *in situ* chemical polymerization of pyrrole on the surface of synthetic textiles in aqueous solutions.

## EXPERIMENTAL

### Materials

Pyrrole and acetonitrile were fractionally distilled. Para-toluenesulfonic acid was used as received. The fibers of silk, cotton, and wool were boiled with water, repeatedly washed with distilled water and acetone to remove foreign substances, and then dried.

### Cyclic Voltammograms

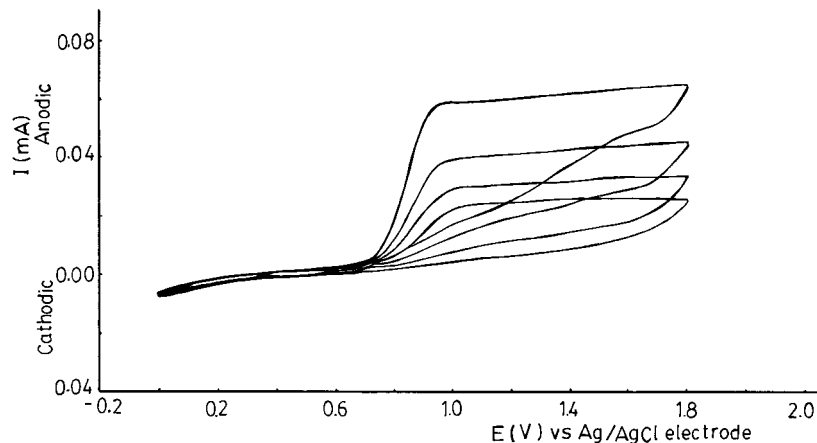
Cyclic voltammograms were recorded with a CV-27 BAS (Bio Analytical System, U.S.A.) cyclic voltammetry system equipped with a BAS X-Y recorder. Cyclic voltammetry work was carried out in a single-compartment three-electrode cell un-

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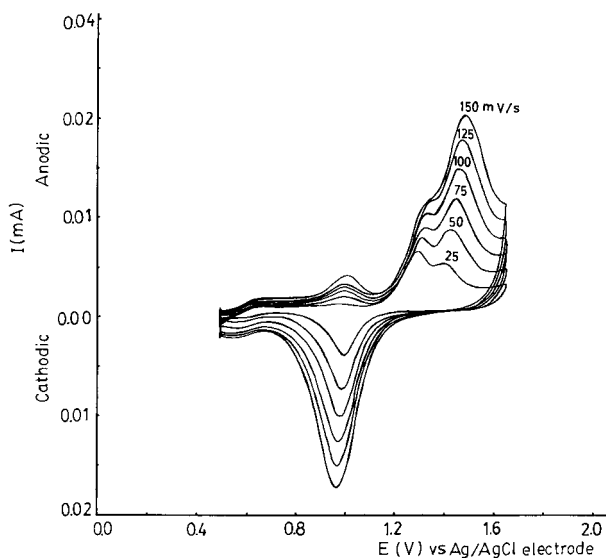
**Figure 1** Multisweep cyclic voltammograms of pyrrole (0.75 mol/L) on a platinum microelectrode in a saturated solution of *p*-toluenesulfonic acid in acetonitrile at 5 mV/s at 30°C. The intensity of oxidation current decreases with the number of scans.

der a N<sub>2</sub> atmosphere. The working electrode was a platinum or gold microelectrode. The counter-electrode was a platinum wire, and the reference electrode was an Ag/AgCl electrode.

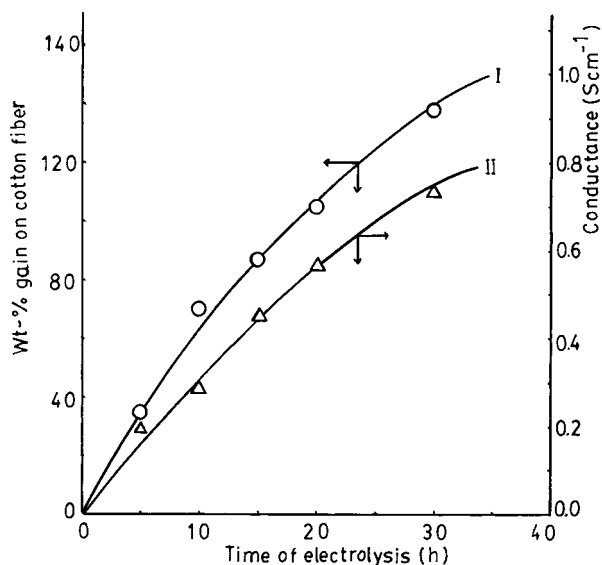
### Polymerization

The polymerization was carried out in an H-shaped electrolytic cell where anode and cathode compartments were divided by a fine fritted glass disk 2 cm in diameter. Two platinum electrodes, each 1.5 × 2.5 cm<sup>2</sup>, housed in the cell, were used

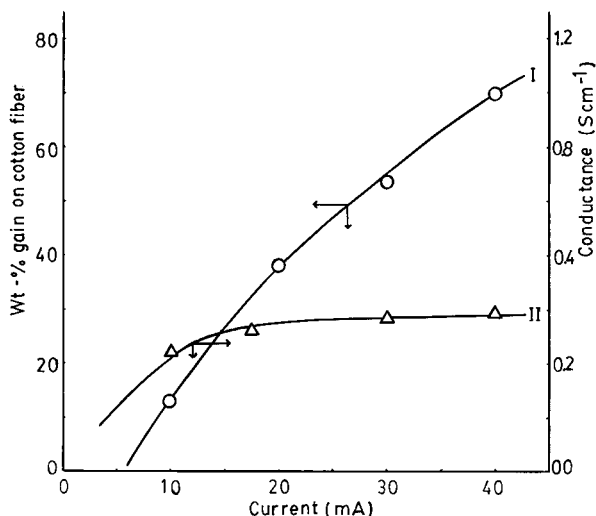
for electrolysis. In a typical run, 100 mg of cotton fiber was tightly wound around the platinum anode. The cell was then charged with the solution of *p*-toluenesulfonic acid (0.51 mol/L) in acetonitrile. The anolyte and catholyte were 20 mL each, and only anolyte contained pyrrole (0.71 mol/L). The electrolyte solution was purged with N<sub>2</sub> gas and thermostated at 30°C. The electrolysis was carried out at 40 mA, unless otherwise mentioned, and it was terminated after the desired time. The fiber was taken out of the anode,



**Figure 2** Multisweep cyclic voltammograms of polypyrrole film on a gold microelectrode in a saturated solution of *p*-toluenesulfonic acid at 30°C and different scan rates.



**Figure 3** (I) The weight percent gain and (II) the increase of conductance (s/cm) of cotton fiber with the duration of electrochemical polymerization of pyrrole (0.71 mol/L) at 40 mA in the solution of *p*-toluenesulfonic acid (0.51 mol/L) in acetonitrile at 30°C.



**Figure 4** (I) The weight percent gain and (II) the increase of conductance (s/cm) of cotton fiber at different current levels during the electrochemical polymerization of pyrrole (0.71 mol/L) at 40 mA in the solution of *p*-toluenesulfonic acid (0.51 mol/L) in acetonitrile at 30°C.

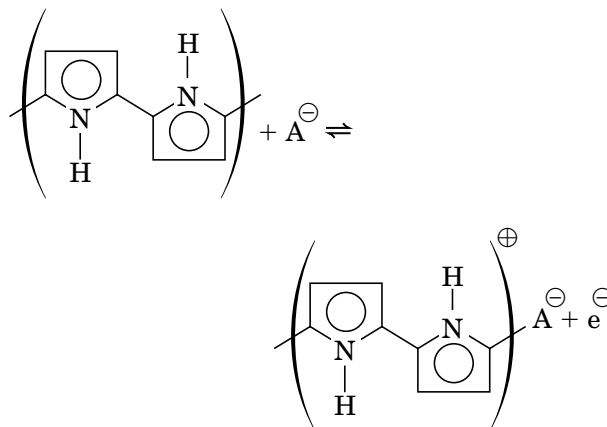
washed three times with distilled water, and finally repeatedly rinsed with acetone to remove loosely adhered polymer materials. The fiber was dried and weighed to constant weight. The resistivity of the fiber ( $\Omega$  cm) was measured as described previously.<sup>8,9</sup> From the knowledge of resistivity and geometry of the fiber, the conductivity (s/cm) was calculated.

## RESULTS AND DISCUSSION

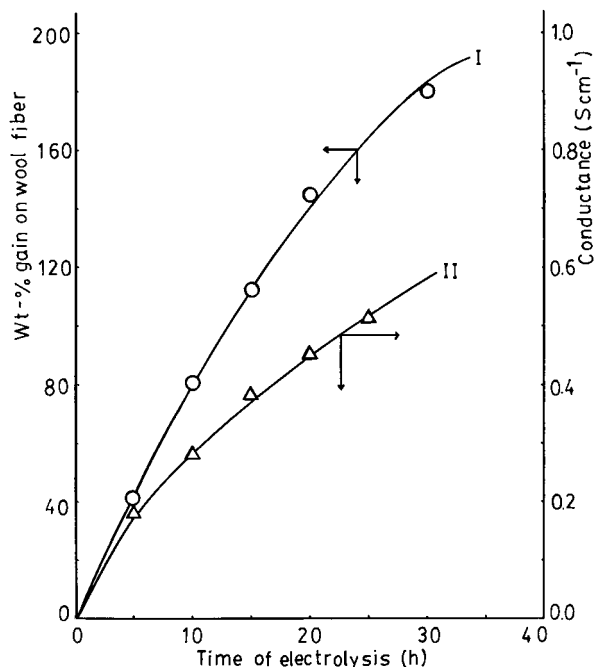
### Cyclic Voltammograms of Polypyrrole Film

The voltammetric behavior of pyrrole in a saturated solution of *p*-toluenesulfonic acid in acetonitrile at 30°C was examined. Figure 1 shows multicycled voltammograms of the solution recorded in the potential range 0.0 to 1.8 V vs. an Ag/AgCl electrode. Pyrrole oxidizes at about 1.0 V. The intensity of the oxidation current regularly decreases with number of potential cycles. Such results were also reported in the literature,<sup>15</sup> suggesting the decrease of the concentration of electroactive species. In another run, the thin green film of polypyrrole was made at 1.0 V on gold microelectrode in acetonitrile with *p*-toluenesulfonic acid. The film was washed repeatedly with acetonitrile to make it free from pyrrole monomer and then immersed in the solution of *p*-tolu-

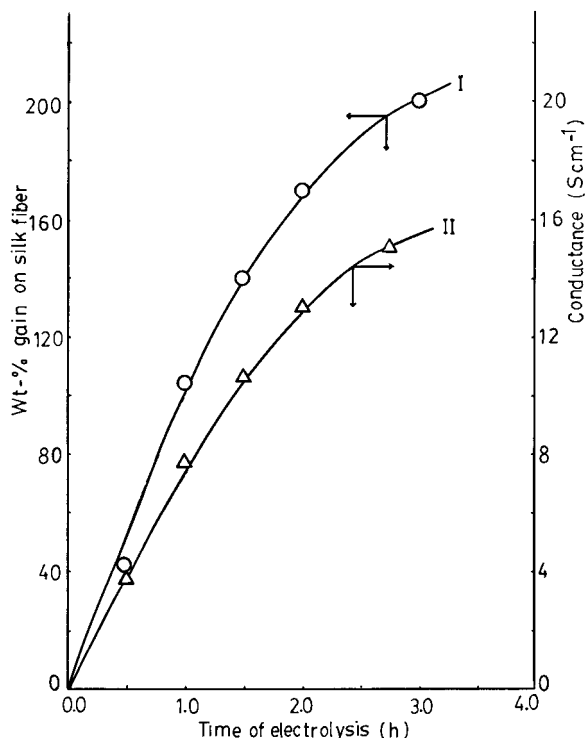
enesulfonic acid in acetonitrile. The voltammograms of the film were obtained and are shown in Figure 2. The redox peak currents gradually increase with the scan rates. Diaz and coworkers<sup>10</sup> have suggested that the properties of polypyrrole film are dependent on its thickness. The thin film (less than 0.1  $\mu$ m thick) of polypyrrole is electroactive and switched between the neutral and the oxidized state at 0.1 V vs. SCE, as follows:



Relatively thick films of polypyrrole are mainly conductive but poorly electroactive. This appears to be the reason for the decrease of oxidation peak



**Figure 5** (I) The weight percent gain and (II) the increase of conductance (s/cm) of wool fiber with the duration of electrochemical polymerization of pyrrole (0.71 mol/L) at 40 mA in the solution of *p*-toluenesulfonic acid (0.51 mol/L) in acetonitrile at 30°C.



**Figure 6** (I) The weight percent gain and (II) the increase of conductance (s/cm) of silk fiber with the duration of electrochemical polymerization of pyrrole (0.71 mol/L) at 40 mA in the solution of *p*-toluenesulfonic acid (0.51 mol/L) in acetonitrile at 30°C.

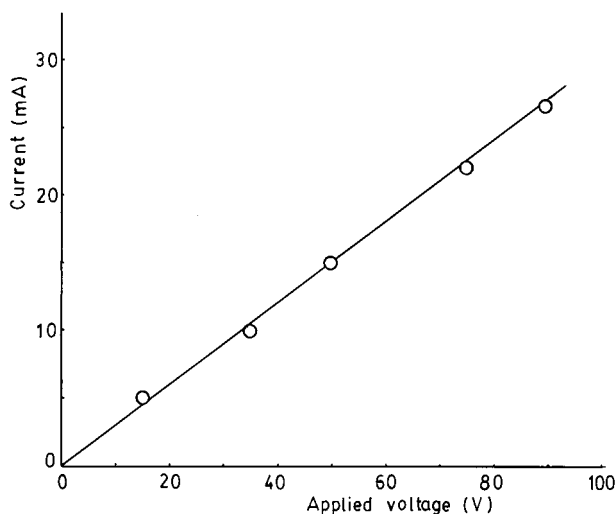
current in Figure 1. The oxidation of pyrrole monomer occurs on the electrode, followed by a polymer formation. The thickness of the polymer film increases with potential cycles, making the electrode passive on the following voltammograms. Furthermore, they pointed out that, in contrast with polyaniline, switching process between electronically insulating (reduced state) and electronically conducting states (oxidized state) is not simple and is associated with structural reorganization in the polymer, plus the limited diffusion of ions in and out of films during anodic and cathodic sweeps. The present work shows that the pyrrole polymerizes electrochemically in the organic electrolyte solution of *p*-toluenesulfonic acid in acetonitrile to yield conducting polypyrrole.

#### Weight Gain and Conductivity of Fibers

As observed with polyaniline,<sup>8,9</sup> the insulating natural fibers become conductive when they are subjected to electrical treatment in the polymerizing solution of pyrrole. Figure 3 shows that the

weight percent gain (curve I) and conductivity (curve II) of the cotton fiber increase monotonically with the time of electrolysis. The polymerization was also carried out at different impressed current levels. Data presented in Figure 4 show that the conductance did not increase appreciably with the increase of current levels, while the maximum weight percent gain was about 70. The results obtained for wool and silk fibers are presented in Figures 5 and 6. The conductivities are in the range 0.2 to 15 s/cm and are dependent on the nature of the fibers. The silk fiber has higher conductivities than those of cotton or wool. The fibers became more conductive with polypyrrole than with polyaniline.<sup>7,8</sup> Figure 7 shows the linear increase of current levels with applied potentials when the conducting cotton fiber, so obtained, was used as the anode and platinum electrode was used as the cathode in the cell containing the solution of *p*-toluenesulfonic acid (0.4 mol/L) in acetonitrile. Above 90 V, the fiber was burnt due to heating.

The polymerization of pyrrole occurs via oxidative coupling and commences in the solution in front of the anode to yield oligomers that precipitate or chemically interact with the fibers wound around the anode. The polymer growth is limited on the fiber surface and interstices. When the fiber was taken out of the anode, no polymer deposits were found on the anode that was completely covered with the fiber. This supports the theory that the polymer growth takes place on the fiber. The polymers may be held with the fibers by either a physical or a chemical interaction, but



**Figure 7** Increase of current level with applied voltage at the conducting cotton-fiber anode.

we have not yet conclusively examined this aspect.

## CONCLUSION

In conclusion, the polymerization of electroactive monomers, such as aniline and pyrrole, with insulating fibers results in the formation of electronic conducting composites. This is a simple method to prepare conducting fibers from intractable conducting polymers.

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