Electrochemistry and Characterization of Conducting Poly(3-methylthiophene) Electrodes Containing Ferrocene Moieties[#]

Ahmed Galal,* Nada F. Atta, Soher A. Darwish, and AbuBakr M. Abdallah

Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

(Received December 9, 1996)

Ferrocenium hexafluorophosphate was used as the supporting electrolyte during the electropolymerization of poly(3-methylthiophene) and poly(1-methylpyrrole). The electrochemical behavior of the resulting polymer electrode indicated the incorporation of the ferrocenium moiety in the polymer film. The appearance and the magnitudes of the voltammetric anodic and cathodic current peaks of the ferrocenium/ferrocenium$^+$ couples were influenced by: (I) the method of ferrocene incorporation into the polymer film, (ii) the concentration of both the ferrocenium and the supporting electrolyte used during the polymer deposition, (iii) the thickness of the polymer film, and (iv) the type of electrolyte used during the polymer film electrochemical characterization. FTIR experiments were performed on polymer films containing the ferrocenecarbaldehyde. The results were compared to the spectrum of ferrocene-free film; the comparison indicated the incorporation of the ferrocene moiety within the polymer film. The structural aspects of the polymer films were studied using XPS experiments, which indicated the presence of iron for films containing ferrocenium. The morphological aspects of the films were studied by SEM technique which indicated that "ferrocenium-free" film morphologies are similar to those of "ferrocenium-containing" films. A model for the charge transfer within the polymer film is described. The method described in this work resulted in a stable ferrocenium-bound to the polymeric film.

Studies of the electrochemical behavior of electrodes modified with polymeric materials are one of the most rapidly growing and advancing areas of modern electrochemistry.[1] This is due to both the stability of these films produced electrochemically and to their interesting electrochromic and conducting properties.[2,3] The "unique" advantage of the electrochemical synthesis is that this procedure leads directly to the conductive polymers in a single-stage process without the isolation of the basic structure. The selective response of this class of polymers towards dissolved ions has made them useful in various applications as a new and important class of ion and molecular sensors.[4] Another important feature of the electrosynthesis of conducting polymers is the incorporation of the ions of the supporting electrolyte into the film during its formation. The electrical and electrochemical properties of the film are affected by the nature of electrolytic species employed.[5,6] The results obtained by the authors[5,6] showed that the nature of the cation affected essentially the behavior of the polymer film during the charge-discharge processes. Thus, the positive charge on the chain of the conducting polymer is neutralized by the doping anions. On the other hand, cations of the supporting electrolyte will be loaded into the polymer film upon switching its potential to a sufficiently negative value. The incorporation of electroactive anions, such as tetrasulfonated iron phthalocyanines and ferro-/ferricyanide redox couple, into conducting polymer films was reported in the literature.[7—9] However, similar attempts to

incorporate electroactive cations into the conducting poly(heteroarylene)s are rather few. Recently, several research groups described the electrochemical behavior and applications of ferrocene-modified polymer electrodes.[10—16] The authors included in their studies different polymeric systems such as phosphazenes.[11] However, the methods described by the authors for the ferrocene incorporation into the polymer film were primarily adopted for the poly(silane) and poly(phosphazene)s. Moreover, chemical modification of the heteroarylene monomer could be time consuming or rather difficult to achieve.[17]

In this work we report the electrochemical polymerization of 3-methylthiophene and the incorporation of ferrocene moieties in the polymer film. We studied different polymerization conditions and their effects on the resulting polymer electrodes and their electrochemical characteristics. Moreover, we will describe the structure of the polymer film using IR and XPS spectroscopies. The morphology of the resulting film was examined by the SEM technique. The electrochemical behavior of the poly(3-methylthiophene) electrode containing the ferrocene moieties (P3MT/Fc) will be compared to that of the P3MT electrode.

Experimental

3-Methylthiophene, ferrocenecarbaldehyde (FcCHO), tetrabutylammonium tetrafluoro-borate (TBATFB), tetrabutylammonium hexafluorophosphate (TBAHFP), ferrocenium hexafluorophosphate (FcPF), potassium hexacyanoferrate(III), and HPLC grade acetonitrile (AcN) were purchased from Aldrich (Milwaukee, WI, USA). Other chemicals used in this work were obtained from Fisher

---

1770 *Bull. Chem. Soc. Jpn., 70, No. 8 (1997)*

Conducting Polymer Electrodes Containing Ferrocene

Scientific (USA) and were used without further purification. Distilled deionized water was used to prepare aqueous solutions.

A platinum disk electrode (apparent area, 0.03 cm^2) obtained from Bioanalytical Systems, Inc. (West Lafayette, IN, USA) was used for electropolymerizing the film in a three electrode setup. P3MT/Fc films were formed using the double potential step technique by applying a potential of 0.8 V for 30 s and then stepping the potential to 2.4 V for 5 s. The electrolyte consisted of 0.08 M each of P3MT and FcCHO, and 0.1 M TBATFB (or TBAHFP) (1 M = 1 mol dm^{-3}) in AcN. Films of P3MT were formed by applying a constant potential of 1.7 V to the Pt working electrode for 30 s. In order to incorporate the ferrocenium into the polymer film, an alternative procedure was used; P3MT films were formed as described previously, followed by holding the film at a constant applied potential of -0.5 V in an electrolytic solution containing 0.05 M FcPF/AcN for 20 min. The polymer thus formed was rinsed thoroughly with water and dried in air for further usage. Polymer films were prepared for surface characterization according to the above-mentioned procedure using a special holder which contained a 1 cm^2 Pt electrode sheet. The film was dried for 24 h prior to further experiments.

Electrochemical experiments were performed using a PRT 40-1X potentiostat, and a GSTP3 function generator, and the data were recorded using a TRP XY/Yt recorder supplied by Tacussel Electronics (France) or a BAS-100 electrochemical analyzer (BAS, Inc., USA). The working electrode was in the form of a Pt disc with an apparent surface area of 0.03 cm^2; the auxiliary electrode was a platinum flag (2×2 cm^2) and all potentials were recorded versus a saturated Ag/AgCl reference. All electrochemical measurements were performed in a conventional one compartment three-electrode cell. Some cyclic voltammetric measurements were collected using a CMS 100 electrochemical system (Gamry Instruments Inc., USA). The CMS 100 system was connected to a PC where data were collected, processed and analyzed using the CMS 100 system data analysis software. Electron spectroscopy for chemical analysis (ESCA) was performed using the Perkin–Elmer ESCA-5300 Spectrometer with a pass energy of about 25 eV ($\Delta E = 0.5$ eV). A Cambridge Stereoscan 600 instrument was used to obtain scanning electron micrographs (SEM) of the polymer films, and a Burleigh Instruments, Inc. scanning tunneling microscope was used along with "True Image" software to produce surface morphological images. IR experiments were performed using a Nicolet Impact 400 FTIR instrument (Nicolet, Inc., USA). All film conductivities were measured using a four-point probe unit.[18]

Results and Discussion

P3MT Films. Double potential step experiments were carried out on polished Pt in AcN-containing 0.05 M 3-methylthiophene, 0.05 M FcPF and 0.10 M TBAHFP. Figure 1A shows the *I–t* transient curve from an experiment where the potential was pulsed from -0.5 V to a value of $+1.7$ V. When the potential reaches a value of $+1.7$ V, the current increases rapidly (part bc), drops slightly (after point c) and increases with a different slope (part cd) in the following minutes, as can be depicted from Fig. 1A. The first part of these results (part bc) are in good agreement with those reported earlier by Tourillon and Garnier.[19] However, the second part of the curve (part cd) of Fig. 1A is different from the results obtained by these authors,[19] who found a stabilization in the same region of the curve. From the data shown in Fig. 1A it can be
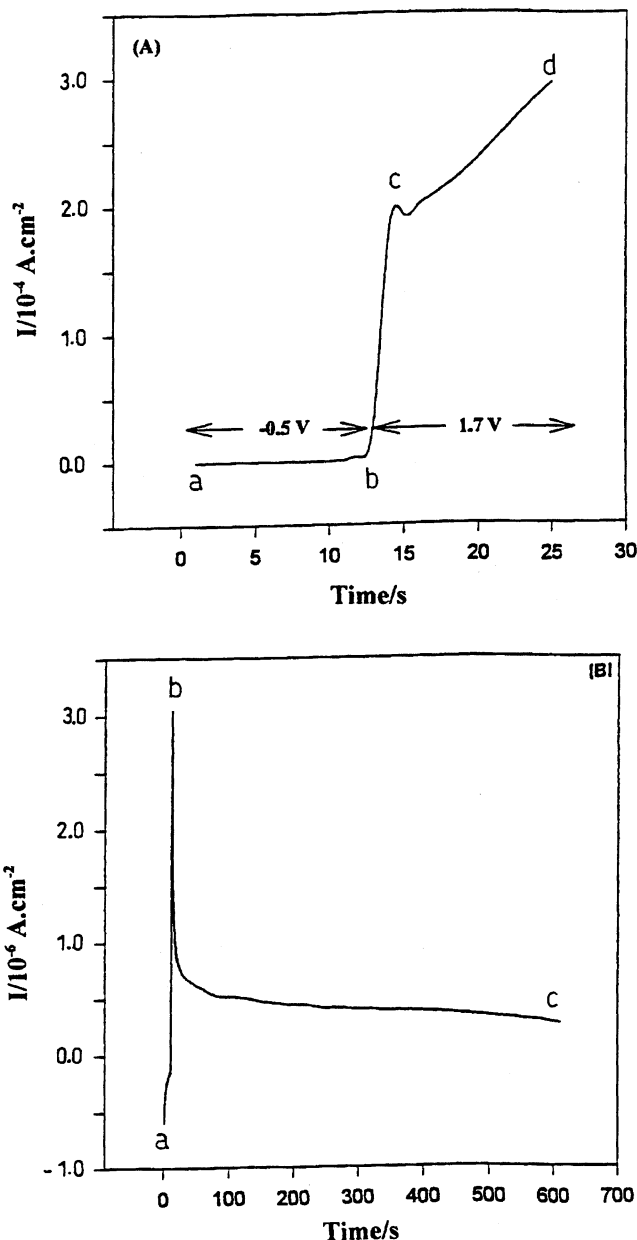

Fig. 1. (A)*I–t* transient curve for 0.05 M 3MT, 0.05 M FcPF in 0.10 M TBAHP/AcN. $E_i = -0.5$ V, $E_f = +1.7$ V. (B) *I–t* transient curve for the polymer filmed formed under the same conditions as in Fig. 1A. Electrolyte is 0.10 M TBAHP/AcN.

seen that a well-defined transient is obtained when analyzing the rising part of the *I–t* curve; an excellent fit to a linear *I–t*^{2} relationship was obtained. Therefore, a three-dimensional growth of the polymer phase is expected, with a possible incorporation of the ferrocenium moieties within the polymer film which catalyzes its further growth. The polymer film thus obtained was adherent to the surface of the electrode and its thickening was controlled by diffusion from the solution. Figure 1B shows the *I–t* transient in 0.01 M TBAHFP for the polymer film formed under the same conditions as in Fig. 1A. The response passes through a peak and falls sharply to reach a steady state current at longer times. In this case the polymer

transforms from the reduced insulating form to the oxidized conducting form. It was indicated in the literature[20,21] that a substantial pseudocapacitive current must flow to charge the double layer at the quasimetallic interface formed at positive potential values. This behavior is a typical indication of the charging–discharging process predominating at the polymer surface when it is cycled within the polymer redox potentials.

P3MT/Fc Films.   Three methods were compared for incorporating the ferrocenium moieties within the polymer film: (i) polymerization of the 3MT, as described above in the presence of 0.05 M of FcCHO/AcN; (ii) applying the FcCHO or FcPF onto the P3MT surface by the spin coating technique; or (iii) the optimum conditions for incorporating the ferrocenium within the polymer film were to hold the polymer film (formed under the same conditions as in Fig. 1A) at a constant applied potential of −0.5 V for 30 min in 0.05 M FcPF/AcN. Both methods (i) and (ii) were not reproducible and the lifetime of the resulting catalytic effect (which is manifested by an increase in the current signal measured) due to the ferrocenium ion within the polymer film was relatively short. Figure 2A shows the cyclic voltammogram of the P3MT/Fc film electrode in 1 mM $[Fe(CN)_6]^{3-/4-}$ using 0.1 M H_2SO_4 as the supporting electrolyte. The film thickness was estimated roughly from the charge passed during the electrosynthesis step; a typical thickness for the P3MT is 0.2 μm. The potential window of the cyclic voltammogram of Fig. 2A shows two pairs of peaks; the first pair at 0.08 and 0.12 V corresponds to the redox ions Fc/Fc$^+$, and the second appeared at 0.28 and 0.41 V, which could be related to the redox ions $[Fe(CN)_6]^{3-/4-}$ in solution. The oxidation

of the polymer film itself is expected to take place at potential values higher than 0.50 V.[21] Thus, the observed rise in the anodic current, after the second peak (peak c), could be attributed to the corresponding oxidation of the polymeric film. A large imbalance of anodic and cathodic charges for the P3MT/Fc electrodes was noticed; this was also reported for the P3MT films earlier.[5] The remarkable property of the poly(thiophene)s over other classes of poly(heteroarylene)s such as poly(pyrrole)s is the stability of both their oxidized conducting and neutral undoped forms,[22] especially to the presence of oxygen. Therefore, unlike poly(1-methylpyrrole) (PNMP), P3MT/Fc retained its electrochemical activity when exposed to oxygen, as will be indicated later.

As mentioned above, the ferrocenium ion of the supporting electrolyte used in preparing the corresponding P3MT/Fc st was injected into the P3MT film as its potential became more negative. Thus, the ferrocenium is reduced under this applied negative potential. However, for the purpose of gaining neutrality of the polymer film (which is negatively charged), the Fc$^+$ will be incorporated first into the film prior to its reduction. Another evidence of the incorporation of the ferrocenium moiety into the film is depicted in Fig. 2B, which shows the repeated cycling of the P3MT/Fc electrode in 0.1 M sulfuric acid for one hour. Three conclusions could be drawn from the data of the cyclic voltammogram of Fig. 2B: (i) the reversibility of the response is maintained in the absence of the redox couple ($[Fe(CN)_6]^{3-/4-}$) from the solution, indicating the presence of another(i.e Fc/Fc$^+$), which is highly reversible at the surface of the electrode; (ii) the cyclic voltammogram shows a high stability after cycling for
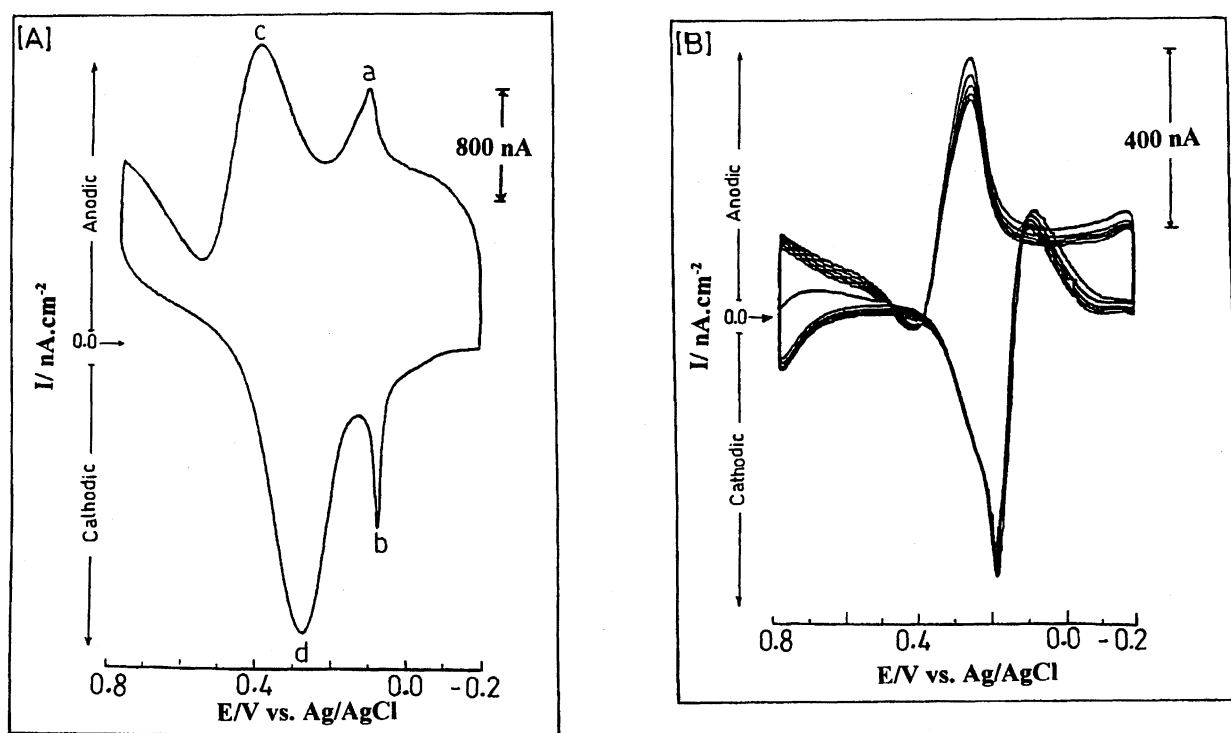

Fig. 2.   (A) Cyclic voltammogram of P3MT/Fc film electrode in 1.0 mM $[Fe(CN)_6^{3-/4-}]$ in 0.1 M H_2SO_4. Scan rate 50 m V s^{-1}.
(B) P3MT/Fc electrode repeatedly cycled in 0.1 M H_2SO_4 for one hour. Scan rate 50 mV s^{-1}.

a relatively extended period of time, which could be related to a chemisorbed redox species at the electrode surface; and (iii) the imbalance of the anodic and cathodic charges persists on continuous cycling and also shows some crossover effects which could be attributed to the presence of some Fc/Fc$^+$ couples imperfectly bound to the polymer film. The redox process at the electrode surface can be expressed in the following way:

$$P3MT^*/Fc^+ + e^- \rightleftharpoons P3MT^\otimes/Fc \qquad (1)$$
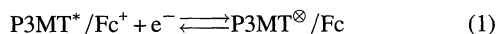
(For this cycling window, the potential limits did not reach the expected complete oxidized or reduced states. Thus, P3MT* is partially oxidized and P3MT$^\otimes$ is partially reduced). It could also be observed from the cyclic voltammetric data that the electron transfer occurs through the polymer film at potentials well negative of its "completely" doped (oxidized) state, where the film becomes highly conducting.[23] An explanation of such a phenomenon can not be provided at this stage of the work. Similar observations were previously reported in the literature.[24,25]

Effect of [Fe(CN)$_6$]$^{3-/4-}$] Concentration. In order to illustrate the catalytic effect of the incorporated Fc moiety within the P3MT film electrode and its contribution to the magnitude of the current signal, we conducted a series of experiments in which we varied the corresponding [Fe(CN)$_6$]$^{3-/4-}$ concentration in solution. Two independent techniques were used; CV (data not shown) and square wave voltammetry (SWV). The P3MT/Fc electrode was prepared as described previously, and the concentration of the [Fe(CN)$_6$]$^{3-/4-}$ in solution was varied between 5.0×10^{-5} M and 5.0×10^{-3} M. The experimental conditions for the SWV were as follows: initial potential 0.0 V, final potential 0.7 or 0.8 V, sample width amplitude of 25 mV, frequency of 15 Hz, and a step potential of 4 mV. Figure 3 shows the SWVs of the P3MT/Fc in (a) 5.0×10^{-5} M, (b) 1.0×10^{-4} M, and (c) 1.0×10^{-3} M [Fe(CN)$_6$]$^{3-/4-}$, respectively. From the data depicted in Fig. 3, we can draw the following conclusions: (i) the general shapes of the SWVs did change upon changing the [Fe(CN)$_6$]$^{3-/4-}$ concentration; (ii) the first anodic peak is due to the redox charge transfer of the Fc/Fc$^+$ couple, which was retained for all concentrations used; this observation should indicate a chemically adsorbed redox couple that is capable of charge mediation; (iii) the position of the redox peaks for the surface and the solution redox couples shifted slightly, as did their corresponding peak separations (ΔE); and (iv) the large current increase at the very positive end of the SWV illustrates the initiation of the oxidation of the P3MT film and its reduction. On the other hand, Fig. 4 shows the repeated cyclic voltammograms (200 cycles) of 5.0×10^{-3} M [Fe(CN)$_6$]$^{3-/4-}$ at the P3MT/Fc electrode. Two important observations can be gained from Fig. 4: (i) only one pair of redox peaks appears, and (ii) the peaks are sharp and similar to the first couple of peaks shown in Fig. 2A. The last two observations could be explained by assuming that the total concentration of Fc in the polymer film, which constitutes the active site for charge mediation (see the fol-
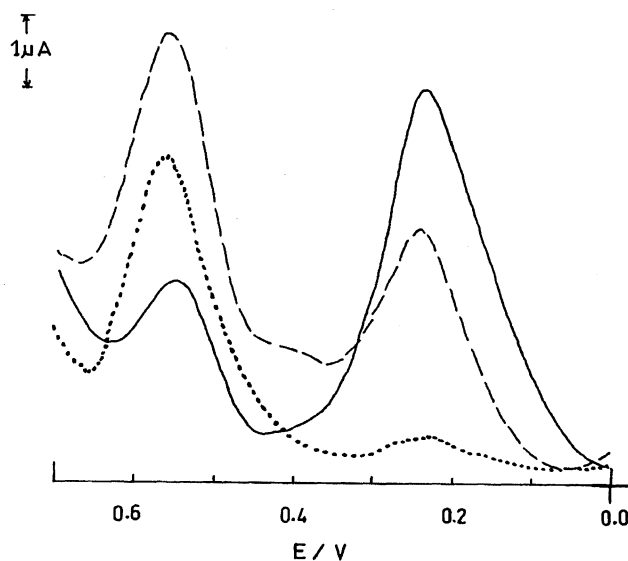
Fig. 3. Square wave voltammogram of P3MT/Fc film electrode in 0.1 M H$_2$SO$_4$ (supporting electrolyte). $E_i = 0.0$ V, $E_f = 0.7$ V, amplitude 25 mV, frequency=15 Hz, $\Delta E = 4$ mV. 5.0×10^{-5} M [Fe(CN)$_6$$^{3-/4-}$] (——), 1.0×10^{-4} M [Fe(CN)$_6$$^{3-/4-}$] (- - -), 1.0×10^{-3} M [Fe(CN)$_6$$^{3-/4-}$] (····).

Fig. 4. Repeated cyling of P3MT/Fc film electrode in 5.0×10^{-3} M [Fe(CN)$_6$$^{3-/4-}$]/0.1 M H$_2SO_4$. 200 cycles, scan rate 50 mV s^{-1}.
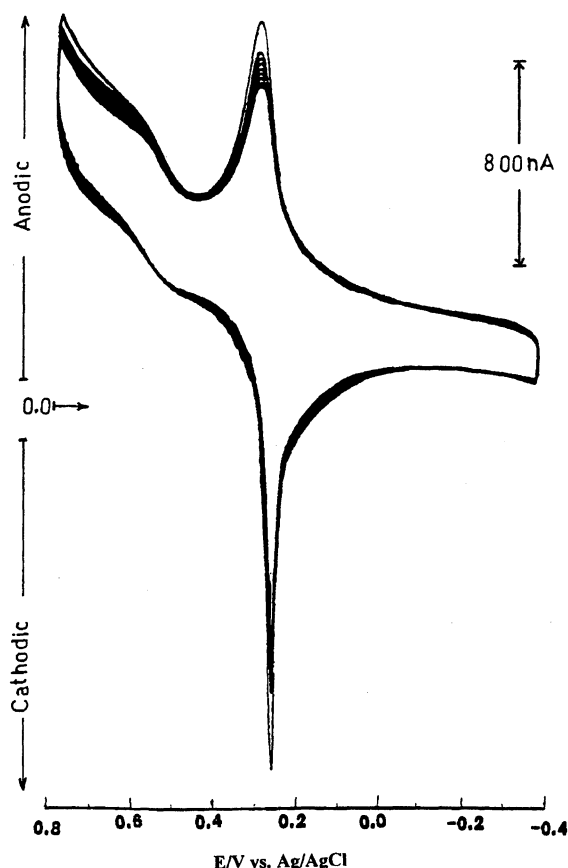
lowing section); is in the range of 1.0×10^{-3} mol L^{-1}.[26—28] Therefore, when the concentration of the redox species in the solution exceeds that within the film, the charge transfer due

A. Galal et al.

*Bull. Chem. Soc. Jpn., 70, No. 8 (1997)* 1773

to the Red/Ox couple with the Fc/Fc$^+$ will predominate, when compared to that due to their diffusion within the polymer film, as will be explained in the following section.

**Mechanism of Charge Transport in the P3MT/Fc.** The mechanism of the charge transfer will be discussed on the basis of the following assumptions: (i) the polymeric film on the electrode surface is "conducting" when it is in the oxidized state; (ii) the P3MT film can be reversibly oxidized and reduced according to:

$$P3MT + A^- \rightleftharpoons P3MT^+A^- + e^- \tag{2}$$

$$P3MT^+A^- + A^- \rightleftharpoons P3MT^{2+} (A)_2{}^{2-} + e^- \tag{3}$$

P3MT being the neutral polymer, P3MT$^+$ and P3MT^{2+} the cationic sites, and A$^-$ the anion in solution; and (iii) redox couples in solution can be reversibly oxidized and reduced at the polymer electrode surface,

$$Red + P3MT^+ \rightleftharpoons Ox + P3MT \tag{4}$$

$$Red + P3MT^{2+} \rightleftharpoons Ox + P3MT^+ \tag{5}$$
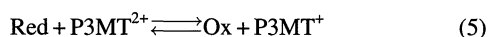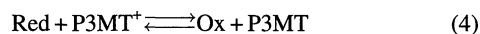
where Red and Ox are the reduced and oxidized forms of the given species in the bulk solution. Now, we should consider the redox reaction involving the Fc incorporated into the P3MT and designated by P3MT/Fc. For simplicity we will write the reaction as:

$$Red + P3MT/Fc^+ \rightleftharpoons Ox + P3MT/Fc \tag{6}$$
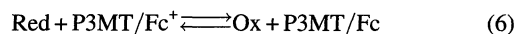
In redox polymeric systems, the rate-determining step is when the charge migrates, or rather hops, between redox sites.[29,30] Moreover, the counter-anion charge transport will not affect the interchain hopping of the charge.[31,32] The incorporation of a redox system, such as Fc/Fc$^+$, within the polymer matrix should result in an increase in the electronic conduction and, consequently, the film electronic conduction will be relatively higher compared to that of the counter anions. Therefore, treating the polymer electrode in the presence of the Fc/Fc$^+$ as a porous film[33] will not be applicable here. Thus, the total current, I_T, will result from the contribution of the following components: (i) the current due to the charge exchange of the couple Red/Ox at the Pt substrate, $I_{Red/Ox}$; (ii) the catalytic current due to the charge transfer between the couple Red/Ox and the polymer oxidized states (as in equilibria 4 and 5), I_{CAT}; (iii) the current due to the reversible redox reaction of the polymer film (as in equilibria 2 and 3), $I_{Red/Ox}^{POL}$; and (iv) the charging/discharging current of the electrical double layer (for both the polymer/Pt and polymer/solution interfaces), I_{dl}. Thus,

$$I_T = I_{Red/Ox} + I_{CAT} + I_{Red/Ox}^{POL} + I_{dl} \tag{7}$$

in the case of P3MT electrode. On the other hand, when the Fc/Fc$^+$ couple is introduced in the polymer film, the current increased due to the following additional contributions: (i) the catalytic current due to the charge transfer between the couple Red/Ox and the Fc-containing polymer oxidized states (as in equilibrium 6), I_{CAT}^{Fc}; and (ii) the current due to the

reversible redox reaction of the P3MT/Fc polymer film (as in equilibrium 1), $I_{Red/Ox}^{POL/Fc}$. Therefore, in the case of the P3MT/Fc the total current, I_T, is given by:

$$I_T = I_{Red/Ox} + I_{CAT} + I_{Red/Ox}^{POL} + I_{dl} + I_{CAT}^{Fc} + I_{Red/Ox}^{POL/Fc} \tag{8}$$

The distinct catalytic effect exhibited by the P3MT/Fc electrode over the P3MT and that of the Pt is illustrated in Fig. 4. This catalytic effect is advantageous in the area of biosensors for the determination and detection of biological and organic molecules.[34]

P3MT/Co Films. P3MT films were formed under a constant applied potential of 1.7 V, as previously described. The electrode was then subjected to a constant potential of −0.2 V for 20 min in an electrolyte containing 0.05 M cobaltocene hexafluorophosphate (CoPF/AcN). Figure 5 shows the cyclic voltammograms of the poly(3-methylthiophene) containing cobaltocene (P3MT/Co) (I) and that for the P3MT/Fc (II) in 5.0×10^{-4} M [Fe(CN)$_6$]$^{3-/4-}$ in phosphate buffer. Two redox couples of waves appeared in the voltammograms for both electrodes; they correspond to the ferrocenium and cobaltocenium systems and to the [Fe(CN)$_6$]$^{3-/4-}$ system, respectively. However, the P3MT/Co electrode exhibited a relatively improved catalytic effect over that of the P3MT/Fc, as indicated by the increase in the current observed at the former electrode. This observation could be attributed to the difference in the reactivity of both the cobaltocene and the ferrocenium because of the relative difference in the atomic size of the metals.[35]

PNMP/Fc Films. The Fc/Fc$^+$ system was electrochemically incorporated in a poly(1-methylpyrrole) film following the procedure adapted for that of the P3MT/Fc system. Figure 6 shows the cyclic voltammogram obtained at the PNMP/Fc electrode in 5.0×10^{-4} M [Fe(CN)$_6$]$^{3-}$ in phoshate
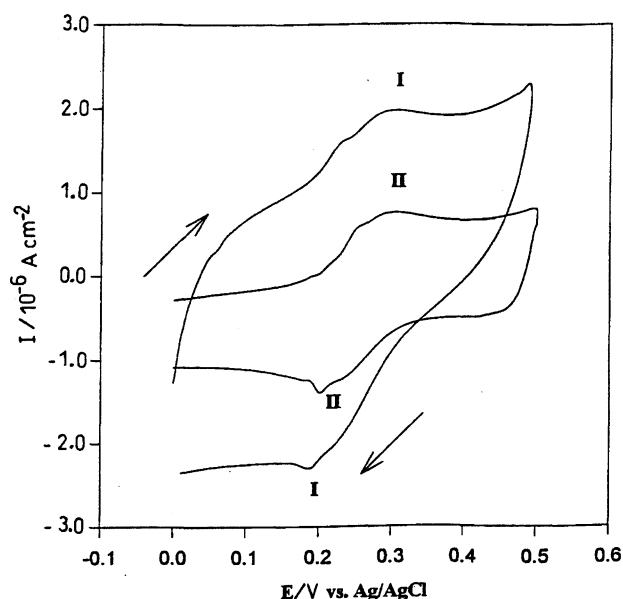

Fig. 5. Comparison between the cyclic voltammograms of P3MT/Co (I) and P3MT/Fc (II) film electrodes in 5.0×10^{-4} M [Fe(CN)$_6$$^{3-/4-}$]/phosphate buffer (pH=6.7). Scan rate 50 mV s^{-1}.
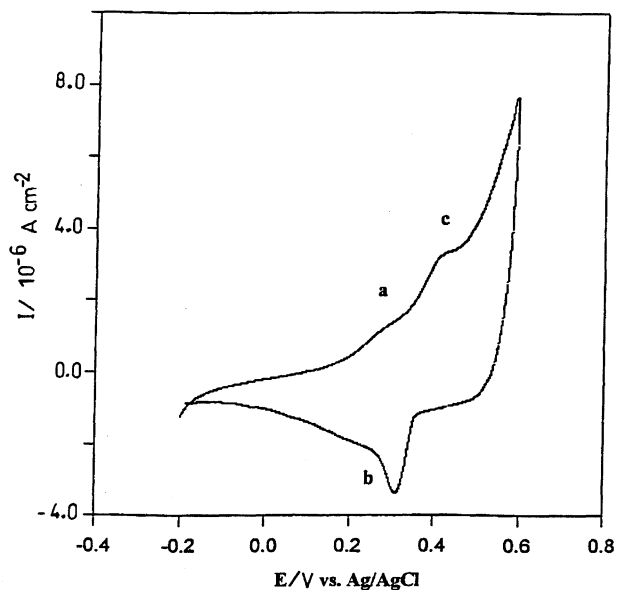
Fig. 6. Cyclic voltammogram of PNMP/Fc film electrode in 5.0×10^{-4} M [Fe(CN)$_6$$^{3-/4-}$]/phosphate buffer (pH=6.7). Scan rate 50 mV s^{-1}.

buffer. The data reveals the following: (i) the general shape of the CV for the PNMP/Fc is not comparable to that obtained for the P3MT/Fc, as shown in Fig. 2A; (ii) the first anodic peak appearing at 0.28 V (a) corresponds to the oxidation of the Fc/Fc$^+$, while the second pair of waves at 0.40 and 0.3 V (b and c) corresponds to the redox ions [Fe(CN)$_6$]$^{3-/4-}$;[36] and (iii) the PNMP/Fc electrode showed less electrocatalytic effect, as depicted by a decrease in the current signal, when compared to that of the P3MT/Fe electrode; only one peak appeared for the Fc/Fc$^+$ redox couple and the peaks separation (b and c) is greater than in the case of the P3MT/Fc electrode for the [Fe(CN)$_6$]$^{3-/4-}$ redox couple. Moreover, the PNMP film is sensitive to the presence of oxygen;[37] the solution and the electrode were extensively deaerated prior to running the above experiments. The electrochemical response showed

extensive decay of the current signal upon cycling and with oxygen diffusion to the electrolytic medium.

Structural and Morphological Studies. Polymer films were characterized using FTIR, XPS, and SEM. All experiments were performed on as-grown film formed under potentiostatic conditions. The film thickness was estimated from the charge passed during the electrolysis step, assuming 100% efficiency.

Infrared Spectroscopy. The structural regularity of the polymer chain and bonding sites were examined by infrared spectroscopy. The number of scans collected at a resolution of 2 cm^{-1} and with an accuracy of 0.004 cm^{-1} was 16 scans for all samples. The FTIR spectrum was measured for a KBr pressed pellet of the poly(3-methylthiophene) grown at a constant applied potential of 1.65 V. The assignments of the principal absorption bands are as follows: the bands appearing between 856 and 633 cm^{-1} are characteristics of the C–H out-of-plane vibrations. The sharp absorption band at 842 cm^{-1} is attributed to the ring C–H out-of-plane bending vibration which is specific for the 2,5-disubstituted thiophene rings. The peak appearing at 1473 cm^{-1} is attributed to the stretching vibration of the 2,3,5-trisubstituted thiophene rings. The band at 1388 can be attributed to the deformation vibration of the methyl group. Two other groups of ill-defined bands appeared; the first between 2975—1850 cm^{-1} are due to the stretching vibrations of the methyl group, while the second at 3061 cm^{-1} could be attributed to the C–H aromatic stretching mode. The foregoing results are in good agreement with those published earlier.[38—41] The FTIR spectrum was also measured for the P3MT/Fc film grown with the incorporation of ferrocenecarbaldehyde, as described above. The spectrum reveals the appearance of two peaks (actually one peak split into two) at 1664 and 1681 cm^{-1}, respectively. Those peaks are clearly indicating the presence of the aldehydic group due to the incorporation of the ferrocenium moiety within the film. Other peaks could be attributed to the same modes of vibrations as described
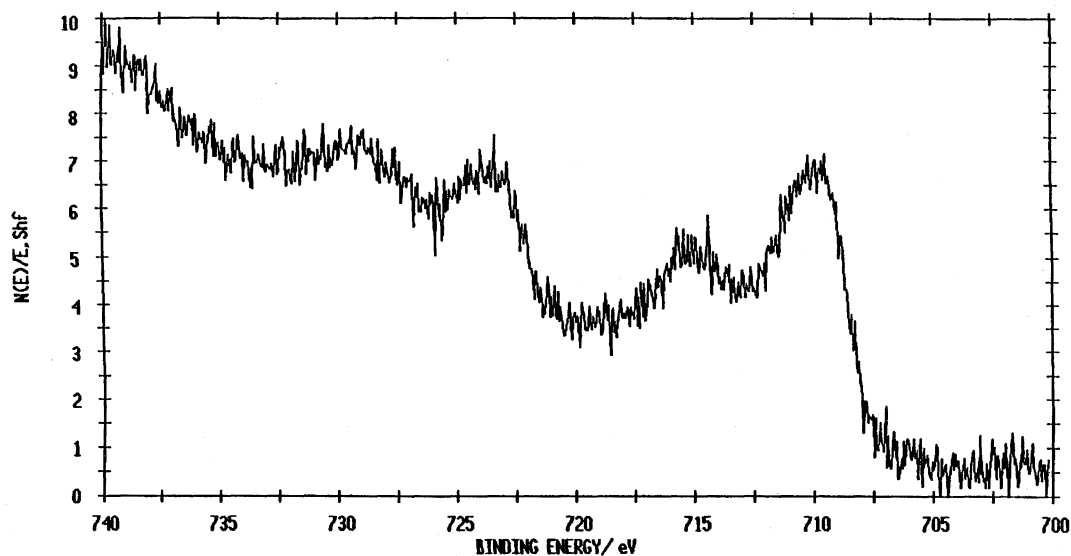

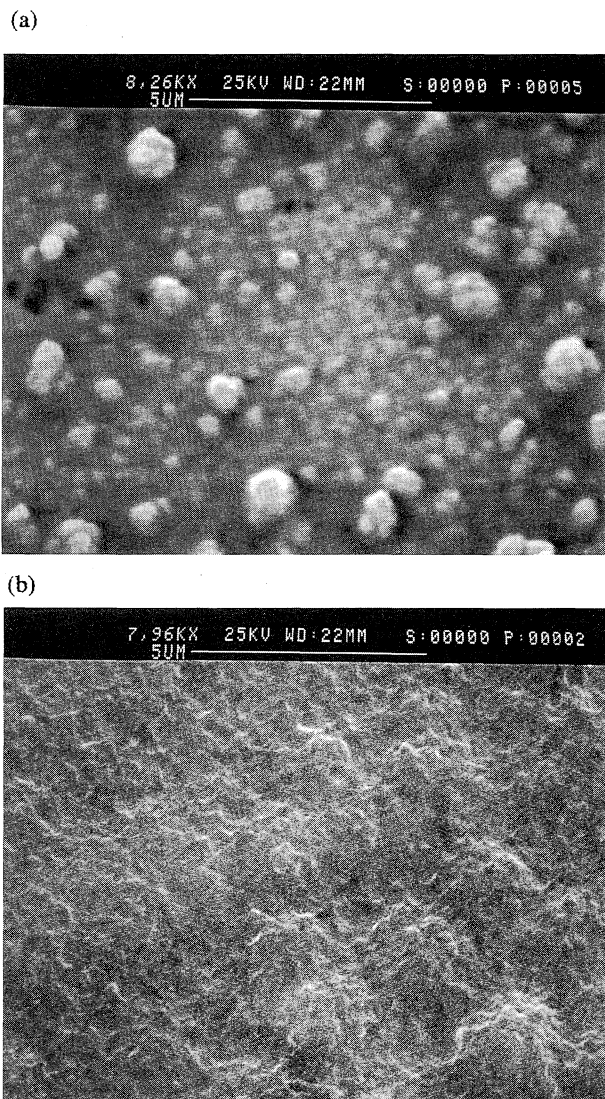Fig. 7. XPS multiplex spectrum of iron of the P3MT/Fc film.

(a)

(b)

Fig. 8. (a) SEM of P3MT film. (b) SEM of P3MT/Fc film.

for the P3MT film.

X-Ray Photoelectron Spectroscopy. XPS measurements were performed on as-grown P3MT and P3MT/Fc oxidized films, respectively. It was noticed from the results that the XPS spectra of the P3MT and P3MT/Fc films are generally similar in accord with the atomic concentration of the respective elements of both films. Another piece of evidence of the incorporation of ferrocenium moiety within the polymer film is illustrated in Fig. 7; the data reveals the XPS multiplex of the iron element, with well-resolved peaks at 710.0, 715.0, and 724.0 eV. However, we can not conclude at this stage the nature of the chemical composition of the ion in the film. Moreover, the chemical nature of the sulfur atom in both films showed an identical chemical environment around the sulfur atom. Previous data showed two sulfur S1 peaks appearing at down field (ca. 164.0 and 169.0 eV) in the case of P3MT grown on stainless steel, compared to only one peak in the case of the film grown on Pt (at 164.0 eV).[42] These results led us to conclude that while the ferrocenium moiety is included within the film, no evidence was shown

for possible complexation of ferrocenium moiety with the polymer backbone.

Morphological Structure of the Conducting Polymer Films. The morphology of the conducting polymer films of P3MT and P3MT/Fc was examined and compared using the SEM technique. Figures 8a and 8b show the scanning electron micrographs of P3MT and P3MT/Fc films, respectively. Five-membered heterocycles electropolymerize through an α–α' coupling. This results in a highly ordered chain, provided that the coplanarity of the units within the chains is also respected. This latter property could be controlled by restricting the electrochemical synthesis conditions and more importantly by planning the number and extent of substitution in the β-positions in the monomeric starting compounds. This is due to the fact that, among the structural defects which can affect the "regularity" of the configuration, are the unlikely α–β' couplings. Thus, thick films (>3000 Å) of the polymers grown potentiostatically on platinum substrates appeared fully amorphous when examined with the SEM, regardless of the nature of the electrolyte used for the synthesis.[5,42] Comparing the results obtained for both the P3MT and P3MT/Fc films grown on platinum from SEM experiments, we can conclude the following: (i) the films showed relative similarities in their general morphological appearance, (ii) the inclusion of ferrocenium moieties did not affect the morphology nor the general conductivity of the surface, and (iii) only some precipitations appeared on the surface of the P3MT, which are mainly due to the supporting electrolyte adsorption at the polymer film. It is assumed that the incorporation of the ferrocenium moieties did not take place with an enough concentration to alter the surface morphology.

The film conductivities were measured on the "as-grown" films formed on a Pt sheet. The surface conductivities of the "ferrocenium-free" polymer and those containing the ferrocene moiety were nearly identical and ranged between 950 to 1150 S cm^{-1}. Thus, the results indicated no appreciable difference in conductivities between the two types of polymer films. The non-linear decrease in the conductivity of the ferrocenium-containing films was similar to that observed for the ferrocenium-free polymer.

In conclusion, the incorporation of the ferrocenium to the poly(3-methylthiophene) affected the rate of the charge transfer at the polymer–electrolyte interface. There is no evidence of the complexation of the ferrocenium with the polymer film backbone. However, the ferrocenium proved to be stable within the polymer film. The inclusion of the ferrocenium within the conducting polymer with the described technique was confirmed from the FTIR and XPS results. A model was described to explain the electrochemical catalytic activity of the surface; in this model, we proposed that the ferrocenium added a faradaic component to the process of charge transfer. The morphology of the surface of the polymer film was not altered by the addition of the ferrocenium and maintained its general appearance.

to Prof. J. F. Boerio of the department of material science at the University of Cincinnati for allowing us the use of the surface analysis facilities. We are also indebted to Prof. H. B. Mark, Jr., for useful comments and discussions.

References

1) "Molecular Design of Electrode Surfaces," ed by R. W. Murray, John Wiley & Sons, Inc., New York (1992).

2) "Electroresponsive Molecular and Polymeric Systems," ed by T. Skotheim, Marcel Dekker, New York (1988).

3) K. Hyodo, *Electrochim. Acta*, **39**, 265 (1994).

4) M. D. Imisides, R. John, P. J. Riley, and G. G. Wallace, *Electroanalysis*, **3**, 879 (1991), and references therein.

5) P. Marque, J. Roncalli, and F. Garnier, *J. Electroanal. Chem.*, **218**, 107 (1987).

6) K. Imanishi, M. Satoh, Y. Yasuda, R. Tsushima, and S. Aoki, *J. Electroanal. Chem.*, **260**, 469 (1989).

7) R. A. Bull, F. R. Fan, and A. J. Bard, *J. Electrochem. Soc.*, **130**, 1683 (1983).

8) F. Mizutani, S. Iijima, Y. Tanabe, and K. Tsuda, *Synth. Met.*, **18**, 111 (1987).

9) G. Lian and S. Dong, *J. Electroanal. Chem.*, **260**, 127 (1989).

10) S. Nakahama and R. W. Murray, *J. Electroanal. Chem.*, **158**, 303 (1983).

11) R. A. Saraceno, G. H. Riding, H. R. Allock, and A. G. Ewing, *J. Am. Chem. Soc.*, **110**, 980 (1988).

12) A. Mertz and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 3222 (1978); D. Albagli, G. Bazan, M. S. Wrighton, and R. R. Schrock, *J. Am. Chem. Soc.*, **114**, 4150 (1992); D. Albagli, G. Bazan, M. S. Wrighton, and R. R. Schrock, *J. Am. Chem. Soc.*, **115**, 7328 (1993); D. Albagli, G. Bazan, R. R. Schrock, and M. S. Wrighton, *Mol. Cryst. Liq. Cryst.*, **216**, 123 (1992); D. Albagli, G. C. Bazan, R. R. Schrock, and M. S. Wrighton, *J. Phys. Chem.*, **97**, 10211 (1993).

13) A. L. Crumblis, D. Cooke, J. Castillo, and P. Wisian-Neilson, *Inorg. Chem.*, **32**, 6088 (1993).

14) C. M. Casado, I. Cuadrado, M. Moràn, B. Alonso, F. Lobete, and J. Losada, *Organometallics*, **14**, 2618 (1995).

15) A. D. Ryabov, A. Amon, R. K. Gorbatova, E. S. Ryabova, and B. B. Gnedenko, *J. Phys. Chem.*, **99**, 14072 (1995).

16) C.-L. Wang and A. Mulchandani, *Anal. Chem.*, **67**, 1109 (1995).

17) W. E. Rudzinski, M. Walker, C. P. Horwitz, and N. Y. Suhu, *J. Electroanal. Chem.*, **335**, 265 (1992).

18) L. J. Holtzknecht, H. B. Mark, Jr., T. H. Ridgway, and H. Zimmer, *Anal. Instrum.*, **18**, 23 (1989).

19) G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, **135**, 173 (1982).

20) C. D. Paulse and P. G. Pickup, *J. Phys. Chem.*, **92**, 7002 (1988).

21) R. J. Waltman, A. F. Diaz, and J. Bargon, *J. Phys. Chem.*, **88**, 4343 (1984).

22) R. B. Kauer, in "Electrochemical Science and Technology of Polymers," ed by R. G. Linford, Elsevier, New York (1990), Vol. 2, Chap. 3, pp. 97—147.

23) J. M. André, J. L. Brédas, J. Delhalk, J. Ladik, G. Levoy, and C. Moser, in "Recent Advances in the Quantum Theory of Polymers," Vol. 13 of Lecture Notes in Physics, Springer, Berlin (1980).

24) H. B. Mark, Jr., N. Atta, Y. L. Ma, K. L. Petticrew, H. Zimmer, Y. Shi, S. K. Lunsford, J. F. Rubinson, and A. Galal, *Bioelectrochem. Bioenerg.*, **38**, 229 (1995).

25) J. Wang and R. Li, *Anal. Chem.*, **61**, 2809 (1989).

26) N. Oyama and F. C. Anson, *J. Electrochem. Soc.*, **127**, 247 (1980).

27) R. P. Buck, *J. Electroanal. Chem. Interfacial Electrochem.*, **243**, 279 (1988).

28) K. Doblhofer, *J. Electroanal. Chem.*, **331**, 1015 (1992).

29) C. P. Andrieux, O. H. Hass, and J.-M. Savéant, *J. Am. Chem. Soc.*, **108**, 8175 (1986).

30) E. F. Dalton, N. A. Surridge, J. C. Jernigan, K. O. Wilbourn, J. S. Facci, and R. W. Nurray, *Chem. Phys.*, **141**, 143 (1990).

31) C. P. Andrieux and J.-M. Savéant, *J. Phys. Chem.*, **92**, 6761 (1988).

32) G. Wegner and J. Rühe, *Faraday Discuss. Chem. Soc.*, **88**, 333 (1989).

33) W. J. Albery, Z. Chen, B. R. Horrocks, A. R. Mount, P. J. Wilson, D. Bloor, A. T. Monkman, and C. M. Elliott, *Faraday Discuss. Chem. Soc.*, **88**, 247 (1989).

34) A. Galal, manuscript submitted to the *J. Solid State Electrochem.*, (1997).

35) N. N. Greenwood and A. Earnshaw, "Chemistry of the Elements," Pergamon Press, Oxford (1984), p. 1287.

36) N. F. Atta, A. Galal, E. A. Karagozler, H. Zimmer, and H. B. Mark, Jr., *Biosens. Bioelectron.*, **6**, 333 (1991).

37) S. Holdcroft and B. L. Funt, *J. Electroanal. Chem. Interfacial Electrochem.*, **240**, 89 (1988).

38) T. Yamamoto, K. Sanechika, and A. Yamamoto, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 9 (1980).

39) S. Hotta, T. Hosaka, M. Soga, and W. Shimotsuma, *Synth. Met.*, **9**, 381 (1984).

40) T. Yamamoto, K. Sanechika, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **56**, 1497 (1983).

41) K. E. Schulte, A. Kreutzberger, and G. Bohn, *Chem. Ber.*, **97**, 3263 (1964).

42) A. Galal, H. Zimmer, O. Y. Attaman, and H. B. Mark, Jr., "Effect of Supporting Electrolyte on the Properties of Conducting Polyheterolene Films," presented at the Pittsburgh Conference, New Orleans, Louisiana (1988).