

Phase transitions in polypyrrole and polythiophene conducting polymers demonstrated by magnetic susceptibility measurements

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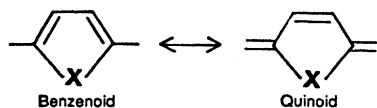
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Magnetic susceptibility measurements conducted by the superconducting quantum-interference device (SQUID) technique in the temperature range 6–300 K on electrochemically synthesized polypyrrole and polythiophene doped with tetrafluoroborate (BF_4^-) are reported. The temperature-dependent susceptibility results indicate the possibility of phase transitions occurring at about 75 K in polypyrrole and at about 130 K in polythiophene. These possible phase transitions are analyzed in terms of electronic and morphological structures of polyheterocyclics. The spin susceptibility clearly changes from a Curie to a Pauli-like behavior in polypyrrole as the temperature rises, while polythiophene only exhibits a Curie behavior. In addition, the ESR measurements performed on polypyrrole, polythiophene, and polyfuran at room temperature are also discussed. The exceptionally narrow ESR linewidth of 0.14 G in polypyrrole indicates the presence of highly mobile unpaired spins in the doped state. A significant effect of environmental conditions on magnetic behavior was also observed. The present susceptibility results are similar to those on arsenic-pentafluoride-doped *cis*-polyacetylenes. The SQUID measurements also indicate the possibility of the coexistence of unpaired spins, i.e., paramagnetic species and paired spins in conducting state. The temperature-dependent susceptibility demonstrates to some extent a dominant spin-coupling type of phenomenon, particularly in polypyrrole. The existence of spinless bipolarons and their contribution to the conduction mechanism are discussed in light of the present results.

I. INTRODUCTION

Highly conducting organic polymers, such as polyacetylene, polyheterocyclics, polyphenylenes, etc., all possess an essential common feature of extended π -electron conjugation in their backbone, which imparts unique electroactive properties in these materials. In their undoped state, these highly conjugated polymers are insulating or semiconducting, but their electrical conductivity increases up to metallic regime simply by electron-acceptor or electron-donor doping.^{1–4} The conductivity of poly(*p*-phenylene), for example, increases by 18 orders of magnitude from 10^{-16} to 500 S/cm by doping with arsenic pentafluoride.⁵ The conduction mechanism in these materials, particularly in their oxidized state, has been a subject of great interest. The conduction process in these conjugated systems is believed to occur via π -electron delocalization along the polymer chain. The highly mobile charge-carrying species have been modeled as solitons in polyacetylene.¹ For brevity, a neutral soliton (radical ion) has a spin $\frac{1}{2}$, while the charged soliton is spinless.⁶ In doped polyacetylene the existence of a soliton band in the midgap state has been evidenced experimentally as well as theoretically.^{7–10} On the other hand, contrary to the *trans*-polyacetylene, in polyheterocyclics the ground state is nondegenerate.^{11,12} The resonance structure for polypyrrole ($X=\text{NH}$) and polythiophene ($X=\text{S}$) can be expressed as follows:

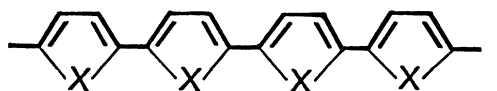


The aromatic (benzenoid) structure has a lower-energy state than the quinoid structure, and a difference of approximately 0.40 eV per ring has been calculated for polypyrrole.^{13,14} This precludes the existence of solitons in polyheterocyclics. However the presence of another species, termed “polaron,” has been proposed. Similar to the soliton, a polaron has a spin $\frac{1}{2}$ and its interaction with the identical species energetically favors the formation of a bipolaron (spin 0).¹¹ The appearance of a bipolaron band structure in the oxidized states of polypyrrole and polythiophene has been evidenced by optical^{15–17} and ESR measurements.¹⁸ In general, bipolarons have been suggested as the charge-carrying species responsible for the conduction process in polyheterocyclics.^{14,19} Large research efforts have been focused on examining the conduction mechanism in polyacetylene, polypyrrole, and polythiophene. The majority of investigators favor the solitonic model (degenerate ground state) for polyacetylenes and bipolaronic (nondegenerate ground state) contributions in polyheterocyclics.

It is well known that organic polymers have very complicated molecular, crystalline, and morphological structures which induce their electrophysical properties to vary over a very wide range depending on synthetic techniques. For example, polyacetylenes synthesized under similar conditions strongly differ in their physicochemical properties; hence it is rather difficult to obtain identical material.⁴ In doped polyacetylene several conduction mechanisms have been proposed only because of the structural problems originating from material preparation and doping.^{1,4,20–24} Like polyacetylene, electrophysical properties of polyheterocyclics are also influenced by synthetic methods and conditions.^{25–27}

Because of the simplicity of the polyacetylene conjugated system, its structure is of considerable interest to the chemist both from the theoretical and experimental points of view. Polyacetylene is environmentally unstable, thereby making practical applications difficult. On the other hand, polyheterocyclics have twofold advantages over polyacetylene. First, they have more architectural flexibility in order to develop a structure-property relationship. Secondly, they are environmentally quite stable systems and therefore can be used in applications under ambient conditions. Recently, more attention has been focused on the derivatized polyheterocyclics, which not only retain the initial conductivity of the conjugated system, but can be extensively characterized in solutions and processed into ultrathin films ($\sim 20 \text{ \AA}$) for qualitative electrophysical investigations.²⁸⁻³⁰

Electrochemically synthesized polyheterocyclic films are obtained in their conducting state due to their *in situ* doping during electro-oxidation of monomers. Usually the cationic polymers comprise $\sim 70\%$, and 30% are counteranions (dopant).^{1,31} The stoichiometric ratio of the polymer units to counteranions is $\sim 4:1$. This ratio is strongly influenced by the synthetic variables, particularly by the nature of the solvent and electrolyte; hence their electrical conductivity varies widely. The conductivity of *in situ* doped polyheterocyclics ranges between 1 and 200 S/cm depending on the synthetic conditions.^{1,25,32,33} The polyheterocyclics, particularly polypyrrole, have been extensively characterized by a number of analytical techniques such as x-ray-photoemission spectroscopy,^{34,35} ^{13}C nuclear magnetic resonance,³⁶ electron-spin resonance,³⁶ and optical³⁷ and infrared spectroscopy.³⁶ Because of the insolubility and infusibility of polypyrrole, its solution characterization is restricted and a direct molecular-weight determination through the solution route cannot be accomplished. Both polypyrrole and polythiophene have linear-chain structures, and the analytical techniques evidence that the monomer units are linked together through α, α' coupling (at 2 and 5 positions).^{38,39} These polyheterocyclics possess a highly conjugated π -electron carbon skeleton similar to polyacetylene. If the heteroatoms are not incorporated in the polymer chain π -electron system, they can be viewed as a linear polymer of acetylene ($sp^2 p_z$ polyene chain) closely related to a structural isomer of *trans-cisoid* type such as shown below.^{1,27} These polyheterocyclics have very close chemical structure as presented below, and the nature of the heteroatom plays a significant role in electroactivity and, hence, they behave differently at their molecular levels:



X=NH, Polypyrrole, X=S, Polythiophene and X=O, Polyfuran

The spin paramagnetism in these conducting polymers results from the existence of unpaired spins along the carbon backbone similar to polyacetylene. The incorporated heteroatom has been found to influence the electrical properties of polyheterocyclics. If the paramagnetism in these polyheterocyclics occurs only along the polymer

chain without any significant contribution from heteroatom spin orbitals, then their magnetic behavior may have some similarities to *cis*-polyacetylene. The ESR measurements have been performed in various laboratories in order to study the nature of polymer-chain defects and their feasible relation to conduction mechanisms in polyacetylene⁴⁰⁻⁴³ and polyheterocyclics,⁴⁴⁻⁴⁷ both in their oxidized and reduced states. The temperature-dependent electrical-conductivity measurements also provide first-hand information about the possibility of involved conduction processes in a variety of materials. A theoretical model of Mott's variable-range-hopping conduction in disorder materials predicts the probable conduction mechanism operating in the materials.²⁰ The results are generally plotted as $\log_{10}\sigma$ versus T^{-x} , where σ is the electrical conductivity, T is the temperature, and x is a constant ranging from 1 to $\frac{1}{4}$. The $x = -\frac{1}{2}$ behavior shows a pseudo-one-dimensional conduction, while $x = -\frac{1}{3}$ predicts two-dimensional system and $x = -\frac{1}{4}$ evidences the three-dimensional conduction process most often observed in conducting polymers. In addition to variable-range hopping, other conduction processes have been considered. In conducting polymers some of the results are still contradictory due to the complexity of polymeric materials. In the present investigation a more precise technique using a superconducting quantum-interference device (SQUID), which can differentiate between charge-carrying species and unpaired spins, has been employed to examine the nature of dynamic defects occurring along the polymer carbon chains of polypyrrole and polythiophene. The available literature was searched to explore the novelty of present experimental results and to find a suitable correlation between reported results on magnetic properties. A possible explanation from the chemical as well as physical points of view have been interpreted in order to explore the nature of dynamic defects in polymer carbon chains of polyheterocyclics.

Magnetic measurements by various researchers have been conducted on polypyrrole to establish a relationship between the charge carriers and conductivity. The ESR technique, which quantitatively distinguishes between magnetic species, also provides information about the transport properties of polypyrrole, as extensively reported by Scott *et al.*^{18,44} For simplicity, a polaron is a radical ion carrying spin $S = \frac{1}{2}$, while a bipolaron (spin 0) is a dication formed by the recombination of two polarons. Bipolarons have been considered to be the fundamental charge-carrying species in the conduction process. These bipolarons transport charge via interchain hopping and thus contribute to conduction. A schematic representation of a polaron and a bipolaron as well as the interchain bipolarons hopping in polypyrrole is given in Fig. 1. Bredas *et al.*¹⁴ also supported the spinless conduction through bipolaron formation in polypyrrole. In polypyrrole at relatively low doping concentrations, paramagnetism arises from the neutral defects in the carbon π -electron system which disappears as the doping level considerably increases. Scott *et al.*¹⁸ reported that absence of an ESR signal in conducting polypyrrole evidences the formation of spinless (diamagnetic) bipolarons. The authors concluded that paramagnetic species (polarons) are

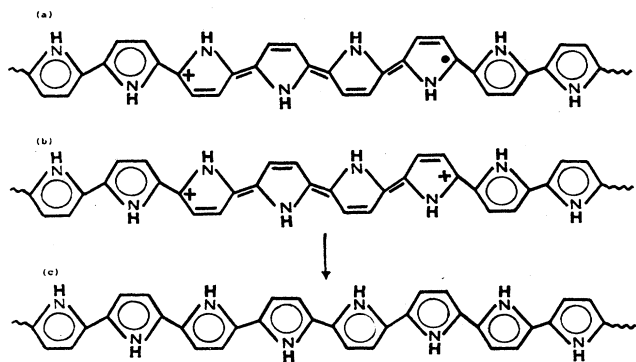


FIG. 1. Systematic representation of (a) a polaron, (b) a bipolaron, and (c) interchain bipolarons hopping in the polypyrrole system (Refs. 14, 18, and 44).

not current carriers. Instead, they suggested that bipolarons are responsible for the conductivity of polypyrrole. In other words, there is no clearcut correlation between the charge carriers and unpaired spins of polypyrrole. The question of which charge carriers are responsible for transport properties is still a very stimulating subject that merits further investigation. For this reason it was of considerable interest to the author to authenticate the previous ESR findings by carrying out the magnetic-susceptibility measurements on polyheterocyclics. In this article the magnetic-susceptibility and ESR measurements of polypyrrole, polythiophene, and polyfuran, all doped with tetrafluoroborate, are reported. These materials exhibit a Curie-like behavior at low temperature, while in the case of polypyrrole Pauli susceptibility is witnessed as temperature rises towards room temperature.⁴⁸ Surprisingly enough, the temperature-dependent susceptibility clearly indicates the possibility of phase transitions both in polypyrrole and polythiophene. Are bipolarons responsible for conductivity or is some other mechanism operative? These magnetic measurements may be able to highlight some predictions for the conduction mechanism in polyheterocyclics.

II. EXPERIMENTAL TECHNIQUES

Electroactive films of polypyrrole, polythiophene, and polyfuran were electrochemically synthesized by the already established synthetic routes.^{26,49,50} A single-compartment cell equipped with platinum as a working electrode and copper wire as a counterelectrode was used for polymerization of monomeric heterocyclics. The monomers of pyrrole, thiophene, and furan were used as received without any further purification. The highly dissociative tetraethylammonium tetrafluoroborate salt was used as the electrolyte in all cases except polypyrrole, where, in addition, *p*-bromobenzenesulfonate was also used. The reactions were performed in acetonitrile. The reaction mixture was thoroughly degassed by passing nitrogen through solution for almost 30 min. The polymer films were generated at platinum electrodes under appropriate electrical potentials. These films were peeled off from the electrode and further purification was done

in acetone using a Soxhlet apparatus. All the films obtained via this procedure are in their doped (oxidized) state due to the incorporated tetrafluoroborate counteranions. The neutral films were obtained using aqueous ammonia solution. This chemical method was found to be more suitable in order to reduce fully the films since a change in their electrophysical properties was noticeable.

The ESR measurements on the doped (oxidized) as well as the undoped (reduced) films were conducted on a Varian X-band ESR spectrometer (model E-12) using a TE₁₀₂ cavity. All the samples were sealed in the quartz ESR tube under vacuum. These tubes were thoroughly checked by ESR before loading the samples to examine the free radical neutrality of tubes. Some of the samples were also exposed to air to examine the effect of paramagnetic oxygen on the ESR spectrum. Only the polypyrrole samples were exposed to radiation using a ⁶⁰Co source. The *g* values of polyheterocyclics were determined by comparison with 1,1-diphenyl-2-picrylhydrazyl (DPPH), for which the *g* value is known to within 2.0036.⁵¹ The magnetic susceptibilities of polypyrrole and polythiophene were measured in the temperature range 6–300 K by a S.H.E. Corporation superconducting SQUID susceptometer. The magnetic-susceptibility data were corrected for the magnetization of the sample cavity used during the magnetic measurements. The electrical-conductivity measurements were performed at room temperature by a standard four-probe technique on free-standing films as obtained from synthesis which were *in situ* doped during the electrochemical polymerization.

III. RESULTS AND DISCUSSION

A typical curve showing the variation of magnetic susceptibility (χ_g) versus temperature is represented in Fig. 2. The susceptibility-versus-temperature plot indicates a strong transition at about 75 K. In addition to this well-defined transition, susceptibility also exhibits some

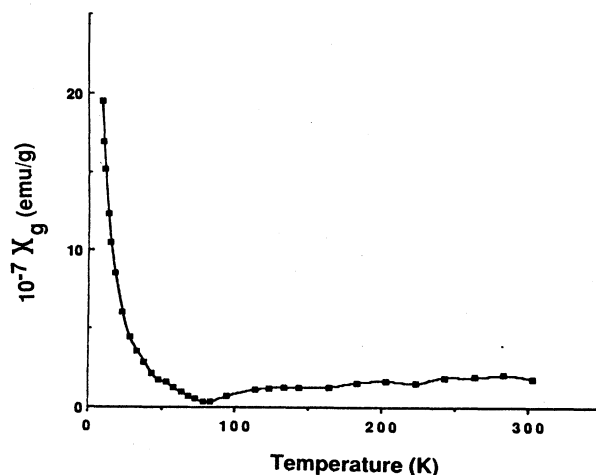


FIG. 2. Typical curve of magnetic susceptibility (χ_g) as a function of temperature obtained by the SQUID technique for a polypyrrole tetrafluoroborate (BF_4^-) sample. The polymer is in the conducting state due to *in situ* doping during electrochemical polymerization.

unusual behavior as the temperature of the polypyrrole sample further rises beyond 75 K. The present susceptibility results of polypyrrole show very peculiar temperature-dependent behavior. However, the temperature-dependent conductivity measurements reported in the literature show no anomaly around these temperatures; therefore the possibility of any transitions have been completely ruled out. The data suggest that the charge-carrying species and unpaired spins in these two observations are not identical. The exact nature of these physicochemical phenomena require more detailed investigations by x-ray diffraction or neutron scattering techniques. The transition at 75 K is probably related to magnetic as well as structural changes occurring in the polymer. For temperatures between 6 and 75 K, the susceptibility obeys the Curie-Weiss law, $\chi_g = C/(T - T_C)$, where C is the Curie constant and T_C is the Curie temperature. It indicates that in this temperature range the unpaired spins are localized and uncoupled due to their noninteraction. Above 75 K susceptibility is again temperature dependent, exhibiting a Pauli-like behavior which deviates as the temperature rises towards room temperature, and also, to some extent, evidences a weak coupling of unpaired spins.

The observation of temperature-dependent Pauli susceptibility indicates the existence of a nondegenerate state in polypyrrole and therefore a finite Fermi density of states of spin carriers. In addition to a clear transition at 75 K, some other physicochemical changes also occur at higher-temperature regions in polypyrrole. The temperature-dependent Pauli contribution is very unusual, which may involve dynamic and/or structural phenomena. An accurate evaluation of polymer chain length is quite difficult due to the insolubility of polypyrrole. Therefore it may be anticipated that polypyrrole system is composed of numerous oligomeric as well as polymeric products. The crystallinity, which strongly contributes to the enhanced intermolecular interaction, varies as the chain length of the pyrrole system increases. It is a well-known fact that electro-oxidation of pyrrole imparts a very high degree of disorder into the polymer.¹ The oligomers of pyrrole possess highly crystalline structure and are usually incorporated with extremely poorly crystalline polypyrrole.

Presumably, the microcrystalline regions embedded into the nearly amorphous matrix of the polymer may generate an utterly chaotic state of magnetic species. Thus observation of cooperative phenomenal changes simultaneously occurring in the polypyrrole system seems highly improbable. As a consequence of the enigmatic nature of the material, a very unusual temperature-dependent Pauli-susceptibility behavior such as that observed in the present study can be anticipated. Even an interpretation of present results in terms of true matter physics seems rather difficult. Devreux *et al.*⁴⁵ reported the magnetic susceptibility of polypyrrole perchlorate (ClO_4^-) samples, which obeys Curie-Weiss law from 30 to 300 K, and a sharp transition around 30 K was noticed. Both the temperature-dependent susceptibility and linewidth clearly indicate a transition about 30 K. The exact nature of the above-mentioned transition has not

been interpreted by the authors. The polypyrrole system has structural similarities to the *cis*-polyacetylene; if the heteroatom is not present in the carbon backbone, then it resembles the *trans-cisoid* isomer. Interestingly enough, the present observations are nearly similar to the results of Tomkiewicz *et al.*⁵² reported for the 0.90% arsenic pentafluoride-doped *cis*-polyacetylenes studied by the double integration of ESR measurements. In these *cis*-polyacetylenes, magnetic susceptibility is strongly temperature dependent below 35 K; however, this effect is not dominant as temperature rises towards room temperature ($T > 35$ K). The authors interpreted the data in terms of a few localized electrons for the low-temperature Curie behavior and the possible origin of Pauli susceptibility from an impurity band. However, the present results more clearly differentiate between a Curie- and a Pauli-like susceptibility of oxidized polypyrrole. A possible interpretation of such observations from chemical and physical viewpoints has been discussed.

The values of the spin susceptibility at three different temperatures for polypyrrole and polythiophene are listed in Table I. At low temperature, susceptibility varies by a factor of ~ 500 between 6 and 75 K, while this difference is approximately ~ 40 from 75 to 300 K. In other words, the population of unpaired spins changes by approximately more than 2 orders of magnitudes from 6 to 75 K and further increases as the temperature rises above 75 K, resulting in a partial decoupling of spins. Such a contribution probably arises from magnetic changes. These results indicate that the pairing of spins takes place with a change of temperature. The SQUID technique is more precise and is able to identify the magnetic species on a more quantitative and qualitative basis. From the present reported results, the sample shows a Curie-like component at the low-temperature tail and a Pauli susceptibility towards room temperature. The origin of this unusual magnetic behavior increases the inquisitiveness concerning the coexistence of unpaired spins and charge-carrying species as well as existing disorder in polypyrrole.

As previously discussed, in the highly doped polypyrrole, the coupling of unpaired electrons (polarons, spin $\frac{1}{2}$) leads to the formation of spinless bipolarons, which is diamagnetic in nature and, hence, shows no ESR signal. A conductivity mechanism due to these spinless bipolarons has been suggested.^{1,44,53} The previously reported results are consistent with the spinless bipolaron theory and support a hypothetical bipolaron band of the order of 0.25 eV.⁵³ Various researchers have conducted temperature-dependent conductivity measurements in order to examine the conduction mechanism in oxidized polypyrrole.

TABLE I. Values for susceptibility of polypyrrole and polythiophene at three different temperatures.

Temperature (K)	χ_g (10^{-7} emu/g)	
	Polypyrrole	Polythiophene
6	19.05	15.62
75	0.04	3.03
300	1.52	1.33

The temperature-dependent conductivity data do not show any anomalies from 1.3 to 300 K and the results fit Mott's variable-range-hopping (VRH) conduction process quite well.⁵⁴⁻⁵⁶ However, in a recent study made by Shen *et al.*,⁵⁷ the temperature-dependent thermopower measurements do not fit into this model and it has been suggested that the VRH model may not be appropriate for oxidized polypyrrole. Similar to polyacetylene, several other possibilities for conduction have been suggested. Owing to the complexity of the polymer morphological structure, it has been rather difficult to draw any definite conclusions for a conductivity mechanism. In addition to the SQUID measurements, which show the paramagnetism in polypyrrole samples, which will be discussed below, the ESR technique also shows a very strong signal of the ESR linewidth, 0.14 G, indicating the presence of highly mobile dynamic defects. These results suggest that there are uncoupled polarons which are not able to recombine to form bipolarons due to Coulombic repulsion or some other energetic mechanism. If the dynamic defects are not extrinsic due to impurities, then the only other possible explanation is the existence of unpaired polarons. The present results show consistency with previously reported ESR data, and, to some extent, the magnetic-susceptibility measurements also substantiate the so-called bipolaron hypothesis. Genoud *et al.*⁵⁸ studied the magnetic properties of polypyrrole using a more quantitative method by performing an *in situ* ESR-electrochemical experiment and excluded the possibility of the spinless-bipolaron hypothesis. These authors suggested the presence of polarons on odd chains of polymer, which may be appropriate due to the average-molecular-weight consideration in polymeric systems. The exclusion of either possibility seems unreasonable since coexistence of polarons and bipolarons cannot be completely ruled out. Moreover, the exact length of polypyrrole chains cannot be defined due to their limited characterization only in the solid state. However, various chain lengths between four units to several hundreds of units have been suggested.^{1,59} The present magnetic measurements show that dynamic defects are delocalized over several monomer units and, therefore, polypyrrole has an extended conjugation.

Polypyrrole tetrafluoroborate shows an exceptionally narrow ESR linewidth of the order of 0.14 G at room temperature (Fig. 3), even comparatively narrower than *trans*-polyacetylene (0.2 G).⁴ For the tetrafluoroborate-doped polypyrrole, the ESR spectrum is symmetrical, possessing a nearly Lorentzian line shape, but deviates when the counteranions are exchanged by *p*-bromobenzenesulfonate anions. Such a narrow peak-to-peak ESR linewidth (H_{pp}) indicates the higher degree of conjugation and even more perfection of the polymer chain. The electrical conductivity, g value, and peak-to-peak ESR linewidth recorded at room temperature for polyheterocyclics are shown in Table II. A linewidth of 0.20–0.30 G in polypyrrole perchlorate has been reported by Street *et al.*³⁶ A variation in the linewidth of polypyrrole, depending on the synthetic conditions, has been observed during several investigations. For example, polypyrrole doped with sulfate anions exhibits a

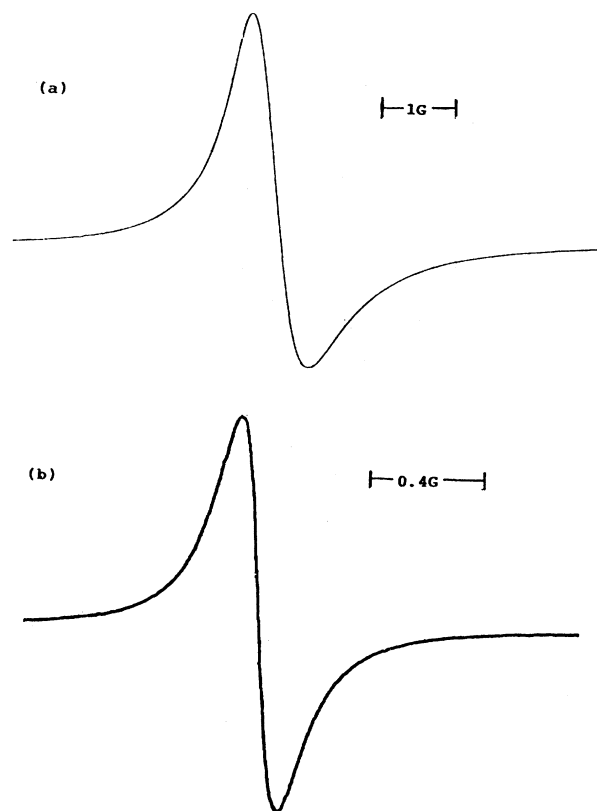


FIG. 3. ESR spectra of electrochemically synthesized polypyrrole samples recorded at room temperature; (a) polypyrrole contains *p*-bromobenzenesulfonate counteranions, and (b) polypyrrole contains tetrafluoroborate counteranions.

linewidth of 5.5 G, as reported by Hyodo and MacDiarmid.⁶⁰ Also, in the present study, when tetrafluoroborate anions were replaced by *p*-bromobenzenesulfonate anions, a linewidth of 0.75 G was obtained. The ESR signal has a Dysonian line shape, and the asymmetric ratio (A/B) amounts to about 2.5 at room temperature (Fig. 3), indicating the metallic characteristics of the polymer. This suggests that the linewidth is affected by the nature of the incorporated anions and is an extrinsic property. When the polypyrrole films containing counteranions were reduced in aqueous ammonia, a more than tenfold increase (from 0.14 to 1.8 G) in ΔH_{pp} was observed.

The influence of radiation on the BF_4^- -doped samples was also investigated in order to examine the dynamic defects occurring due to chains breaking or cross linking.

TABLE II. Electrical conductivity, g value, and peak-to-peak linewidth of polypyrrole, polythiophene, and polyfuran recorded at room temperature.

Polymer	Conductivity (S/cm)	g value	Linewidth (G)
Polypyrrole	100	2.0028	0.14
Polythiophene	20	2.0026	2.0
Polyfuran	20	2.0030	6.0

The ΔH_{pp} of polypyrrole tetrafluoroborate show a slight variation with exposure time. A 2-h exposure time raises the ΔH_{pp} to 0.28 G, while its further exposure for 24 h increased up to 0.40 G. Exposure to radiation results in inter- and intrachain breakage, thus limiting the mobility of the charge carriers due to reduced chain length. The shorter chain-length segments would hinder the propagation of paramagnetic defects and thus will localize them. The broadening of the ΔH_{pp} could be explained by these short chain segments. The conductivity of polypyrrole tetrafluoroborate when aged in an oxygenated atmosphere for 36 months decreases by at least 3 orders of magnitude (from 100 to 0.1 S/cm). Diaz and Hall²⁶ also studied the effect of atmospheric conditions on various samples, and conductivity was found to decrease from 50 to 7 S/cm within a period of 27 months. In another study, the conductivity of unprotected polypyrrole only declined by 20% over a period of 12 months.¹ Such a negligible change indicates good stability of polypyrrole under ambient conditions. A significant effect of oxygen atmosphere on the ESR spectrum was also observed since its ΔH_{pp} increases by a factor of 40 (from 0.14 to 5.7 G). The broadening of the ESR line reflects the interaction of the unpaired spins with the paramagnetic impurities such as oxygen. The g values determined were 2.0031 different from the pristine sample (g value of 2.0028). The present observation of the oxygen effect is not in agreement to the results of Street *et al.*³⁶ and Devreux *et al.*,⁴⁶ who reported a very strong influence of oxygen on polypyrrole since ΔH_{pp} increased at least by a factor of 100 upon very short exposure. The influence of atmospheric conditions (radiation and paramagnetic oxygen) on the ESR spectrum of polypyrrole is not surprising since chemical degradation contributes to several physicochemical processes occurring in materials.

The magnetic susceptibility (χ_g) of polythiophene tetrafluoroborate plotted against temperature is shown in Fig. 4. The temperature-dependent susceptibility shows a Curie-like behavior over the entire range, except for a cusp at about 130 K. These results show a high density of uncoupled and dominantly localized spins in polythiophene. This may be a possible phase transition since polythiophene has been reported to possess partially crystalline structure.¹ A study made by Tourillon *et al.*⁶¹ on poly(3-methylthiophene) doped with trifluoromethylsulfonate anions (SO_3CF_3^-) also indicates the possibility of a phase transition near 200 K. The polythiophene systems in these two studies are quite different due to the substituted methyl group in the thiophene ring and incorporated counteranions. Such variations in the phase-transition temperature can be anticipated due to the resulting differences in polythiophene materials and the measurement techniques employed for magnetic investigations. Figure 5 represents the X-band ESR spectra of electrochemically synthesized polythiophene in oxidized and neutral states. The g value was found to be 2.0026, which corresponds to nearly a free-electron g value, which is also in agreement with the other reported results on polythiophene samples. An asymmetric ESR line (Dysonian shape) observed in a tetrafluoroborate-doped sample indicates the metallic

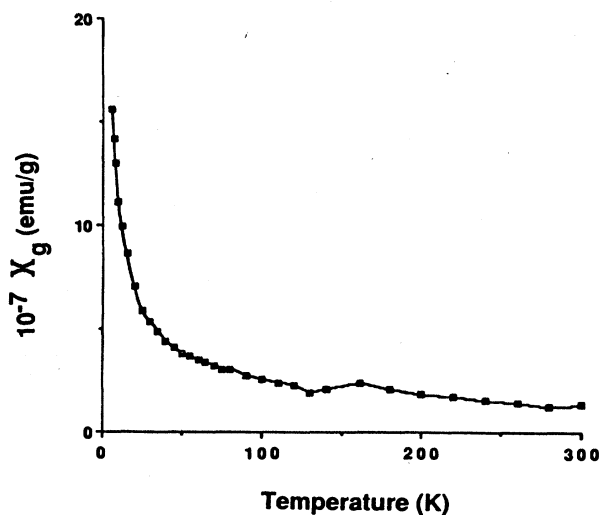


FIG. 4. Temperature dependence of magnetic susceptibility (χ_g) of electrochemically prepared polythiophene tetrafluoroborate (BF_4^-) obtained by the use of the SQUID method.

state of polythiophene, which gradually becomes symmetric after reducing the sample in aqueous ammonia. In the present case, oxidized samples show a ΔH_{pp} of 2 G, which broadens to 7 G after reduction. In another ESR observation made by Scharli *et al.*⁶² on poly(3-methylthiophene) doped with tetrafluoroborate, the temperature-dependent magnetic susceptibility shows a change from Curie-like to Pauli-like behavior with increasing dopant concentration. The authors reported

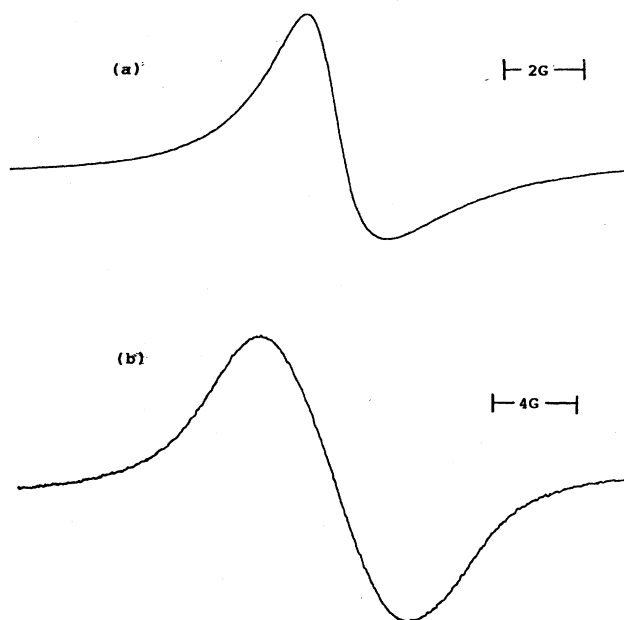


FIG. 5. ESR spectra of electrochemically synthesized polythiophene samples recorded at room temperature; (a) polythiophene is in an oxidized state containing tetrafluoroborate counteranions, and (b) polythiophene after reduction with aqueous ammonia solution.

that at higher doping levels the Pauli susceptibility appears in the temperature range ~ 80 – 100 K, which is nearly consistent with present data. The highly mobile polarons have been suggested as the dominant charge-carrying species by the authors, and in these BF_4^- -doped samples the spin density accounts for about 3×10^{19} spins/cm³, i.e., 1 spin per 300 thiophene rings, which reduces to 1 spin per 10 000 upon reduction with aqueous ammonia.

Moraes *et al.*⁶³ reported the determination of magnetic susceptibility in the iodine-doped polythiophene. The temperature-dependent susceptibility shows Curie behavior over the entire temperature range (10–300 K). A Dysonian ESR line shape at room temperature for the arsenic pentafluoride-doped polythiophene has been reported. The g value is slightly shifted and is of the order of 2.008. Tanaka *et al.*⁶⁴ reported that the g values and ΔH_{pp} of poly(3-methylthiophene) range between 2.0021–2.0026 and 2.75–6.53 G, respectively, depending on the oxidized and reduced states. The ΔH_{pp} in polythiophenes varies between 1.0 and 8 G, depending on materials preparation and the presence of counteranions.¹ The present results on oxidized polythiophene are in good agreement with those reported in the literature.

The polyfuran films were dark brown and very brittle. Typical ESR spectra of polyfuran in oxidized (conducting) and reduced (neutral) states are shown in Fig. 6. The ESR signal of polyfuran tetrafluoroborate had a peak-to-peak linewidth of 6 G, which increases to 10 G after re-

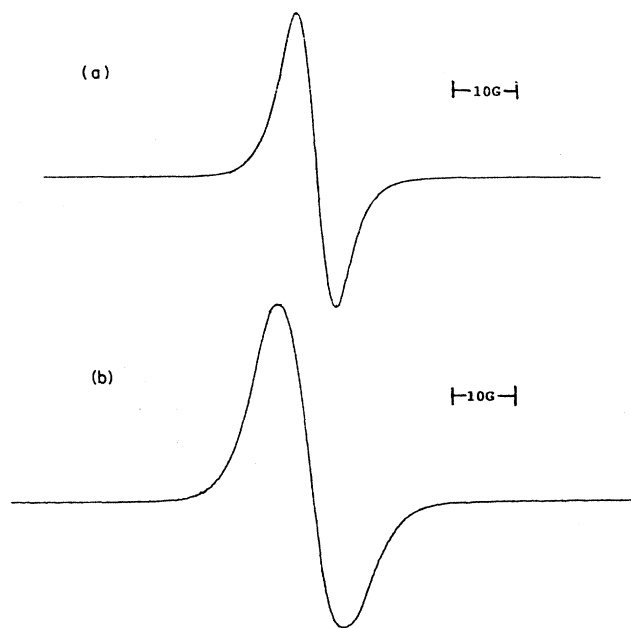


FIG. 6. ESR spectra of electrochemically prepared polyfuran samples at room temperature; (a) polyfuran contains tetrafluoroborate counteranions and, hence, is in its oxidized state, and (b) polyfuran after reduction with aqueous ammonia solution.

ducing the sample with aqueous ammonia. The oxidized, as well as the reduced, polymer, when exposed to air, shows a variation in ΔH_{pp} . The exchange of paramagnetic oxygen leads to the broadening of the ESR line, and the interaction also shows a Lorentzian shape. For the doped sample it increases to 7.5 G, while for an aqueous ammonia-reduced sample it approaches 10.5 G. This shows that oxygen affects the polyfuran in a way similar to the way it affected the polypyrrole system. Street *et al.*³⁶ reported that in perchlorate- (ClO_4^-) doped polypyrrole, ΔH_{pp} changes from 0.20 to 30 G within a very short exposure time. However, in polyfuran, oxygen was not that effective. In addition to the close proximity in electrical conductivity (~ 20 S/cm), the broad ΔH_{pp} indicates a low degree of conjugation in polyfuran, in contrast to polypyrrole and polythiophene. It is well known that electrical conductivity originates within the defined chain length but paramagnetic defects are influenced by a variety of factors, such as, average molecular weight, degree of cross linking, attachment of defect to the lattice, etc. The g value calculated for polyfuran was found to be 2.0030. The difference in g factor is accountable due to the replacement of the heteroatom in the polymer carbon chains. If the transport behavior is associated with the heteroatom spin orbitals, then a change in g value is more likely. For a free electron, the g value corresponds to 2.0023. The g factor shows a remarkably small change as the conjugation system changes from polyacetylene ($g = 2.0026$) to polypyrrole ($g = 2.0028$), indicating that spin orbitals of heteroatoms which contribute to dynamic defects occurring in the polymer chains have an almost negligible effect.⁶¹ The ESR results are nearly consistent with earlier reported work on polyheterocyclics.

Since the temperature-dependent susceptibility results are very peculiar in polypyrrole, it requires more efforts to clarify the transport and magnetic species. Certainly the use of a SQUID is one of the most sensitive techniques for studying the existing paramagnetic species in a variety of materials and, similarly, its use can distinguish between existing polarons and bipolarons in these conducting polymers. Two approaches will be taken into consideration for polypyrrole: one from a chemical viewpoint and the other in terms of physical effects such as the existence of polarons and bipolarons (or any other species?). Polypyrrole has been intensively characterized by various analytical techniques in order to investigate its morphological structure. A very high degree of disorder has been seen in polypyrrole, as reported in the literature.¹ In polypyrrole tetrafluoroborate samples, the elemental analytical data indicate that in most cases the fluorine contents are relatively lower than the expected values.^{1,33,55,65,66} In such a case, then, the question arises as to how the chemical stoichiometric factor would affect the physicochemical properties of the polymer. Do the unpaired spins result from the stoichiometric imbalance due to compensatory factors?

The analytical techniques indicate a high degree of structural disorder (cross linking and branching) in polypyrrole. Therefore, in polypyrrole structural disorder may be associated with the imperfect conjugations.^{67,68} Also, higher contents of hydrogen

($\sim 10\%$),^{1,66,69} determined by elemental analysis, indicate that there are some saturated pyrrole rings in the polymer that would limit the mobility of the charge carriers. If saturated rings are in the main polymer chain, then it would localize the defects, while their existence at the end of the polymer chain would be less effective. Usually, in polymers, segments of different chain length are found. It may be that Curie behavior at low temperature appears from the localized spins in short chain segments and the higher-temperature Pauli susceptibility is a contribution of long polymeric chain segments. If there is no correlation between unpaired spins and charge carriers, then neutral defects may originate from the stoichiometric imbalance. If paramagnetic defects are due to the chemical composition, such as stoichiometric imbalance and impurities, then paramagnetism should be of an extrinsic nature and a large difference in magnetic parameters with a variation in synthetic conditions can be expected. On the other hand, if defects are intrinsic, resulting only within the carbon-carbon chains, then magnetic behavior must have some similarities to the doped *cis*-polyacetylenes. Because of the complexity of polymeric materials, it is not evident from where the paramagnetic defects originate; however, the carbon-backbone contribution cannot be ruled out. The available experimental data on polypyrrole are still not sufficient for quantitative consideration. In particular, the chemical components need to be studied in conjunction with magnetic behavior to validate such possibilities.

A large variety of experiments have been conducted in order to study the magnetic behavior, and several possibilities have been considered for conduction in oxidized polypyrrole. Scott *et al.*⁴⁴ showed the existence of spinless bipolarons in polypyrrole perchlorate which contribute to conductivity. Polaronic characteristics for highly doped polypyrrole have been suggested by Kaufman *et al.*¹⁷ The above results on oxidized polypyrrole are inconsistent with one reported by Genoud *et al.*⁵⁸ Kahol and Mehring⁷⁰ in keeping with their experimental results, proposed an exchange-coupled-pair model for non-Curie-like susceptibility in conducting polypyrrole. Nechtschein *et al.*⁷¹ conducted a more quantitative study for the existence of polarons and bipolarons in polypyrrole by simultaneously performing *in situ* ESR-electrochemical experiments and suggested a non-Nernstian behavior due to interparticle charge-repulsion interactions. A theoretical model has been proposed for such characteristic behavior by these authors.^{71,72} The question of the existence of bipolarons and their contribution to conduction is still unresolved and, therefore, more quantitative explanation is required, particularly in terms of magnetic aspects. At least the present results are able to further elucidate the bipolaronic hypothesis on a quantitative basis, particularly in regard to the paramagnetic spin concentration. The high sensitivity of the SQUID technique also cautions us about the coexistence of polarons. Whether or not they really contribute to conduction still remains questionable.

The physical aspects of the origin of unpaired spins and their probable relationship with charge-carrying species have been discussed for the present results. It is

well established that conduction takes place through interchain hopping of bipolarons, and that such a process is energetically blocked for polarons. Bipolarons are formed in the system when two polarons appear on the same polymer chain. It is quite possible that some of polarons are trapped in the lattice defects and are therefore unable to form bipolarons. In other words, polarons and bipolarons may coexist in polymeric systems which have an abundance of neutral defects. It is also possible that with increasing temperature the thermal excitation exceeds the binding energy of the bipolaronic state and that this may dissociate some of the bipolarons into unpaired spins or polarons. It is not unusual to observe a small increase in susceptibility as temperature rises beyond 75 K. Such a remarkable change may not be visible in conductivity measurements⁵⁴ simply if the charge-transport process only involves bipolarons. As pointed out above, ESR and SQUID techniques detect the presence of polarons. Although these polarons coexist in the system, they may or may not participate in the conduction mechanism. Therefore, conductivity measurements will not shed any light on their existence or nonexistence, which implies that a transition state in the conductivity may not be observed. Since the SQUID technique is only sensitive to magnetic species, and conductivity measurements only reveal the nature of the charge carriers, similar temperature-dependent phenomena cannot be observed. If the charge-carrying species in doped polypyrrole are bipolarons, then temperature-dependent conductivity may have a few similarities to these magnetic observations.⁵⁴⁻⁵⁶ Kaneto *et al.*⁴⁷ also suggested the possibility of two different kinds of polarons, i.e., shallow polarons and deep polarons in the case of polythiophene, but which types of polarons occur in relation to their contribution to magnetic and conducting behaviors is not clear. In fact, these hypotheses are nearly identical to those reported by Genoud *et al.*⁵⁸ One possible explanation is based on energetic considerations since if the energy for the formation of a doublet of polarons is somehow different, then bipolarons may not be involved. Bredas and Street¹¹ reported that formation of a bipolaron is energetically favored over two polarons by 0.45 eV, and this theoretical consideration has been supported by ESR measurements.¹⁸ The present susceptibility results clearly show a predominantly spin-coupling type of phenomenon, which probably involves formation of bipolarons, but in addition, coexistence of polarons in the polymer system is also apparent. The temperature dependence of spin susceptibility exhibits unusual behavior in oxidized polypyrrole and possible interpretation in terms of bipolarons and polarons have been discussed above. The low-temperature Curie behavior shows a high population of uncoupled and localized spins in polymers. As temperature increases towards 75 K, the coupling of unpaired spins (identical species, i.e., polarons) takes place; however, some uncoupled spins remain, possibly due to their trapping into lattice defects. The uncoupled spins never reach a clear steady state of spinless species because immediately after 75 K partial decoupling of paired spins starts, since the number of spins increases by a factor of approximately 40 from 75 to 300 K. Although the

present situation seems much more favorable to the bipolaron hypothesis, quantitatively the possibility of the existence of polarons still cannot be excluded, and thus—relatively—a slightly muddled picture of the coexistence of magnetic and nonmagnetic species develops. From these susceptibility data, over the entire temperature range the existence of spinless bipolarons (if they are assumed to be the coupled spins) contributing to conduction is apparently visible around and after 75 K in oxidized polypyrrole. As discussed earlier, a strong transition occurring at 75 K may be of magnetic type. Although it has not yet been established, microcrystallites of oligomers probably embedded in a nearly amorphous matrix of the polymer may lead to such unusual temperature-dependent Pauli-susceptibility behavior.

In the case of polythiophene, a different situation is likely to be encountered. A phase transition above 130 K is observed, but a significant change in spin density similar to polypyrrole was not found. However, the Curie behavior observed in the present case of polythiophene is in agreement with previously reported results.^{1,62-64} It also indicates that two polymers are not identical; the significant differences may occur owing to a variety of factors.⁴⁸ The nature of unpaired polarons (spins) is a very important factor to be considered here, since magnetic behavior would be influenced by the average conjugation length, the degree of polymer cross linking, and the number of polarons and the way in which they are bound to the lattice. Moreover, these possible phase transitions in polypyrrole and polythiophene may also result from a change in microcrystalline structure,^{1,58,69,73} as discussed earlier in the text. The inconsistency in magnetic properties may be associated with the complex crystalline and morphological structures of polyheterocyclics since synthetic routes play an important role.^{29,74} If it is assumed that abstraction of some heteroatoms from polyheterocyclics takes place during electropolymerization, then extremely low segments closely related to *cis*-polyacetylene may also be present in the polymeric system. Under such circumstances polypyrrole or polythiophene would not only be composed of their own oligomeric products, but may also contain an extremely low concentration of *cis*-polyacetylene segments. It is known that polyacetylenes possess highly crystalline structure.^{1,4} Therefore, in the present case, if any assumptions are made, then the crystalline structure of *cis*-polyacetylene needs to be considered. However, due to the complexity of polyacetylene materials various inconsistencies have been observed, but *cis*-polyacetylenes show reasonably high crystallinity.^{4,75-77} While not established so far, the possibility of polymorphism has also been suggested in polyacetylenes. If—due to the abstraction of heteroatoms—some *cis*-polyacetylene segments are formed, then regions of microcrystallinity may be generated into the polyheterocyclics. In addition to their oligomers, they may be associated with the observed phase transitions in polyheterocyclics. An analogous structure between polythiophene and *cis*-polyacetylene has been proposed by Chung *et al.*,⁷⁸ where the abstraction of covalently bonded sulfur heteroatoms from a polythiophene backbone structure should lead to an sp^2p_z polyene chain

structure. Such assumptions have been analyzed by performing the photoinduced absorption measurements on polythiophenes.⁷⁹ However, in the literature so far there is no such evidence for the existence of *cis*-polyacetylene segments in the polyheterocyclic carbon chain.

It has not yet been conclusively established whether bipolarons or polarons are the charge-carrying species responsible for conductivity in polyheterocyclics, but spin-coupling phenomena tend towards bipolaronic contribution. These experiments show that coupling of unpaired spins takes place at some stage, particularly in oxidized polypyrrole. While it is not very clear in the case of polythiophene, we may be dealing with two completely different materials, at least in terms of the chemistry of these two polymers. The characteristic differences in the magnetic susceptibility of polypyrrole and polythiophene are not easily interpretable. Although these conjugated polymers are a class of materials entirely different than inorganics, from the morphological point of view it has been reported that as particle size increases the magnetic susceptibility changes from a Curie- to a Pauli-like behavior.⁸⁰⁻⁸² Therefore, considering the present case, if polypyrrole possesses particles of larger size than polythiophene, then these two polymers may exhibit different magnetic behavior. However, from the present results the possibility of phase transitions has been analyzed through electronic and morphological approaches, still, in order to understand fully the exact nature of these transitions, more quantitative investigations are required.

IV. CONCLUSIONS

In conclusion, the present work describes a magnetic-susceptibility study of tetrafluoroborate-doped polypyrrole and polythiophene conducting polymers. The temperature-dependent susceptibility measurements performed over the range 6–300 K indicate the possibility of phase transitions at about 75 K in polypyrrole and at about 130 K in polythiophene. These possible phase transitions have been interpreted in terms of electronic and morphological structures of polyheterocyclics. Although not yet established, these transitions may be associated with the microcrystallinity of polyheterocyclics arising from the incorporated oligomers and/or *cis*-polyacetylene segments formed during electro-oxidation due to the heteroatom abstraction. The SQUID technique conclusively shows that the charge-carrying species responsible for conductivity and the paramagnetic species contributing to magnetic behavior do not have any significant correlation, and thus these results substantiate previously reported ESR findings. Although the unpaired spins show a strong-coupling tendency, probably due to the formation of spinless bipolarons, the presence of polarons cannot be neglected, whether because of their trapping into lattice defects or for some other physicochemical reasons. Although present results provide a wealth of information, still more quantitative studies are required in order to understand fully the magnetic and electronic properties of these polyheterocyclics. The characteristic difference in the magnetic susceptibility of

oxidized samples of polypyrrole and polythiophene may arise due to various physicochemical properties, such as degree of conjugation, concentration of counteranions, degree of cross linking, and crystalline and morphological structures (particle size, interaction between the particles, etc.). The ESR studies show that polyheterocyclics are paramagnetic in their conducting state, and, to some extent, the intrinsic properties are influenced by the nature of the heteroatom in the conjugated polymer backbone.

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