Electrochemical Formation of Some Conducting Fibers

SURAJ N. BHADANI,* SUMANTA K. SEN GUPTA,† GURU C. SAHU, and MADHURI KUMARI

Department of Chemistry, Ranchi University, Ranchi 834 008, India

SYNOPSIS

A study on the electrochemical grafting of polyaniline onto cotton, silk, and wool fibers was made. These insulating natural fibers became moderately conducting when they were subjected to electrical treatment in the polymerizing solution of aniline in aqueous HBF_4 medium. The weight gain of the fibers increased linearly and electrical resistance decreased with the time of electrolysis. The multiple cycled voltammograms of the solution of aniline in the aqueous solution of HBF_4 at the tip of conducting silk and wool fibers, which functioned as a microelectrode, were successfully recorded. The deep green polyaniline film was deposited on the fiber microelectrodes during electrolysis at +0.85 V vs. an Ag/Ag^+ electrode. The IR spectra suggest the coordination between the polyaniline and fibers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The synthesis of conducting fibers represents a fruitful technologically important area of research in the field of conducting polymers.[1-6] Conducting fibers are not prepared by normal solution or melt techniques because electrical conduction needs conjugated structure that in turn makes the polymer chain rigid, infusible, and insoluble. Several approaches are generally made to circumvent the processing difficulties in preparing conducting fibers.

A soluble conducting polymer is obtained by adding side groups such as a long alkyl group to the chain but usually at the cost of conductivity. The fiber is spun from such a soluble polymer.[7-9]

The precursor route is followed to prepare conducting fibers. An example of this is the fiber is spun from a soluble nonconjugated precursor such as poly(p-phenylene dimethylene)-α-(dimethyl sulfonium chloride). On heating, the conducting fibers of poly(phenylene–vinylene) results.[10]

The blend composite materials are used to form conducting fibers. For example, the conducting fibers were prepared from a polyblend of polyaniline and poly(p-phenylene tetraphthalamide) from homogeneous solution in concentrated sulfuric acid.[11]

Grafting and coating of the conducting polymers onto semiconductors or insulators results in conducting materials.[12-15] The grafting of conducting polyaniline onto glass fabrics and nylon cloth results in formation of conducting fabrics.[16]

Such graftings or coatings can elegantly be carried out by the electrochemical polymerization technique that has the following advantages[17,18]:

1. Chemical synthesis may give powders while electrochemical synthesis results in cohesive films.
2. Film or fiber thickness and homogeneity are easily controlled by the electrical current or potential.
3. Wetting of the fiber surface by the monomer provides a uniform film on the surface and interstices.
4. The electrochemical process is simple and inexpensive and thus can be extended from laboratory scale to continuous industrial scale without major changes.

Previously we briefly reported the electrochemical grafting of polypyrrole and polythiophene onto the insulating surface of cotton, silk, and wool fibers that acquired moderate electrical conductivity.[19] In this article, we describe the preparation of such conducting fibers in the electrochemically polymerizing solution of aniline with aqueous HBF_4 as an electrolyte.

EXPERIMENTAL

Materials

Aniline and water were fractionally distilled prior to use. 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.

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^2, were used for electrolysis. In a typical run, 100 mg of cotton fiber was tightly wound around the platinum anode where the polymer formation was restricted to take place. The cell was then charged with the solution of aniline (0.43 mol/L) in aqueous HBF$_4$ (0.57 mol/L). The volumes of anolyte and catholyte were 25 mL each. The cell was thermostatted at 25°C and purged with N$_2$ gas. The reaction mixture was subjected to electrolysis at a constant current of 40 mA. As soon as the current was impressed through the solution, a blue-green mass started to deposit on the fiber at the anode. The electrolysis was terminated after the desired time. The fiber was taken out of the anode, washed three times with distilled water, and finally repeatedly rinsed with acetone to remove loosely attached polymer materials. The fiber was dried and washed to constant weight. The surface resistivity (Ω cm) of the fiber was determined using a high vacuum tube voltmeter and the average value was noted. Wool and silk fibers were subjected to similar electrochemical treatment with the aniline solution in aqueous HBF$_4$.

Cyclic Voltammograms

Cyclic voltammograms were recorded with a CV-27 BAS (Bio Analytical System) cyclic voltammetry system equipped with a BAS X-Y recorder. All electrical measurements were performed in a single compartment, three electrode cell under N$_2$ atmosphere. The working electrode was a conducting fiber such as a wool, cotton, or silk microelectrode. The counterelectrode was a platinum wire and the reference electrode was an Ag/Ag$^+$ electrode. The fiber microelectrode was prepared by inserting the conducting fiber, prepared electrochemically as stated above, in 1-mm inner diameter Pyrex tubing and sealed with shellac. The surface of the electrode was smoothed on a piece of parchment paper. We prepared a batch of 10 electrodes at a time because about 60% of these constructed electrodes were found unsuitable for voltammetric work because either the high residual currents were too large or useful potential range was too small. Such difficulties were also encountered in the preparation of carbon-paste microelectrodes.[20]

IR Spectra

The IR spectra were obtained using Perkin–Elmer 1330 IR spectrophotometer.

RESULTS AND DISCUSSION

Weight Gain and Conductivity of Fibers

Figure 1(I) shows that the weight percent gain of the cotton fiber increases linearly with time of electrolysis. Weight gain of the fiber was determined gravimetrically by weighing the fiber sample before and after electrochemical treatment of the fiber. No increase in weight of the fiber was noticed after washing and drying when the fiber was not subjected to the electrochemical treatment. Figure 1(II) shows the resistivity (Ω cm) decreases with time of electrolysis, that is, electrical conductivity increases after exposing the fiber to the electrochemical polymerization. The electrical resistance of the fiber before electrolysis was greater than 10^8 Ω cm. Similar results were obtained for wool and silk and pertinent results are shown in Figures 2 and 3. Weight gain
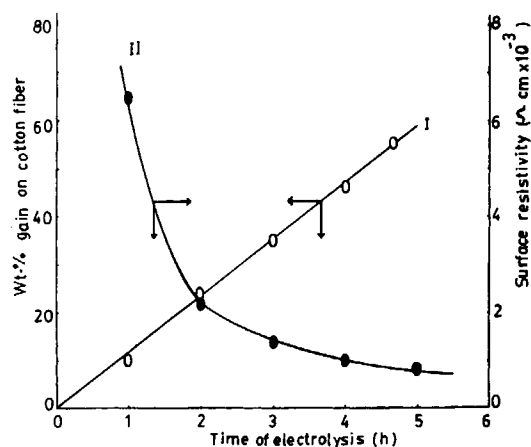

Figure 1 (I) The weight percent gain and (II) the decrease of resistivity (Ω cm) of cotton fiber with the duration of electrochemical polymerization of aniline (0.43 mol/L) at 40 mA in the aqueous solution of HBF$_4$ (0.57 mol/L) at 25°C.
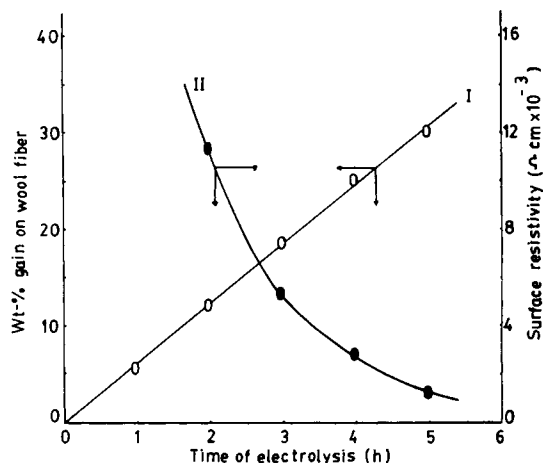
Figure 2 (I) The weight percent gain and (II) the decrease of resistivity (Ω cm) of wool fiber with the duration of electrochemical polymerization of aniline (0.43 mol/L) at 40 mA in the aqueous solution of HBF_4 (0.57 mol/L) at 25°C.

of silk fiber was found to be more than 215 wt %, cotton 55 wt %, and wool 30 wt % under the present experimental conditions.

The electrochemical approach in the formation of fiber–polymer composites has the advantage that the electrical property can be altered simply by changing the electrolysis condition. Therefore, the formation of the conducting fibers *in situ* by electrochemical polymerization of monomer on insulating fibers may be a most promising alternate approach to overcome difficulties of the state of the art fiber fabrication from infusible and insoluble conducting polymers.

Current and Voltage

The wool microelectrode was used as the anode and platinum electrode as the cathode in the cell containing the solution of aniline (0.43 mol/L) in aqueous HBF_4 (0.57 mol/L). Figure 4 shows the increase in current with applied voltage. The current increase is linear. When the applied voltage exceeds 60 V, the fiber is burned because of heating. This result clearly demonstrates that a considerable amount of current could be passed through this conducting fiber. A similar result was obtained in conducting cotton fiber and the current and potential data are exhibited in Figure 5.

Constant Potential Electrolysis

The potentiostatic growth of polyaniline film on the conducting wool microelectrode was followed during 85 min of polymerization. The chronoamperometric
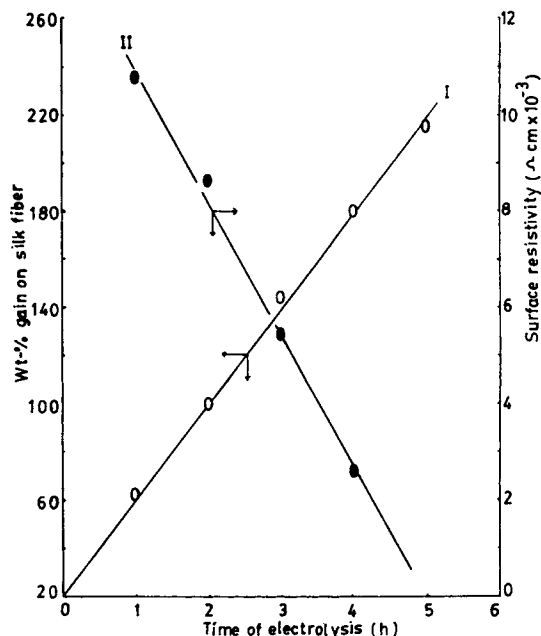

Figure 3 (I) The weight percent gain and (II) the decrease of resistivity (Ω cm) of silk fiber with the duration of electrochemical polymerization of aniline (0.43 mol/L) at 40 mA in the aqueous solution of HBF_4 (0.57 mol/L) at 25°C.

curve is shown in Figure 6. First there is sharp drop of the current and then the current increases. The decrease of the current is the characteristic of nucleus growth kinetics and is due to the charging of the double electric layers on the fiber–solution interface.[17] The zeta potential or electrokinetic potentials of cotton, wool, and silk fibers in aqueous medium were reported to be 38, 48, and 0.8 mV, respectively.[21] As the film grows and consequently the electroactive area increases on the surface of the
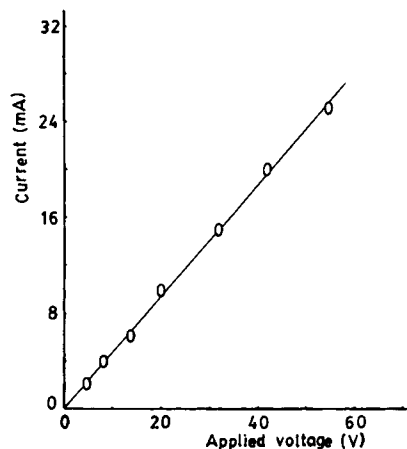

Figure 4 Increase of current level with applied voltage at the conducting wool-fiber anode.
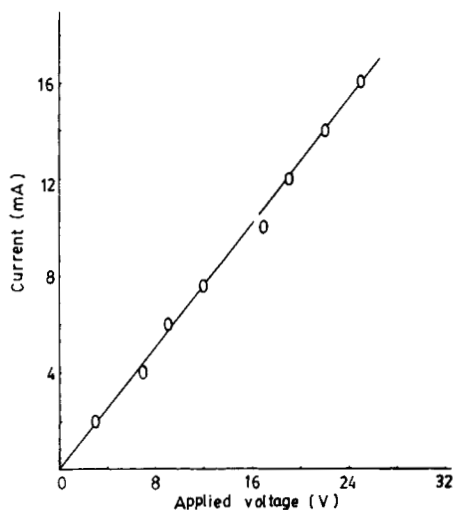
Figure 5   Increase of current level with applied voltage at the conducting cotton-fiber anode.

microelectrode, the current increases. After electrolysis when the electrode was removed, the growth of a deep green mass was indeed observed on the tip of the microelectrode. Figure 7 shows the chronoamperometric curve on the conducting silk microelectrode.

Cyclic Voltammograms

The voltammetric behavior of the solution of aniline (0.2 mol/L) in the aqueous solution of HBF_4
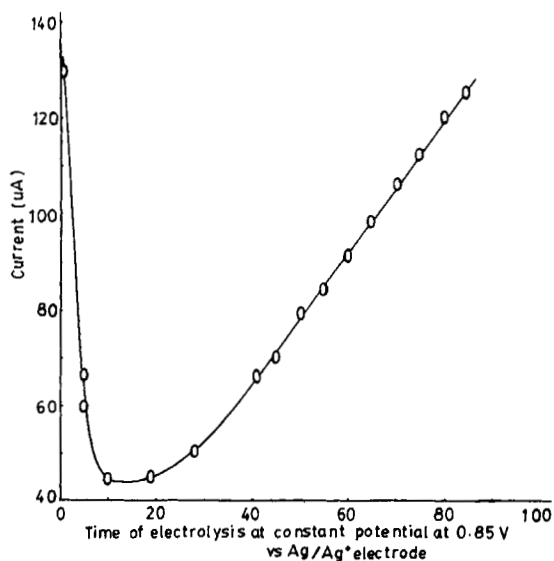

Figure 6   Chronoamperometric behavior during the electrochemical polymerization of aniline (0.2 mol/L) at the conducting microwool-fiber anode at +0.85 V vs. the Ag/Ag^+ electrode in the aqueous solution of HBF_4 (1.4 mol/L).
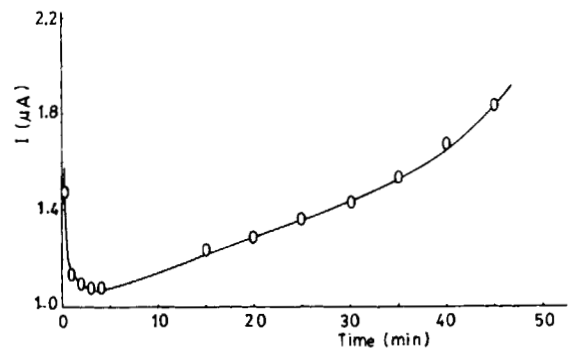

Figure 7   Chronoamperometric behavior during the electrochemical polymerization of aniline (0.2 mol/L) at the conducting microsilk-fiber anode at +0.85 V vs. the Ag/Ag^+ electrode in the aqueous solution of HBF_4 (1.4 mol/L).

(1.4 mol/L) was examined at the silk fiber microelectrode as the working electrode. Figure 8 shows the multiple cyclic voltammograms of the solution recorded in the potential range −0.4 to +1.2 V versus the Ag/Ag^+ electrode. As on the platinum microelectrode,[22] the redox peak currents gradually increase with the number of potential scans, indicating that the conducting polyaniline film formed on the surface of the fiber microelectrode and its thickness increase with the potential cycles. The cyclic voltammograms of polyaniline films on the conducting wool-fiber microelectrode were also recorded and pertinent results are presented in Figure 9. These redox peak currents are attributed to the redox of polyaniline intraconversion of the ben-
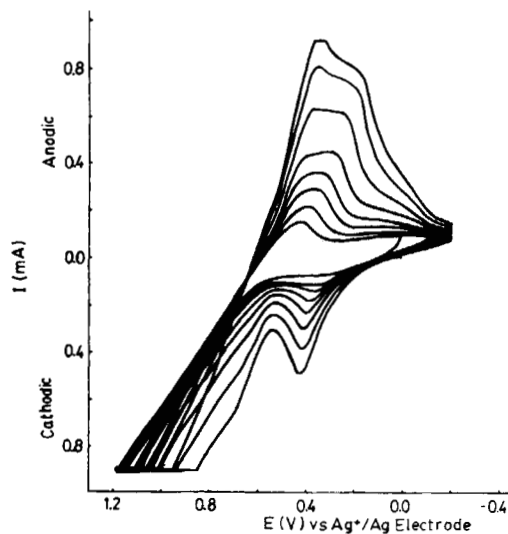

Figure 8   Multisweep cyclic voltammograms of the solution of aniline (0.2 mol/L) in an aqueous solution of HBF_4 (1.4 mol/L) at the tip of the conducting silk fiber acting as a microelectrode at 50 mV/s and 30°C.
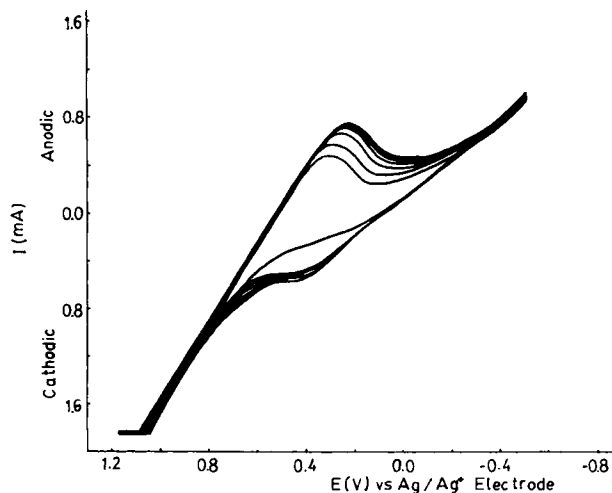
Figure 9   Multisweep cyclic voltammograms of the solution of aniline (0.2 mol/L) in the aqueous solution of HBF$_4$ (1.4 mol/L) at the tip of the conducting wool fiber functioning as a microelectrode at 50 mV/s at 30°C.

zenoid and quinoid structure.[17,22] The oxidation process is accompanied by the insertion of the anion (BF$_4^-$) to maintain the charge neutrality.[22,23] However, the cyclic voltammograms recorded on the fiber electrode differ from those on the nobel electrodes[22] such that redox waves at higher potentials such as +0.85 V are not seen. This is possibly due the loss of flexibility of the chain and hindrance to the mobility of dopants beyond 1 V.

IR Spectra

The IR spectra of the conducting polyaniline, silk, and silk-fiber composite of polyaniline were obtained and are shown in Figure 10. The IR of polyaniline [Fig. 10(I)] shows quinoid and benzenoid vibrational bands at near 1600 cm^{-1} (C—C stretching in the quinoid ring) and 1500 cm^{-1} (C—C stretching in

the benzenoid ring). The band at 1290 cm^{-1} suggests the salt formation between anion (BF$_4^-$) and protonated nitrogen atoms next to the quinoid ring. Analogous results of chemically prepared polyaniline were reported in the literature.[18]

The IR spectrum of raw silk fiber is shown in Figure 10(II). The band at 3300 cm^{-1} is due to the hydroxy group. The bands at 1750 and 1500 cm^{-1} correspond to the carboxyl and amide groups, respectively. Figure 10(III) shows the IR spectrum of silk-fiber–polyaniline composite. The conspicuous absence of absorption bands at around 3300, 1750, and 1500 cm^{-1} confirms the interaction between the polyaniline and silk. Polyaniline has a reactive —NH— group in the polymer chain flanked on either side of the quinoid ring. Hence the polyaniline can coordinate on the fiber surface through the reactive —NH— group. The IR spectra of the cotton and wool-fiber composites of polyaniline suggest similar interaction between the fibers and polyaniline. For the sake of brevity, the spectra are not shown here.

The electrochemical polymerization of aniline proceeds via radical cations formed by anodic oxidation of the monomer. Initially, the coupling of these radical cations generate oligomers in solution that chemically interact at the surface or interstices of the fiber wound around the anode. Finally, the polymer chain progression follows by coupling reaction to newly formed radical cations.[16,22,24] The oxidation potentials correspond to the following order[4]:

$$E^0_{monomer} > E^0_{dimer} > E^0_{oligomer} > E^0_{polymer}$$

Homogeneity in Fibers

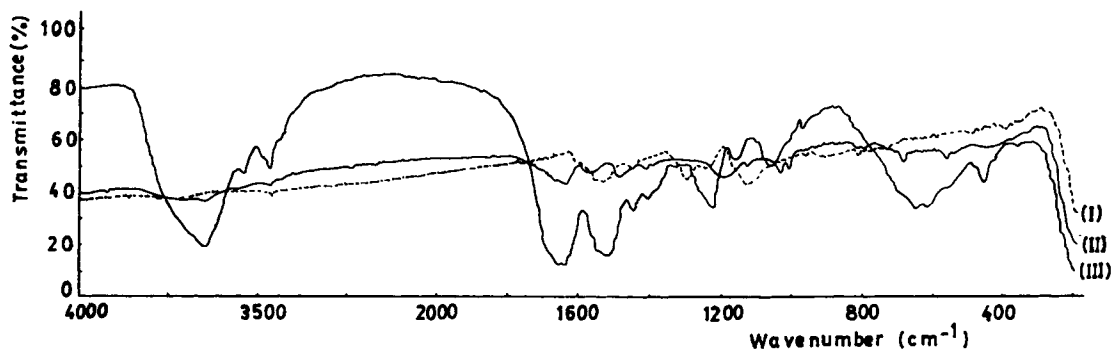The surface resistivity is roughly proportional to the length of the fibers (Fig. 11) indicating that the fiber

Figure 10   IR spectra of (I) polyaniline, (II) silk fiber, and (III) silk-fiber–polyaniline composite in KBr.
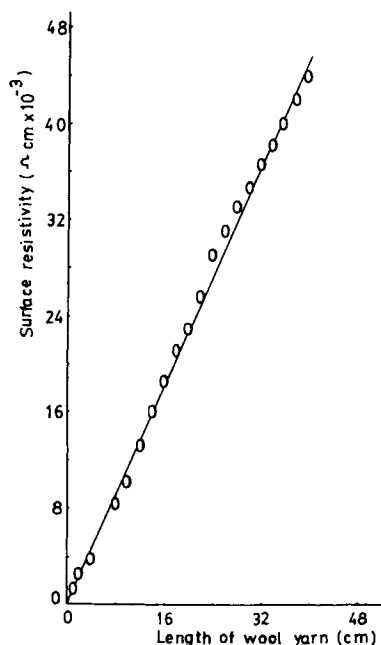
Figure 11   Resistivity (Ω cm) vs. fiber length (cm).

was uniformly grafted onto the polyaniline oxidized form. Because the standard oxidation potential of the polymer is less positive than that of the corresponding monomer, the polymer is always obtained under its oxidized (doped) form.[4]

CONCLUSION

In conclusion, we have shown that natural insulating fibers can be made conductive by the electrochemical technique, which may be an attractive feasible route to synthesize such fibers. These conducting fibers may exhibit the desirable characteristic of electromagnetic interference shielding as antistatic materials[2,16] and may possibly play an important role in this field.

REFERENCES

1. T. A. Skotheim, Ed., *Handbook of Conducting Polymers*, Vols. 1 and 2, Marcel Dekker Inc., New York, 1986.

2. M. Aldissi, Ed., *Intrinsically Conducting Polymers: An Emerging Technology*, Kluwer Academic Publishers, Dordrecht, 1993.

3. J. Ladik and A. K. Bakhshi, Eds., *Ind. J. Chem.*, **33A** (Special issue) (1994) [Entire issue].

4. J. Simonet and J. R. Berthelot, *Prog. Solid State Chem.*, **21**, 1 (1991).

5. M. G. Kunatzidic, *Conductive Polym.*, *Chem. Eng. News*, **68**, 36 (1990).

6. P. N. Prasad, Ed., *Frontiers of Polymer Research*, Plenum Press, New York, 1992.

7. S. Md. Rahmun and S. Maiti, *Eur. Polym. J.*, **20**, 475 (1990).

8. D. Macinnes and B. L. Funt, *Synth. Met.*, **25**, 235 (1988).

9. H. Masuda, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, 725 (1989).

10. D. K. Gagnon, J. D. Capistraw, F. E. Karasz, R. W. Lenz, and S. Antoun, *Polymer*, **28**, 567 (1987).

11. A. Andreatta, A. J. Huger, and P. Smith, *Polym. Commun.*, **31**, 275 (1990).

12. F. Garnier and G. Horowitz, *Makromol. Chem., Macromol. Symp.*, **8**, 159 (1987).

13. A. Nuzzal and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 83 (1984).

14. M. Aldissi, M. Hou, and J. Farrel, *Synth. Met.*, **17**, 229 (1987).

15. W. S. Huang and J. M. Park, *J. Chem. Soc., Chem. Commun.*, 856 (1987).

16. D. C. Trivedi and S. K. Dhawan, *Synth. Met.*, **59**, 267 (1993).

17. B. Zinger, S. Shkolnik, and H. Hocker, *Polymer*, **30**, 628 (1989).

18. Y. H. Park, S. H. Chol, S. K. Song, and S. Miyata, *J. Appl. Polym. Sci.*, **45**, 843 (1992).

19. S. N. Bhadani, S. K. Sen Gupta, and M. K. Gupta, *Ind. J. Fibre Textile Res.*, **18**, 46 (1993).

20. P. J. Kissinger and W. R. Heineman, Eds., *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker Inc., New York, 1984, p. 304.

21. F. Sadov, M. Korchagin, and A. Matetsky, Eds., *Chemical Technology of Fibrous Materials*, Mir Publishers, Moscow, 1973, p. 321.

22. S. N. Bhadani, M. K. Gupta, and S. K. Sen Gupta, *J. Appl. Polym. Sci.*, **49**, 397 (1993).

23. H. Daifuku, T. Kawagoe, T. Matsunaga, N. Yamamoto, T. Ohsaka, and N. Oyama, *Synth. Met.*, **41**, 2897 (1991).

24. P. Lang, F. Chao, M. Costa, and F. Garnier, *Polymer*, **28**, 668 (1987).