

Cyclic Voltammetry and Conductivity Investigations of Polyaniline

SURAJ N. BHADANI,* MANOJ K. GUPTA, and SUMANTA K. SEN GUPTA

Department of Chemistry, Ranchi University, Ranchi-834008, India

SYNOPSIS

The cyclic voltammograms of polyaniline prepared electrochemically were examined in the range -0.2 to 1.0 V vs. SCE in the presence and absence of aniline in the aqueous solution of HBF_4 . Cyclic voltammetry studies show that the polymeric film suffers degradation when the potential exceeds $+0.85$ V, and below this potential, it is quite stable. The redox reaction of the film is reversible. The polymeric film synthesized at low temperature and high acid concentration exhibits higher electronic conductivities. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyaniline synthesized by the chemical or electrochemical oxidation of aniline has been known for last several decades.¹⁻³ However, it is only recently that much interest has been shown in the polymeric product because it is stable with good electrical conductivity in oxidized and protonated forms and seems to be a viable material for many potential uses in electric and electronic devices.⁴⁻¹⁰ In the present study, we describe the cyclic voltammetry and conductivity investigations of polyaniline prepared electrochemically in the aqueous solution of aniline and HBF_4 .

EXPERIMENTAL

Materials

Aniline and water were purified by fractional distillation and middle fractions were collected. Aqueous HBF_4 (48%) was analytical grade and used as received. All solutions were purged with purified N_2 prior to use.

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. All electrical measurements were performed in a single-compartment three-electrode cell under a N_2 atmosphere. The working electrode was a platinum microelectrode; the counterelectrode, a platinum wire, and the reference electrode, a saturated calomel electrode that was isolated from the cell by a KCl salt bridge. The polymer films were grown galvanostatically on a platinum sheet of area 3.6 cm^2 at 0.85 V vs. SCE. The resistivity in ohm-cm of the electrochemically oxidized polymer film was determined using a high-vacuum tube voltmeter. An electronic comparator was used to measure the film thickness. Knowing the area and thickness of the film, conductivity in s cm^{-1} was calculated.

RESULTS AND DISCUSSION

Cyclic Voltammograms of Polyaniline Film in the Presence of Aniline

The voltammetric behavior of the solution of aniline (0.2 mol/L) in the aqueous solution of HBF_4 (1.4 mol/L) was examined. Figure 1 shows multiple-cycled voltammograms of the solution recorded in the potential range -0.2 and 1.0 V vs. SCE. The redox

* To whom correspondence should be addressed.

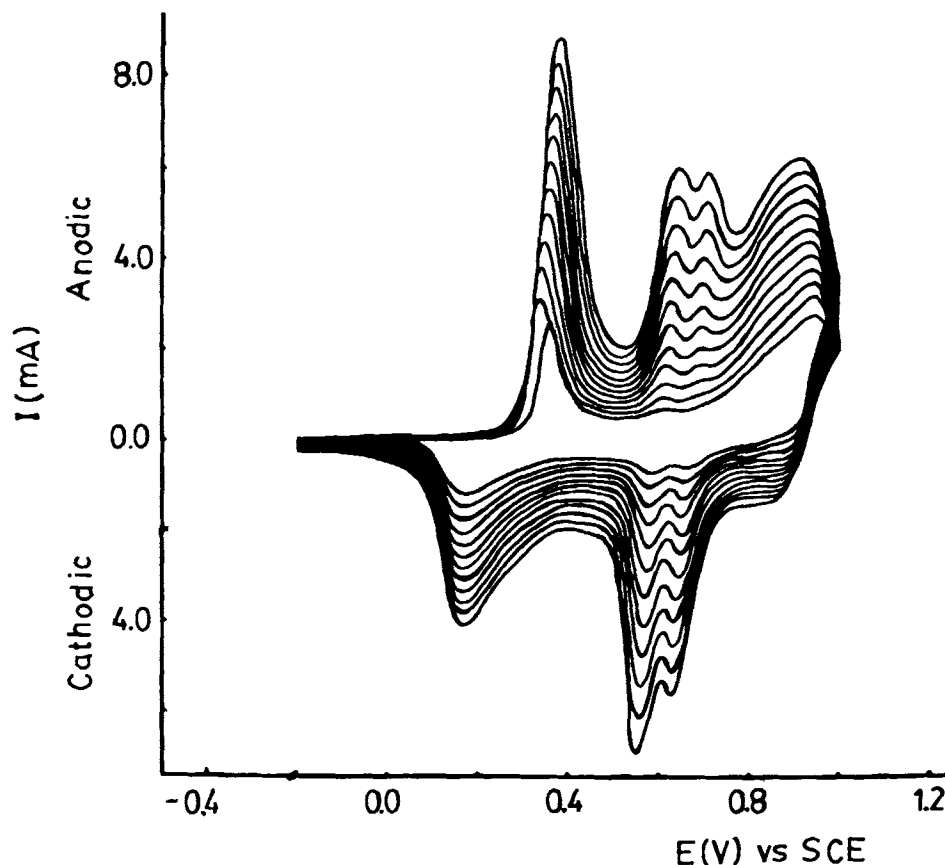


Figure 1 Multisweep cyclic voltammograms of polyaniline film on a Pt microelectrode in an aqueous solution of aniline (0.2 mol/L) containing HBF_4 (1.4 mol/L) at 50 mV/s and 30°C. The redox peak currents increase with the number of scans.

peak currents gradually increased with the number of potential scans, indicating that the conducting polymer film formed and its thickness increased with potential cyclings. All oxidation peaks shifted positively and, reduction peaks, negatively, with cycles. The middle redox peaks did not appear when the potential scan did not exceed 0.85 V, as shown in Figure 2. Therefore, the middle peak current is attributed to electroactive species formed by the partial degradation of the film. The magnitude of the middle redox peak currents decreased with decreasing acid concentration. Therefore, degradation of the film is dependent on the potential and electrolyte concentration. Genies et al.¹¹ also recorded the cyclic voltammograms of the solution of aniline in a concentrated solution of HF and reported that the middle redox peak currents were due to the solvation and desolvation phenomenon of the ion inserted, but our results confirm degradation of the film. Figure 3 shows voltammograms when the scan ranged between -0.2 and 0.5 V. The redox peak currents increase with the increase of scan rates. The anodic

peak currents are sharp and higher, showing that the polymer film is in the conductive state. On the other hand, the cathodic peak currents are smaller and broader than are the anodic peak currents, indicating the conversion of the polymer into an electrically insulating reduced state. The plot of anodic peak currents (data from the voltammetric curves of Fig. 3) is linear with the scan rate, as shown in Figure 4, suggesting that the redox reaction is quite reversible.

Cyclic Voltammograms of Polyaniline Film in Absence of Aniline

The green polyaniline film was deposited on the platinum microelectrode. The film was washed several times with distilled water and then immersed in an aniline-free aqueous solution of HBF_4 (1.4 mol/L). The cyclic voltammograms of the film were recorded and are presented in Figure 5. The redox peak in the first cycle is a little higher than on subsequent scans. The multicycle voltammograms confirm that the film is fairly stable without any severe

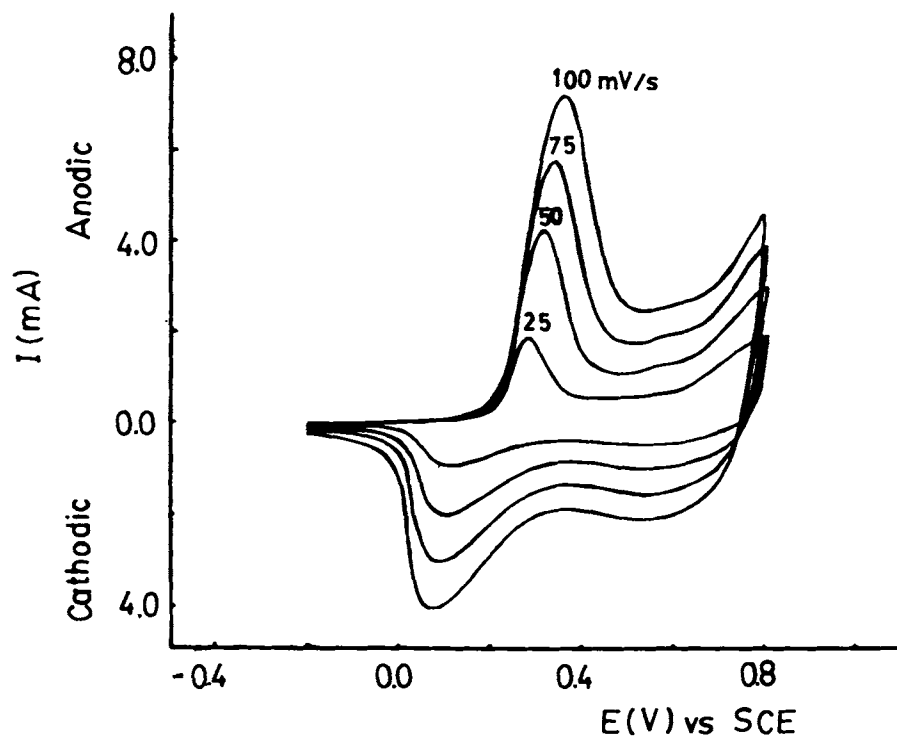


Figure 2 Cyclic voltammograms of polyaniline film on a Pt microelectrode in an aqueous solution of aniline (0.2 mol/L) containing HBF_4 (1.4 mol/L) at different scan rates.

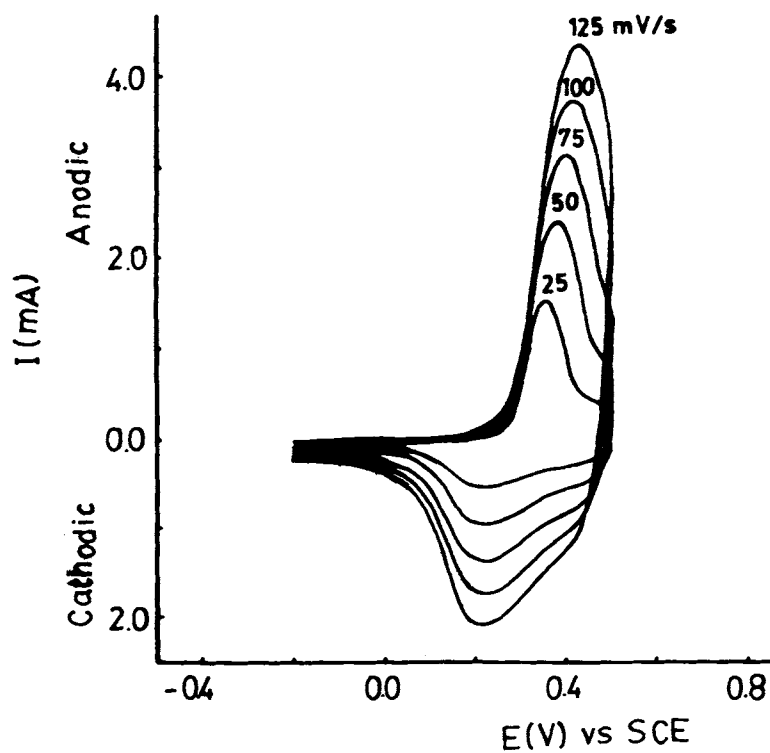


Figure 3 Cyclic voltammograms of polyaniline film on a Pt microelectrode in an aqueous solution of aniline (0.2 mol/L) containing HBF_4 (1.4 mol/L) at different scan rates.

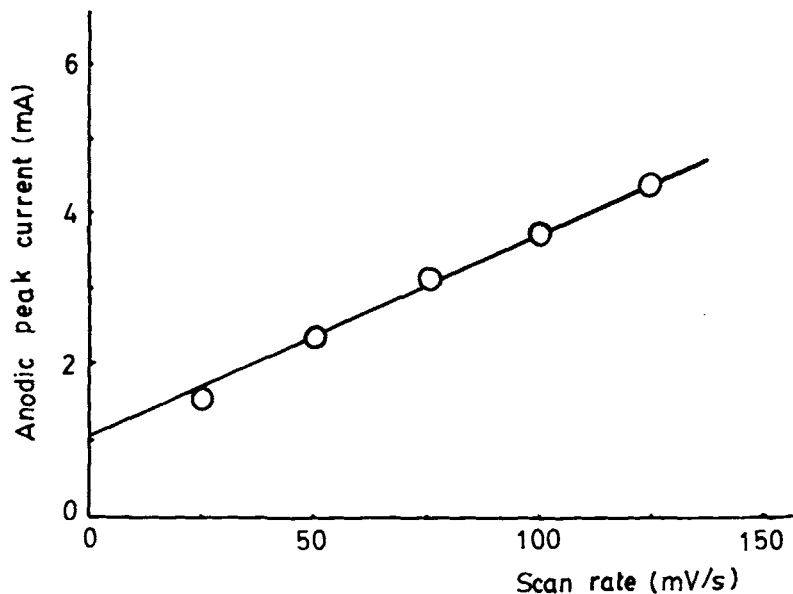


Figure 4 Plot of anodic peak current vs. scan rate.

film degradation. Figure 6 shows the cyclic voltammograms of the film at different scan rates when the scans were in the range -0.2 to 0.8 V. Like poly-

aniline film in the monomer solution, the plot of the anodic peak currents vs. scan rate is also linear, as is evident from Figure 7.

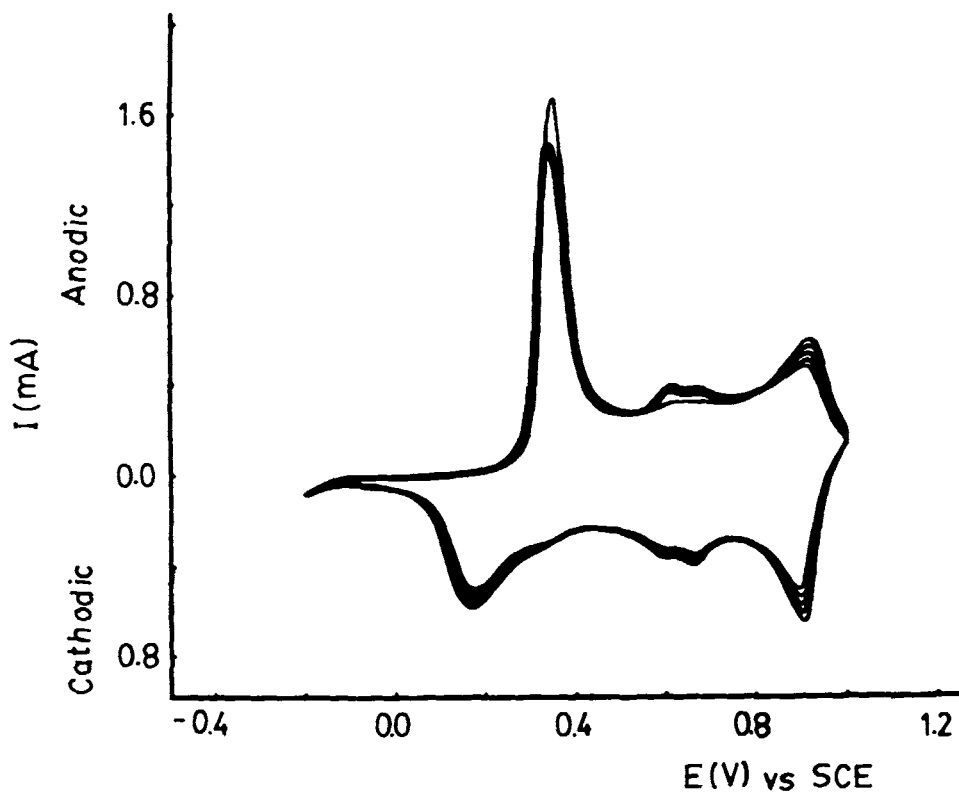


Figure 5 Multisweep cyclic voltammograms of polyaniline film on a Pt microelectrode in an aqueous solution of HBF_4 (1.4 mol/L) at 50 mV/s.

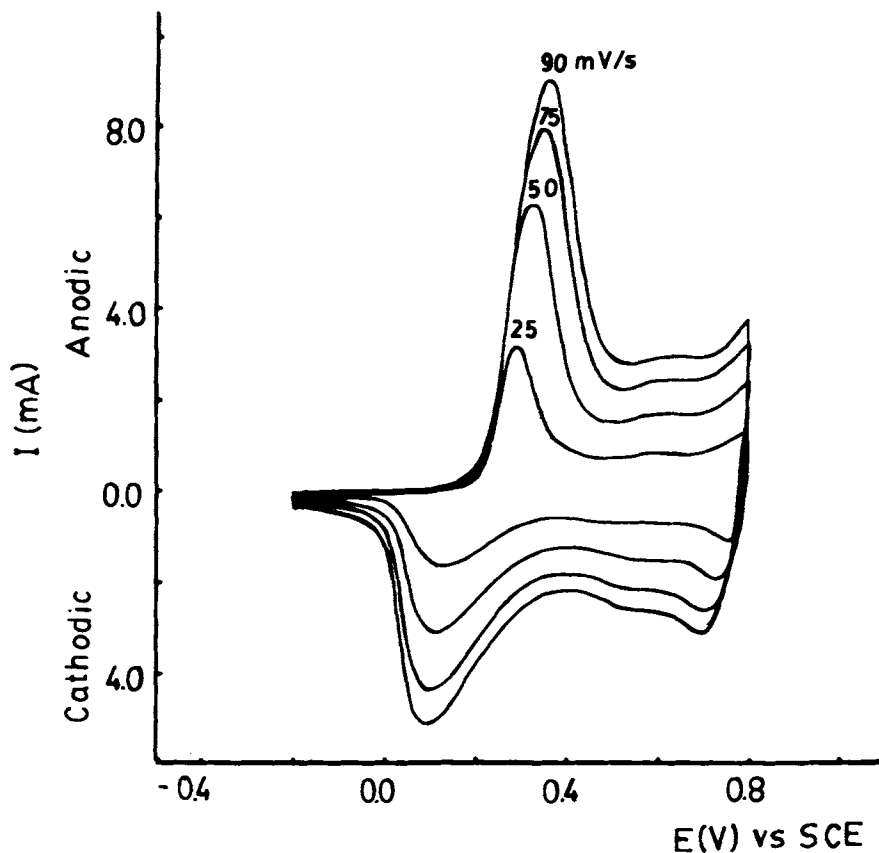
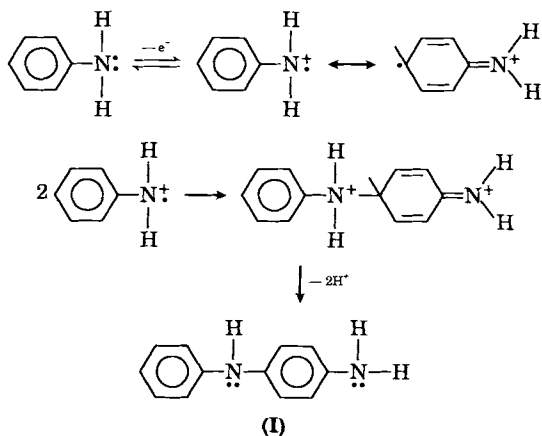


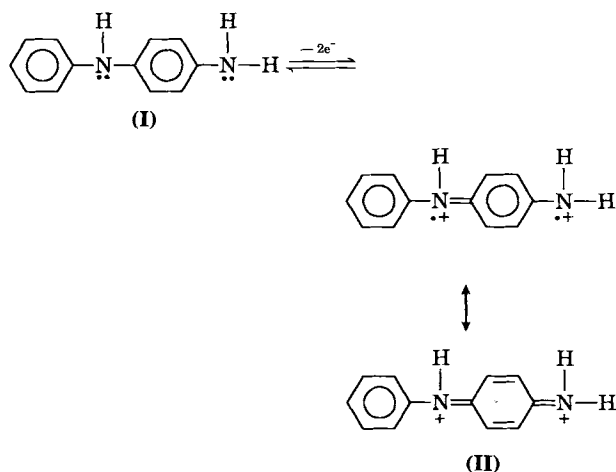
Figure 6 Cyclic voltammograms of polyaniline film on a Pt microelectrode in an aqueous solution of HBF_4 (1.4 mol/L) at different scan rates.

Mechanism of Redox Reaction

The electrochemical polymerization of aniline is believed to proceed via the cation radical. The anodic oxidation of aniline in the aqueous HBF_4 solution gives a radical cation that couples together in a head-to-tail manner to form *p*-aminodiphenylamine (I), according to the following scheme^{2,11}:

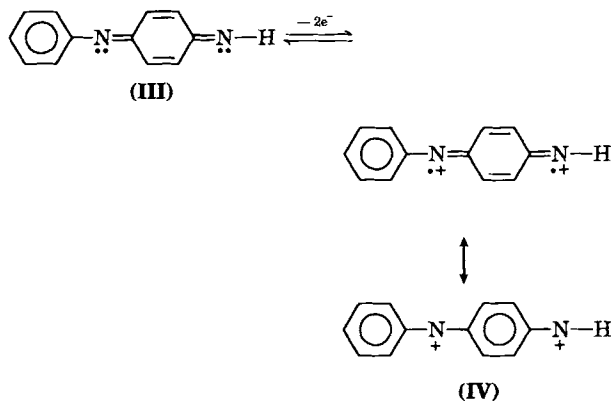


(I) is oxidized at ca. 0.38 V vs. SCE:

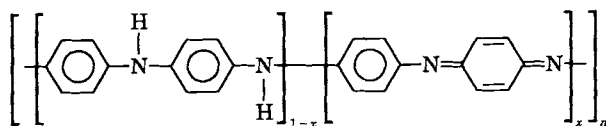


The oxidation process is accompanied by the insertion of anion (BF_4^-) to maintain the charge neutrality.¹² The above oxidation process gives rise to the anodic current peaks at ca. 0.38 V, as illustrated in Figure 1.

The further expulsion of 2H^+ from quinone dication (II) yields quinone diimine (III), which becomes oxidized at a potential of ca. 0.92 V vs. SCE:



The oxidation wave at 0.92 V in Figure 1 is due to this oxidation step. The process is repeated with two electrons and 2H^+ involved in each addition step to form polyaniline, which has been reported to have the following idealized structure⁶:



with $x = 0$ representing the fully reduced form of the polymer; $x = \frac{1}{2}$, polyemeraldine; and $x = 1$, fully oxidized polyaniline. The relative content of the benzenoid and quinoid forms depends on the acid

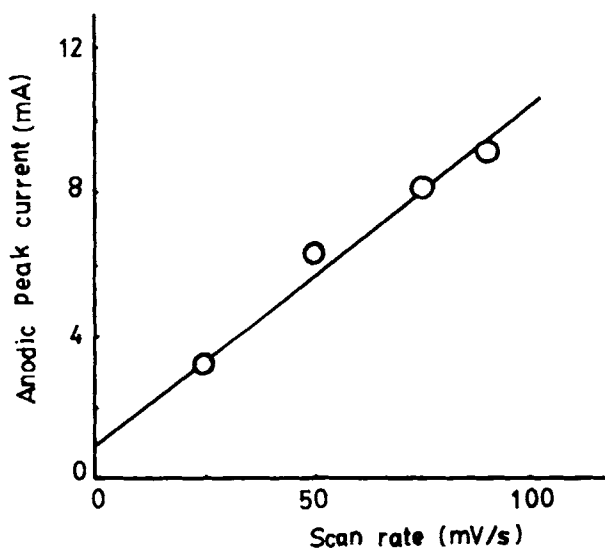


Figure 7 Plot of anodic peak current vs. scan rate.

Table I Conductivity of Polyaniline Formed at 0.85 V vs. SCE^a

pH	Temperature (°C)	Conductivity (s cm ⁻¹)
0.8	30	220
1.5	30	85
2.2	30	69
2.8	30	57
2.8	15	92
2.8	4	175

^a Using a fixed concentration of aniline (0.2 mol/L) and different concentrations of aqueous solutions of HBF_4 at different polymerization temperatures.

concentration and the degree of oxidation of the polymer.

Conductivity of Polyaniline

The conductivities of polyaniline films grown galvanostatically on a platinum sheet of area 3.6 cm² at +0.85 V vs. SCE in the aqueous solution of aniline and HBF_4 at different pH and different temperatures were determined. The results are summarized in Table I. The conductivity of the film increases with the decrease of solution pH and polymerization temperature used to synthesize the film. The polyaniline may exist both in the form of an emeraldine base and emeraldine salt.^{6,7} The latter is found to be more electroactive and conductive and its fraction increases with increasing concentration of the acid. Thus, the observed high conductivity, shown in Table I, is due to the emeraldine salt. The polymerization at lower temperature would yield polymer film with a greater conjugation length and, thereby, a higher conductivity.

The financial support of the Department of Science and Technology, New Delhi, India (Project No. SP/G1/G00/88), to carry out this work is gratefully acknowledged.

REFERENCES

1. H. Lethely, *J. Chem. Soc.*, **15**, 161 (1862).
2. D. M. Mohilner, R. N. Adams, and W. J. Agersinger Jr., *J. Am. Chem. Soc.*, **84**, 3618 (1962).
3. J. Bacon, and R. N. Adams, *J. Am. Chem. Soc.*, **90**, 6596 (1968).

4. T. Kobayashi, M. Yoneyama, and H. Tamura, *J. Electroanal. Chem. Interfacial Electrochem.*, **161**, 419 (1984).
5. J. C. Chiang, and A. G. MacDiarmid, *Syn. Met.*, **13**, 193 (1986).
6. A. P. Monkman, D. Bloor, G. C. Stevens, and J. C. H. Stevens, *J. Phys. D. Appl. Phys.*, **20**, 1337 (1987).
7. M. Kalaji, L. Nyholm, and L. M. Peter, *J. Electroanal. Chem.*, **313**, 271 (1991).
8. A. F. Diaz, J. F. Rubinson, and H. B. Mark Jr., *Adv. Polym. Sci.*, **84**, 114 (1988).
9. K. M. Choi, E. J. Lee, J. W. Park, and K. H. Kim, *J. Appl. Polym. Sci.*, **42**, 2129 (1991).
10. T. Matsunaga, H. Daifuku, T. Nakajima, and T. Kawagoe, *Polym. Adv. Technol.*, **1**, 33 (1990).
11. E. M. Genies, A. A. Syed, and C. Tsintavis, *Mol. Cryst. Liq. Cryst.*, **121**, 181 (1985).
12. H. Daifuku, T. Kawagoe, T. Matsunaga, N. Yamamoto, T. Ohsaka, and N. Oyama, *Syn. Met.*, **41**, 2897 (1991).

Received April 10, 1992

Accepted September 13, 1992