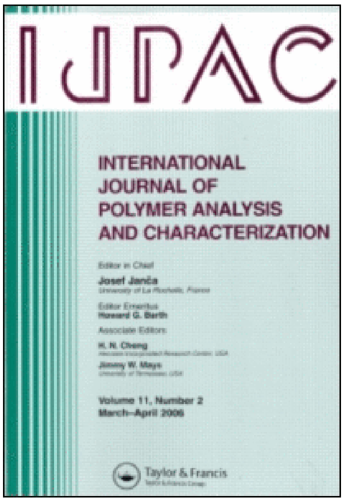

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An Electrochemical Study of Homopolymer, Copolymer and Composite Electrodes of Polypyrrole and Polycarbazoles

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Copolymer and composites of pyrrole with carbazole were synthesized on a platin substrate and an electrochemical study of polymeric films was performed. The characterization of homopolymer, copolymer and composite films was performed by electrochemical methods (i.e., polarization curves and cyclovoltammetric measurements), morphological and elemental analyses, solid-state conductivity measurements and spectrophotometric methods comparatively. The reversibility of electrodes was checked by ferrocene in nonaqueous media. The stability of films was also tested both with corrosion and residual discharge capacity measurements in acidic aqueous solution.

Keywords: Conducting polymers; Electrodes; Electrochemistry; Polypyrrole; Polycarbazoles

INTRODUCTION

Over the past 20 years conducting polymers have been synthesized at an inert anode to yield coherent layers with an electronic conductivity high enough to rule out any excessive ohmic drop for numerous applications. Of all known conducting polymers, polypyrrole is the most frequently used, due to its conductivity and the possibility of forming

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* Corresponding author.

homopolymer, copolymer or composites with optimal properties. However, it is hard and brittle and these poor properties greatly restrict its potential for applications.[1,2] Attempts have been made at composite formation with different polymer matrices[3,4] and at the copolymerization of pyrrole (Py) with other heterocyclic monomers with the aim of improving the properties of the resulting product.[5,6] So far copolymers of pyrrole with heterocyclic monomers have been prepared by electrolytic oxidation.[7–9] The choice of such monomers (i.e., pyrrole, phenol, *N*-vinylcarbazole, etc.) was not random since the oxidation potentials of the monomers are comparable and the electrochemical oxidation of mixed monomers successfully produces the copolymer. Most of the previous work deals with the synthesis of new copolymer and composite of polypyrrole with a second polymer and with the characterization of polymeric film. The electrocoated copolymer and composite films have not been studied in detail as regards to corrosion.

The results of the present investigation are significant, as they describe the corrosion behavior of homopolymer, copolymer and composite electrodes of *N*-substituted carbazoles with pyrrole as well as the synthesis and characterization of them. Following the findings of our previous work on *N*-substituted carbazoles with pyrrole,[10,11] the electrochemical behavior of these materials in acid and nonaqueous medium and their physicochemical properties are discussed in comparison with previous results.

EXPERIMENTAL

Materials

Three carbazole monomers namely (1) *N*-vinylcarbazole (NVCz) (Aldrich > 99%), (2) carbazole (Cz) (BDH > 99%) and (3) *N*-ethylcarbazole (ECz) (Aldrich > 99%) and pyrrole (Py) (Merck > 98%) were employed. Acetonitrile (ACN) (Carlo Erba HPLC grade) and all other chemicals were used as supplied. The prefix ‘P’ indicates the corresponding polymer. Ferrocene (2 mM) was used as the redox reagent. Aqueous corrosion electrolytes were 0.5 M H_2SO_4, which was prepared with distilled and deionized water.

Measurements

FT-IR measurements were performed with a Matson 1000 spectrophotometer. A Jeol JSM 84 scanning electron microscope (SEM) was used for morphological analysis. Solid-state electrical conductivity measurements were performed from films removed from electrode surface on a Keithley 617 electrometer connected to a four-probe head with gold tips and calculated from the following equation:

$$\sigma = V^{-1}I(\ln 2/\pi d_n)$$

where V is the potential in volts, I is current in A, and d_n is the thickness in cm.

Pt wire as the working electrode ($A = 0.345\,\mathrm{cm}^2$), Pt as the counter electrode and saturated calomel electrode as the reference electrode were employed for electrochemical measurements.

Electrodeposition

Potentiodynamic electrodeposition was performed with a Wenking POS 73 model potentiostat connected to an X–Y recorder (Kipp and Zonen). The nominal thickness was 80 μm throughout to verify complete coating of the platinum and calculated electrochemically by using Faraday's equations as suggested in literature.[12] The nominal thickness of polymer layer can be calculated as follows:

$$d_n = m_e Q/FA\rho$$

where Q is charge in Coulombs, F is Faraday constant, A is the area of polymer in cm^2, m_e is the electrochemical equivalent of polymers, and ρ is the density of polymers, which is found to be in the range of 1.42–1.50 for ClO_4^--doped products and agree with the literature value.[12]

The potentiodynamic electrodeposition of homopolymer of Py and carbazoles (carbazole, *N*-vinyl and ethylcarbazole) from ACN onto Pt was carried out as follows: The electrodes were first polarized from 0 mV (vs. SCE) up to 1.2 V and maintained for 100 s, and then subsequently five cycles (each at $50\,\mathrm{mV\,s^{-1}}$) were performed, forming polymer films (Pt/PPy and Pt/polycarbazoles (PVCz, PECz, PCz).

The copolymerization of carbazoles by Py was prepared in the same way with homopolymer in the presence of both monomers. PPy/Polycarbazoles and Polycarbazoles/PPy composites were electrochemically prepared by polymerization of Cz monomers on the precoated PPy and Py monomer on the precoated PCz layers, respectively. A degree of doping y was calculated from the potentiodynamic electrodeposition capacity Q_0, and the first discharge capacity in the background electrolyte (0.1 M tetraethylammonium perchlorate TEAP in acetonitrile) ($Q_{E,0}$) as suggested in the literature.[13]

$$y = 2Q_{E,0}/(Q_0 - Q_{E,0}).$$

The corrosion of polymeric films was investigated experimentally by the determination of potentiodynamic residual redox capacity of films after exposure to corrosion medium as given in literature.[14,15] For this purpose, the electrical potential was swept between 0 and 1400 mV in 0.5 M H_2SO_4 for freshly prepared polymer layers and after 20 h corrosion time in the same electrolyte, with 100 mV s^{-1} scan rates. By the integration of the area under the anodic voltammogram and the line of zero current density, the stored charge Q_{ox} was obtained. Reduction charge Q_{red} was also obtained by the same integration of the area under the cathodic branch. The relative capacities Q_{ox}/Q_{red} were compared.

Corrosion measurements just after coating and after 20 h corrosion time in 0.5 M H_2SO_4 as a corrosion medium were also carried out. From Tafel extrapolation of the anodic and cathodic polarization curves, the corrosion current of bare and coated electrodes was obtained.

RESULTS AND DISCUSSION

Elemental Analysis

Elemental analysis results support the structure of copolymers as $-C_{26}H_{20}N_4-$, $-C_{24}H_{18}N_4-$, $-C_{26}H_{22}N_4-$, for NVCz–Py, Cz–Py, ECz–Py respectively, suggesting they contain three pyrrole unit for each carbazole ring.

FT-IR Results

The FT-IR spectra of products obtained on platinum anodes as substrates were recorded as dispersed polymer in a KBr disc. Results are summarized in Figures 1–3. A significant band at 1100–620 cm^{-1} has been attributed to the presence of ClO_4^- ion as the dopant and bands attributed to 1, 2, 4-substituted benzene[16] appear in the range 750–850 cm^{-1}. These spectrophotometric observations suggest that in the conducting green-colored polymer, the aromatic rings must be involved in polymer propagation and the NVCz vinyl group is not solely responsible for polymerization. Another band at about 950 cm^{-1} appears in all copolymer and composite samples which is attributed to the linkage between the two conductive polymers,

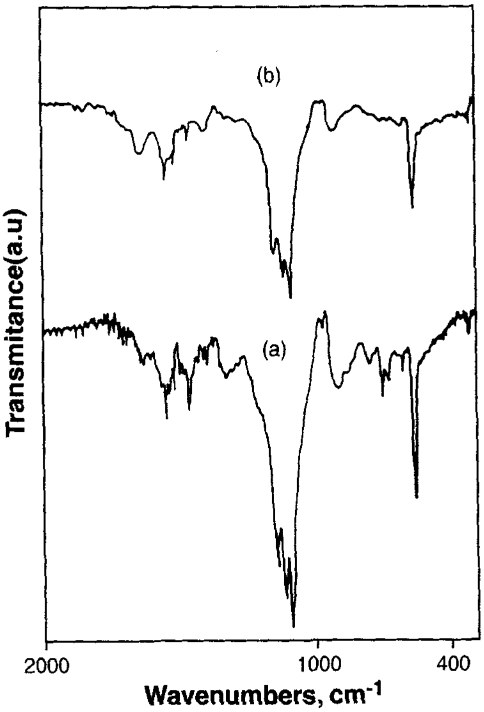

FIGURE 1 FT-IR spectra of electrochemical composites of PVCz/PPy (a) and, PPy/PVCz (b). [Py] = 0.01 M, [NVCz] = 0.02 M, [Cz] = 0.02 M, [ECz) = 0.02 M, applied potential = 1.2 V.

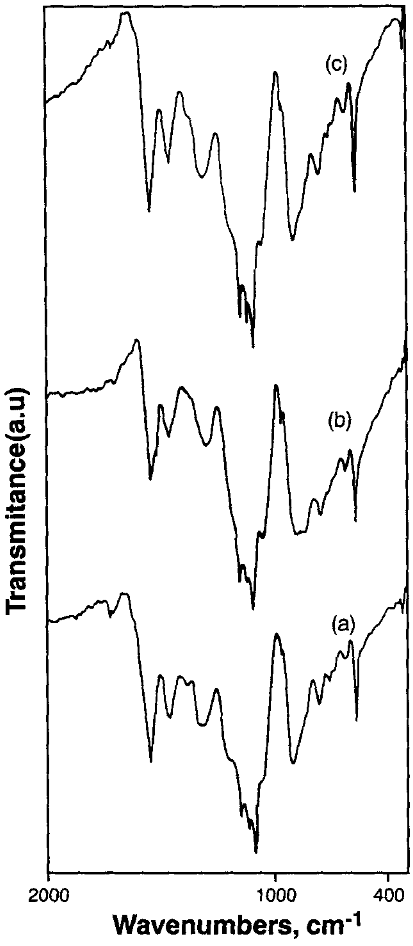

FIGURE 2 FT-IR spectra of electrochemical copolymer of ECz-Py (a) composite of PECz/Py (b) and PPy/PECz (c). [Py] = 0.01 M, [NVCz] = 0.02 M, [Cz] = 0.02 M, [ECz] = 0.02 M, applied potential = 1.2 V.

possibly through their aromatic sites (−3 and/or −6 position of carbazoles and −2 and/or −5 position of Py).[8]

Scanning Electron Micrographs

The SEM micrographs of products show the typical cauliflower structure at the electrolyte surface, which is quite similar to those results

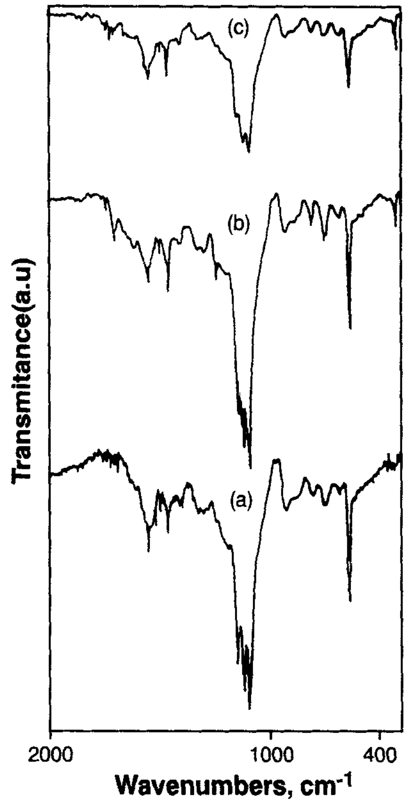

FIGURE 3 FT-IR spectra of electrochemical copolymer of Cz–Py (a) composites of PPy/PCz (b) and PCz/PPy (c). [Py] = 0.01 M, [NVCz] = 0.02 M, [Cz] = 0.02 M, [ECz] = 0.02 M, applied potential = 1.2 V.

reported in the literature.[17] The micrographs of the electrochemically prepared composite and copolymer layer of pyrrole with carbazoles show differences comparable with homopolymers as given in our previous work.[18] These differences indicate the incorporation of carbazoles into the polypyrrole structure.

Electrical Conductivity

The conductivities of the resultant homopolymer, copolymer and composites are given in Table I. The electrocopolymerization of carbazole derivatives with Py can cause some increase in conductivities

TABLE I Conductivity corrosion current I_{corr} and the ratio of relative oxidation and reduction capacities of homopolymer, copolymer and composite coated electrodes in 0.5 M H_2SO_4 before and after 20 h corrosion time

Electrode	(S/cm)	I_{corr}, A × 10^5		Q_{red}/Q_{ox}	
		Before	*After*	*Before*	*After*
PVCz	2.4×10^{-4}	2.0	3.0	2.2	2.2
PCz	8.4×10^{-4}	12.0	10.0	2.2	3
PPy	1.2	10.0	3.5	0.5	0.8
NVCz–Py[a]	1.7×10^{-3}	7.7	6.0	0.9	0.3
Cz–Py[a]	1.3×10^{-4}	5.0	8.0	0.9	2.5
ECz–Py[a]	3.2×10^{-3}	45.0	20.0	1.3	3.0
PPy/PVCz[b]	4.8×10^{-4}	140.0	150.0	4	2.3
PCz/PPy[b]	1.3×10^{-4}	5.5	4.5	0.5	1.0
PPy/PCz[b]	1.9×10^{-4}	9.0	8.0	1.1	0.8
PPy/PECz[b]	2×10^{-4}	40.0	45.0	1.1	3.9
PVCz/PPy[b]	7.2×10^{-4}	7.0	7.2	1.2	0.9

[a]Copolymer; [b]Composite.

and the presence of PPy in composite structure has a positive effect on the conductivities of composites to some extent when PPy is on the upper side.

Cyclic Voltammetric Characterization

Degree of doping The oxidation potentials of monomer during the electropolymerization are in the range of literature values (0.8–1.1 V. vs. SCE).[7] The oxidation potential of the resultant copolymer was somewhere in between the oxidation potential of the two polymers. The oxidation potential of monomers on the precoated polymer layer was slightly different from the oxidation potential on bare Pt, as expected. The oxidation potential during the following sweep became lower since dimer and oligomer can be oxidized at a lower potential, as suggested in the literature.[19] Electrodeposition from monomer containing 0.1 M TEAP solution leads to a doped polymer layer, the dopant being the ClO_4^- ion. From the CV curves, electrodeposition, first discharge and degree of doping were calculated. These values are in the range of 0.23–0.44 which are the highest ratios obtained in the case of copolymer formation. The doping ratio is greater than 0.33, which has been accepted for PPy. The area of the current–potential curve expanded with increased film thickness. In addition, the expansion of the effective electrode area increased the doping of the anions, thus making the film capacity increase proportionally to the thickness of the film.[20] The higher doping ratios might be due to the thickness of the film in this study, which is higher in comparison to those reported in the literature.

Cyclic voltammograms in ferrocene-containing acetonitrile Cyclic voltammograms of polymer-coated electrode in ferrocene-containing

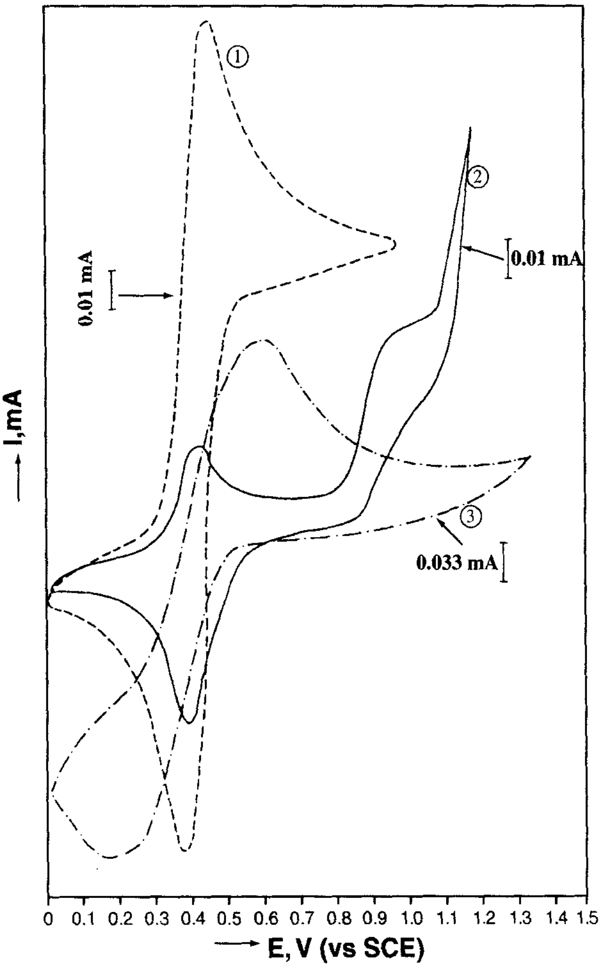

FIGURE 4 Cyclic voltammograms of Pt (1), PVCz film (2) and NVCz-Py copolymer film (3). Supporting electrolyte = 0.1 M TEAP in acetonitrile containing ferrocene (2 mM); scan rate = 100 mV s^{-1}.

(2 mM) acetonitrile solution were also recorded (Figures 4–6). In all cases, the number of electrons corresponding to the oxidation and reduction process of ferrocene is close to unity as expected. The E_a of ferrocene obtained at the polymer layers is more positive than that of the bare Pt considering that the conductivity of polymer layer is far lower than Pt. These results can easily be understood. It has been

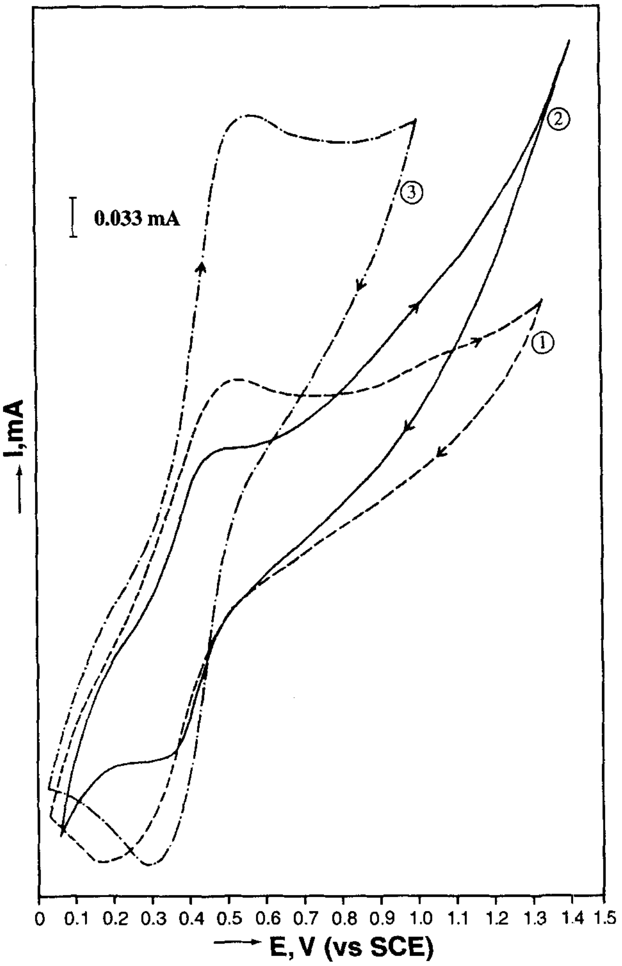

FIGURE 5 Cyclic voltammograms of PPy/PCz film (1), PCz/PPy film (2) and PPy film (3). Supporting electrolyte = 0.1 M TEAP in acetonitrile containing ferrocene (2 mM); scan rate = 100 mV s^{-1}.

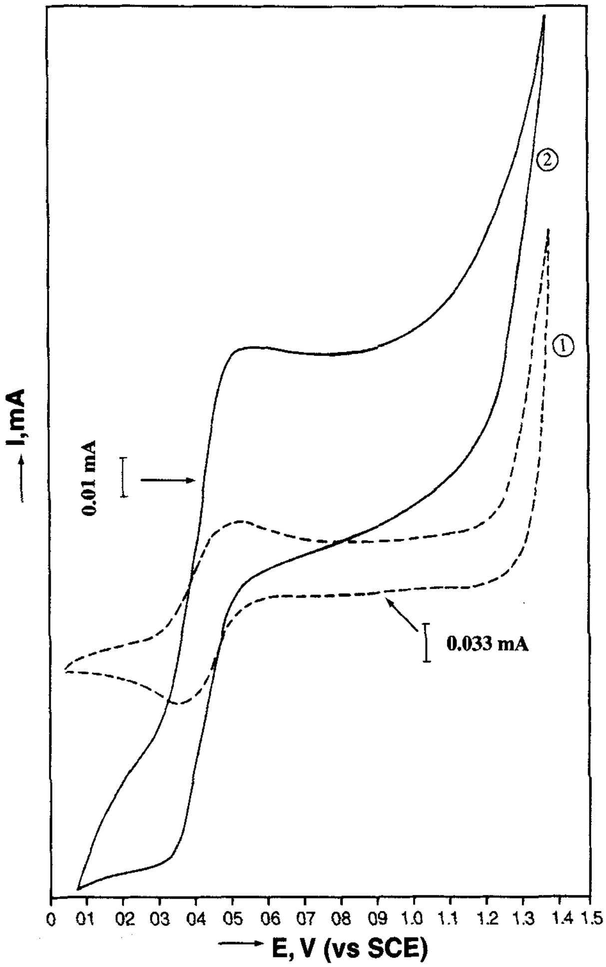

FIGURE 6 Cyclic voltammograms of ECz-Py copolymer film (1), PPy/PECz composite film (2). Supporting electrolyte = 0.1 M TEAP in acetonitrile containing ferrocene (2 mM); scan rate = 100 mV s^{-1}.

reported that the reactivity of ethylcarbazole is higher than the vinyl carbazole in the case of the copolymerization with pyrrole.[8] Better reversibility was observed for ECz-Cz, probably due to the better arrangement of the copolymer chain by the closer proximity of ECz and Py. The differences of the peak potentials of composite electrodes in ferrocene with homopolymer electrodes alone, might be due to the different interaction of the two conducting polymers. Composite electrodes behave similarly with homopolymer which appears on the upper layer of composite coating, except in the case of the PPy/PCz electrode.

Stability of polymer layers The corrosion currents of coated electrodes, which are obtained from Tafel extrapolation of anodic and cathodic curves, are collected in Table I. Only minor alterations in the corrosion currents of coated electrodes can be detected. Differences in corrosion currents from polymer to polymer are probably due to differences in the conductivities of polymer layers. The corrosion potential of the composite electrodes is shifted in the negative direction during the corrosion process. This may be due to anion exchange of polymer film taking place.

Control voltammograms (between 0 and 1400 mV at 100 mV s^{-1}) of polymer films in 0.5 M H_2SO_4 before and after corrosion were recorded. From such experiments, the corresponding total charges were calculated and given as the ratio of total cathodic charge to anodic charge (Q_{red}/Q_{ox}). Results are summarized in Table I. As can be seen from the table, PVCz, PPy, PVCz/PPy, PCz/PPy and PPy/PCz electrodes seem more stable to corrosion in acidic media as their redox capacities are almost the same. Since PCz homopolymer electrodes are not stable, copolymer and composite of Cz with Py are also unstable. In the case of ECz, since ECz does not polymerize under given conditions but form a soluble 3,3′-dimer,[21] the stability of the copolymer and composite of ECz with Py is low.

CONCLUSION

Conducting copolymer and composite films of *N*-substituted carbazole with pyrrole were prepared electrochemically. It was found that homopolymer, copolymer and composite electrodes of *N*-substituted carbazoles with pyrrole seem to be stable and sufficiently electroactive for potentially different applications (i.e., sensors, battery and corrosion inhibition). Studies on using these electrodes as sensors for different uses are in progress. It is known that low doping levels give rise to polarons, whereas higher doping levels produce bipolarons. In this study, due to the thicker films obtained than reported in literature,[20] extended oxidation may occur, which may produce bipolarons giving the possibility of the inclusion of more counter ions. This may result in a higher doping level. However, it should be emphasized that these models were devised assuming ideal structures. The actual structures of conductive polymers need further detailed investigation.

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