PHYSICAL REVIEW B VOLUME 48, NUMBER 1 1 JULY 1993-I

Magnetic studies of $FeCl_4^-$-doped poly(3-alkylthiophenes) and poly(4,4′-dialkyl-2,2′-bithiophenes)

P. Barta and S. Nizioł
Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, 30-059 Kraków, Mickiewicza 30, Poland

M. Zagórska
Department of Chemistry, Technical University of Warsaw, 00-664 Warszawa, Noakowskiego 3, Poland

A. Proń
Department of Materials Science and Ceramics, University of Mining and Metallurgy, 30-059 Kraków, Mickiewicza 30, Poland

Z. Trybuła
Institute of Molecular Physics, Polish Academy of Science, 60-179 Poznań, Smoluchowskiego 17/19, Poland

(Received 27 February 1992; revised manuscript received 8 February 1993)

Two types of soluble conducting polymers doped with $FeCl_4^-$ were investigated, namely, poly(3-alkylthiophenes) and their "head-to-head," "tail-to-tail" coupled analogues: poly(4,4′-dialkyl-2,2′-bithiophenes). The samples were subjected to static magnetic measurements of the magnetic susceptibility (the Faraday balance) and electron-spin-resonance spectroscopy in a wide temperature range (4.2–273 K). A classical paramagnetic dependence of the static magnetic susceptibility can be found at high temperatures. On the other hand, a different magnetic effect appears at low temperatures. This may suggest that below a certain temperature (denoted as T_a), short-range magnetic order affects the magnetic response of the polymer samples.

INTRODUCTION

In recent years conjugated polymers have attracted significant attention mainly because of their interesting nonlinear optical properties and their doping-induced electroactivity. Much of these research efforts were devoted to polyalkylthiophenes, which differ from other conjugated polymers by their solubility in common solvents. This latter property is of extreme importance from an applications point of view, since it strongly facilitates the processability of these materials. Polyalkylthiophenes are most frequently prepared by oxidative polymerization of 3-substituted thiophenes.[1,2] Recently, a new family of these compounds was synthesized, namely poly(4,4′-dialkyl-2,2′-bithiophene).[3] Poly(4,4′-dialkyl-2,2′-bithiophenes) can be formally treated as "head-to-head," "tail-to-tail" coupled analogues of poly(3-alkylthiophenes). Both poly(3-alkylthiophenes) (P3AT's) and poly(4,4′-dialkyl-2,2′-bithiophenes) (PDABT's) may be chemically doped using a suitable doping agent (for example, $FeCl_3$). In the process of doping the polythiophene chain, charge carriers, polarons or bipolarons, are introduced into polymer conjugated chains.[4–6] For this reason, electronic band structure and electronic transport properties fundamentally depend on the dopant concentration.[7] Furthermore, because transport properties of electrically conducting polymers are also limited by interchain and interfibrillar conductivities, the net value of the macroscopic conductivity depends on the dimension of the dopant molecule.

If the polymer matrix is doped with magnetic agents, magnetic measurements may be useful as an additional source of information about the nature of dopant agent-polymer chain interactions. This, in turn can be useful in understanding electrical transport processes. Additionally, in the case of magnetic dopants, influence of the localized magnetic moments on delocalization of charge carrying species (polarons, bipolarons) are expected as a consequence of the dopant-polymer chain interaction. The introduction of an external magnetic moment into the conjugated polymer system was discussed by Jones[8] for polyacetylene. In this case, ferric chloride was chosen as a magnetic impurity candidate. For these samples, there was no evidence for any magnetic interactions. Contrary to this result, Kucharski *et al.*[9] reported an observation of the antiferromagnetic coupling between the dopant species and the polymer chain. These interactions were detected for *PPV* doped with ferric chloride. It is very interesting that the cited results were obtained for two totally different conjugated systems. The fact that magnetic order has been observed for systems with nondegenerate ground states, but has not been reported for systems with degenerate ground states, is motivation for additional studies.

In our research, polythiophene was chosen as the nondegenerate ground-state system. The polymers investigated (see above) were doped with the same magnetic agent: ferric chloride. In the doping process, the negative tetrachloroferrate ($FeCl_4^-$) complex is formed as the counter ion to the positively charged polymer chain. According to earlier observations reported by Proń[10] and by Sakai,[11] the high spin state of the ferric ion with the effective magnetic moment $\mu_{\text{eff}} = 5.92\mu_B$ is to be expected at room temperature.

In this paper we describe the results of the static magnetic susceptibility and the electron spin resonance spec-

0163-1829/93/48(1)/243(7)/$06.00

troscopy measurements carried out on doped poly(3-alkylthiophenes) and poly(4,4′-dialkyl-2,2′-bithiophenes). These magnetic studies were undertaken for several reasons: to address whether the alleged doping specie, $FeCl_4^-$, acts as a free paramagnetic agent with a spin $\frac{5}{2}$; to obtain some information about possible short-range magnetic order; and to obtain information about the character of the charge carrying specie responsible for the transport phenomena.

EXPERIMENTAL

The substrates for the polymerization of the two families of polymers studies were prepared as follows: (i) 3-alkylthiophenes were prepared from 3-bromothiophene by Grinard coupling.[12] (ii) 4,4′-dialkyl-2,2′-bithiophenes were prepared from 3-alkylthiophenes by metalation with butyllithium followed by oxidative dimerization with $CuCl_2$.[3]

The monomers were then polymerized with $FeCl_3$ to the corresponding polymers. Different procedures were used for the monomer compounds than for the dimer ones. The main differences were connected to the purification procedure and the concentration on the substrates. The exact procedure for the preparation procedure for PAT's, used in the present studies was reported by Kulszewicz-Bajer *et al.*[13] The preparation of PDABT's on the other hand, was described in detail by Zagòrska and Krische.[3] The polymers were checked for iron contamination after the synthesis and were found essentially iron free. Free-standing films of undoped polymers were prepared by casting from chloroform solutions.

The films were doped with $FeCl_3$ to give $[P3AT(FeCl_4)_y]_n$ and $[PDABT(FeCl_4)_y]_n$, respectively. The dopings were carried out in $FeCl_3$ solution in dry nitromethane. The doping level was controlled by the time of the direct contact of the doping solution with the film. After doping, the samples were washed repeatedly to remove any excess of the doping agent, and then vacuum dried to constant mass. The doping levels were determined from mass uptake, and verified by elemental analysis for selected samples. The relative error of the dopant concentration determination was estimated to be below 10% for all tested samples. Based upon the elemental analysis of the selected samples, the estimated dopant levels should be regarded as the higher bounds. It should be noted here that in inappropriately doped samples, antiferromagnetic aggregates can exist,[14,15] which of course would influence the measured magnetic susceptibility. The existence of such aggregates can be verified by Mössbauer spectroscopy (ME) studies, as reported by Proń *et al.*[16] The present measurements were carried out at sufficiently low temperatures, i.e., below the Néel temperatures appropriate to $FeCl_2$ and $FeCl_3$ aggregates. The ME studies of the samples indicate that the weight ratio of the "antiferromagnetic contaminants" to the "dopant iron" is the order of 10^{-2} and hence cannot affect the observed magnetic response of the samples.

Static magnetic measurements of the magnetic susceptibility were carried out on a Faraday-type magnetic balance with a Cahn RG type automatic electrobalance. A personal computer was used for computer data acquisition and analysis, allowing the collection of any number of experimental points. The balance was calibrated using Dy_2O_3, and the sensitivity of this magnetometer was estimated to be about 10^{-8} emu/g. Measurements were carried out in the temperature range from 5 K to 300 K, in a flow-gas cryostat, using magnetic fields up to 0.5 T.

The ESR measurements were performed with a standard 10 GHz X-band ESR spectrometer in the temperature range of 4.2 K–40 K. Temperature setting was accomplished using a gas-flow variable temperature cryosystem. The temperature was measured using Au+0.03% Fe-chromel thermocouple with total accuracy better than 1 K.

In all measurements polymer samples were exposed to air for about 15 min during mounting in the apparatus.

RESULTS AND DISCUSSION

As mentioned above, samples were doped with ferric chloride to the different doping levels. The static magnetic susceptibility measurements were carried out for the samples, with dopant concentrations corresponding to medium and high doping levels. In principle, at medium doping, positive bipolarons are expected. Because of interactions between charged excitations, the lowest charge transfer configuration at high (saturated) doping level is expected to correspond to a polaron lattice.[17] The dopant concentration y, defined as the number of dopant anion species per monomer of the polymer, i.e., $[(P3AT)^{+y}(FeCl_4^-)_y]_n$ and $[(PDDBT)^{+y}(FeCl_4^-)_y]_n$. The following samples were subjected to susceptibility measurements:

P3HT: $y=0.02,\ 0.10,\ 0.42$,

P3OT: $y=0.04,\ 0.11,\ 0.41$,

PDDBT: $y=0.03,\ 0.30$.

Samples with the lowest doping levels obtainable in this study correspond to medium dopant concentrations. The remaining dopant compositions belong to the high-doping regime.

In Fig. 1(a) a typical measured temperature dependence of the static magnetic susceptibility is shown, where static magnetic susceptibility is plotted as a function of absolute temperature. The quenching of the magnetic signal for one polythiophene sample is more evident in Fig. 1(b) than in Fig. 1(a). The onset of the change in the magnetic susceptibility with increasing temperature (i.e., near 7 K) is very similar to systems in which paramagnetic to magnetic ordering transitions occur.

Consider the static magnetic susceptibility of a given sample as a function of temperature. This may be described by the following formula:

$$\chi(T)=\chi_0+\chi_{PC}(T)+\chi_{DOP}(T)\ , \qquad (1)$$

where particular contributions are as follows. χ_0 is a sum of temperature-independent contributions; namely, core diamagnetism of the polymer chains and dopant mole-

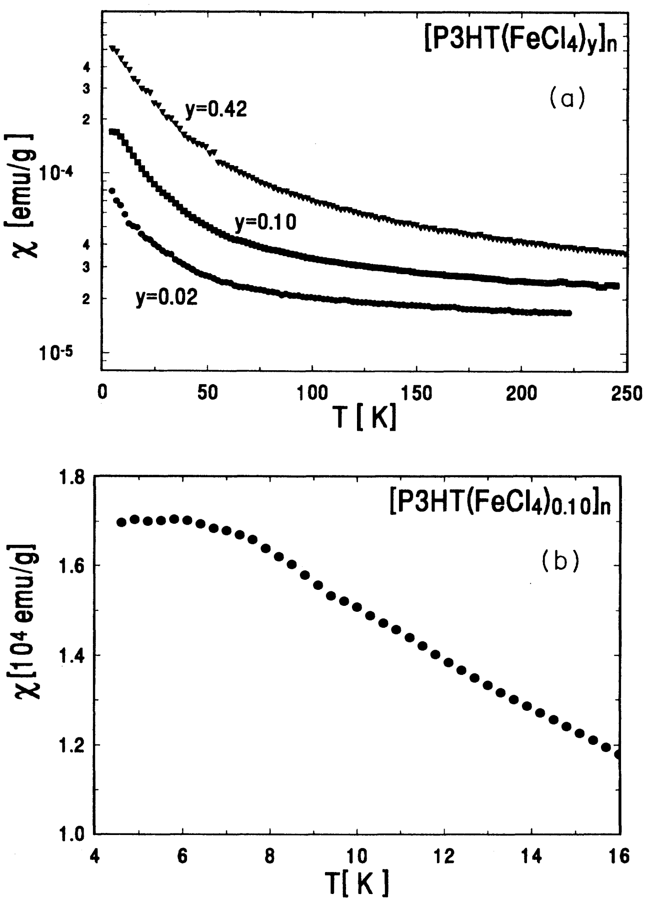

FIG. 1. (a) Temperature dependence of the static magnetic susceptibility for FeCl$_4^-$ doped poly(3-heksylothiophene) (P3HT). Measurements were carried out for three dopant concentrations ($y=0.02$, 0.10, 0.42). Every third point is shown. (b) The temperature dependence of the magnetic susceptibility for [P3HT$^{+0.10}$(FeCl$_4^-$)$_{0.10}$]$_n$. Quenching of the magnetic response of the sample is observed.

cules. Moreover, the Pauli susceptibility of charge carriers should be taken into account. This may be described, to a good approximation, by $\chi_{\rm PAULI}=N(E_F)\mu_B^2$, where $N(E_F)$ is the density of states on the Fermi level and μ_B is the Bohr magneton. The total diamagnetic susceptibility can be obtained by summing all diamagnetic contributions (called Pascal constants) from all atoms and from all bonds in a given functional group, either for polymer chain or the dopant molecule. $\chi_{\rm PC}(T)$ is a Curie-like temperature-dependent susceptibility, which is associated with localized spins existing at polymer chain defects. And finally, $\chi_{\rm DOP}(T)$ is the Curie (Curie-Weiss) temperature-dependent susceptibility of the dopant molecule.

The temperature dependence of localized spin susceptibility can be described by the Curie law (or more generally by the Curie-Weiss law)

$$\chi(T)=\frac{C}{T-\Theta}=\frac{N\mu_{\rm eff}^2}{3\mu_B k_B}\frac{1}{(T-\Theta)} \ . \tag{2}$$

$C=N\mu_{\rm eff}^2\mu_B/3k_B$ is a constant which can be used to obtain the effective magnetic moment $\mu_{\rm eff}=g[J(J+1)]^{1/2}$, where N is the number of ions, J is a total quantum number, and μ_B and k_B are the Bohr magneton and the Boltzmann constant, respectively. The Θ temperature depends on the nature of the magnetic interionic or intermolecular interactions. The value of theta can be correlated with a sum of the exchange integrals of various magnetic interactions.[18]

In order to verify the agreement of the temperature dependence of the susceptibility with the Curie-Weiss law, the following formula was fitted to the experimental data over the entire temperature range:

$$\chi(T)=\chi_0+\frac{C}{T-\Theta} \ , \tag{3}$$

where the temperature-dependent part comes from the Curie-Weiss law, and χ_0 is the sum of all temperature-independent contributions in (1).

In general, a good correlation coefficient (of 0.999) was only obtained in the high-temperature range of the susceptibility data. Below a certain temperature, which we define as T_a, the static magnetic susceptibility did not follow the Curie-Weiss law. Here it should be considered that magnetic susceptibility studies of polythiophene samples doped with nonmagnetic anions such as ClO$_4^-$, the Curie law contribution to the total value of χ was 5×10^{-7} emu per mole thiophene and did not change with doping.[19,20] If it is assumed that stable (bi)polaron excitations exist as the dominant doping-induced charge storage configuration, then the $\chi_{\rm PC}(T)$ contribution to the total value of the measured susceptibility is of the same order of magnitude as the accuracy of our measurement technique, and, consequently, can be neglected. Furthermore, for polyalkylthiophene samples with the highest dopant concentration one can expect a finite density of states at the Fermi level.[21] This means that transport properties possess bandlike character. Accordingly, their influence on the magnetic properties should be manifested in the temperature-independent part of the magnetic susceptibility [Eq. (1)]. Consistently, only contributions to the temperature-dependent part of the fitted expression, which come from the dopant species, were taken into consideration.

All of the fit parameters obtained are shown in Table I. The values of the effective magnetic moment are also collected in this table. These values were calculated from the value of the Curie coefficient C obtained according to Eq. (2). Errors of the effective magnetic moment δ_μ also were estimated. It should be stressed here that the influence of the error of the dopant concentration determination on the estimated values of the magnetic moment errors was most pronounced for the lowest dopant concentrations. Despite the errors obtained, the values of $\mu_{\rm eff}$ shown in Table I are smaller than expected values for pure spin state ($\mu_{\rm eff}=5.92$). This is probably caused by the incomplete quenching of the orbital angular momentum of ferric ion because of distorted tetragonal ligands arrangement. Since for $3d^5$ atoms the spin-orbit coupling favors an antiparallel arrangement of L and S angular

TABLE I. Magnetic parameters derived from the Curie-Weiss law fitting above T_a.

Sample	P3HT			P3OT			PDDBT	
Dopant concentration	0.02	0.10	0.42	0.04	0.11	0.41	0.03	0.30
T_a (K)	21.7	22.8	20.8	33.9	31.3	33.6	34	35.6
Θ (K)	0.25	1.79	1.81	1.37	1.11	1.72	1.2	1.5
χ_0 (10^{-5} emu/C mol)	1.18	1.35	0.76	0.91	0.92	0.61	0.09	0.34
C (emu K/Fe mol)	5.42	2.98	3.32	3.41	4.27	3.36	4.16	3.52
μ_{eff} (μ_B/Fe ion)	6.6	4.89	5.16	5.23	5.85	5.19	5.78	5.31
$\delta_{\mu\,\mathrm{eff}}$ (μ_B/Fe ion)	1.77	0.56	0.33	1.77	0.34	0.17	1.72	0.35

TABLE II. Diamagnetic and Pauli susceptibilities of doped polythiophenes.

Sample		χ_{dia} (10^{-7} emu/C mol)	χ_{Pauli} (10^{-5} emu/C mol)
P3HT	$y=0.02$	-5.6	1.3
	$y=0.10$	-5.0	1.4
	$y=0.42$	-3.4	0.8
P3OT	$y=0.04$	-4.9	1.0
	$y=0.11$	-4.4	1.0
	$y=0.41$	-3.2	0.7
PDDBT	$y=0.03$	-4.5	0.1
	$y=0.30$	-3.4	0.4

momenta, one observes a reduction of the effective magnetic moment. For temperatures below T_a, the temperature dependence of the static magnetic susceptibility does not follow the Curie-Weiss law. In addition, a dependence of T_a on the length of the alkyl group is observed. This behavior is not entirely understood. The fact that T_a does not depend on the dopant concentration can be explained by the fact that the samples were doped to medium and high regimes. Since doping is inhomogeneous and bulk samples were doped, the dopant agents are located within areas with different dopant concentrations. Some areas within a sample are doped to high (saturation) level, while others are doped to the doping level well below the average estimated for the bulk sample. The size of such highly doped "clusters" increases upon doping, with almost constant dopant concentration within an individual "cluster." Thus, the molar magnetic response of a single cluster should not depend upon the dopant concentration. For all samples, the values of Θ obtained are all positive and are of the same order of magnitude as the estimated temperature error. Therefore, the existence of positive values of the factor representing magnetic interactions cannot be interpreted as an effect of ferromagnetic interactions in the polymer samples.

The Pauli susceptibility is the last quantity which can be extracted from the static magnetic measurements. It was obtained from χ_0 values by subtraction of the diamagnetic contribution to the total value of temperature-independent susceptibility. This contribution was estimated from the Pascal constants. The values of the Pauli susceptibility obtained are shown in Table II. They are comparable to those reported by Chen, Heeger, and Wudl[19] and by Moreas *et al.*[22] For the highest dopant concentrations, smaller values of χ_0 are observed. This may suggest that for dopant concentrations close to the saturation state bipolaronic rather than polaronic excitations are responsible for transport processes. Smaller values of the Pauli susceptibility for PDDBT, relative to other samples, may be explained by taking into account the experimentally proved lower conjugation length in PDDBT.[3] Then, the lower Pauli susceptibility may be caused by an expected concentration of barriers, resulting in a hindrance to movement of charge carrying species along the chain. This behavior was confirmed experimentally by electrical conductivity measurements on P3AT and PDDBT.[23]

To summarize the susceptibility data, $(\chi-\chi_0)(T-\Theta)$ as a function of temperature is shown in Fig. 2 in order to better illustrate the magnetic susceptibility deviation from the Curie-Weiss law. This disagreement indicates a complicated behavior of the magnetic moments of ferric ions at temperatures below T_a. The shape of the susceptibility curves [Figs. 1(a), 1(b), and 2] suggests rather antiferromagneticlike interactions. Furthermore, the measured effective magnetic moment μ_{eff} is lower than expected for pure paramagnetic dopant species. It should be mentioned here that a magnetic dipole interaction between dopant molecules ought to be excluded at once, since the energy of two directly interacting magnetic dipoles ($S_i=\frac{5}{2}$) about 10 Å apart is two orders of magnitude lower than the measured value of T_a.

Consider the behavior of paramagnetic spins in high magnetic fields at low temperatures. In this case, magnetization per unit volume can be described by the following formula:[18]

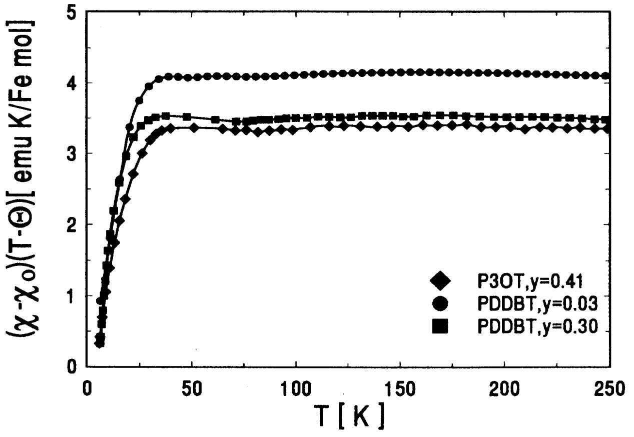

FIG. 2. Curves of $(\chi-\chi_0)(T-\Theta)$ vs temperature are shown for selected P3OT and PDDBT samples. The nonlinear parts illustrate the discordance with the fitted Curie-Weiss law. The fitting parameters are shown in Table I.

$$M = NgJ\mu_B B_J\left[\frac{gJ\mu_B H}{k_B T}\right], \tag{4}$$

where B_J is the Brillouin function,

$$B_J(\eta) = \frac{1}{J}\left[\left[J+\frac{1}{2}\right]\coth\left[J+\frac{1}{2}\right]\eta - \frac{1}{2}\coth\frac{\eta}{2}\right], \tag{5}$$

where

$$\eta = g\mu_B H/k_B T . \tag{6}$$

B_J describes the saturation of paramagnetic moments of total quantum number J. Therefore, if one assumes that the ferric ion acts as a pure paramagnetic ion, a similar dependence of the magnetization would be observed as a function of ratio H/T independent of temperature. In such a case, even if accessible magnetic fields do not suffice to reach the saturation state, the magnetization ought to follow the onset of the Brillouin function, especially of low temperatures. Any disagreement observed in the H/T dependence of the magnetization may be caused by the effect of magnetic interactions.

Accordingly, for two samples, P3HT ($y=0.42$) and P3OT ($y=0.41$), static magnetization measurements were carried out as a function of magnetic field at five temperatures below T_a. To obtain a strong and pronounced magnetic signal in weak magnetic fields, samples with the highest dopant concentration were chosen. Measurements were performed in magnetic fields from 0 up to 0.5 T. The dependences are shown in Figs. 3(a) and 3(b). The measured dependence of the magnetization on the ratio of magnetic field and absolute temperature should have followed the linear onset of the Brillouin function, if the paramagnetic state had been achieved. Any disagreement in the observed H/T dependence of the magnetization is caused by magnetic interactions. In fact, it can be seen that at higher temperatures, the magnetization increases linearly with the H/T ratio, with a slope depending on the measurement temperature. This means that magnetic phenomena can be roughly described by the Curie law, as approximated in the magnetization formula. The effective magnetic moment, evaluated from the highest temperature results, is very close to the value obtained from the temperature dependences of the susceptibility ($\mu_{\text{eff}}=5.30$ and 5.64 for P3HT and P3OT, respectively). The fact that the slope of the magnetization curve depends on temperature leads to the following conclusion: a transition from a paramagnetic state to a state in which the short-range magnetic interactions affect the pure paramagnetic response of the polythiophene samples is observed. This explanation is reasonable, especially because of the nonlinear behavior of the magnetization for the lowest measurement temperatures. Thus, the static magnetic measurements suggest an accentuation of magnetic interactions among ferric ions at low temperatures.

Additionally, the electron spin resonance also was carried out. There were several reasons to undertake such measurements. One goal was to exclude the possibility of the high-spin–low-spin evolution of the electronic state of the ferric ion. Moreover, the existence of (bi)polaronic state responsible for the transport properties can also be detected. Another reason was the desire to observe possible asymmetry of the g factor corresponding to the ferric ion. This may suggest the distortion of the tetrahedral ligand arrangement which, in turn, may cause the incomplete quenching of the orbital angular momentum. This, in turn, was suggested by the magnetic studies discussed above. Thus, the ESR measurements were carried out at low temperatures for selected samples with specified dopant concentrations:

POT $y=0.04$ and 0.41 ,

PDDBT $y=0.03$ and 0.30 ,

i.e., for the highest and the lowest doping levels. Results obtained for the polyoctylthiophene samples are shown in

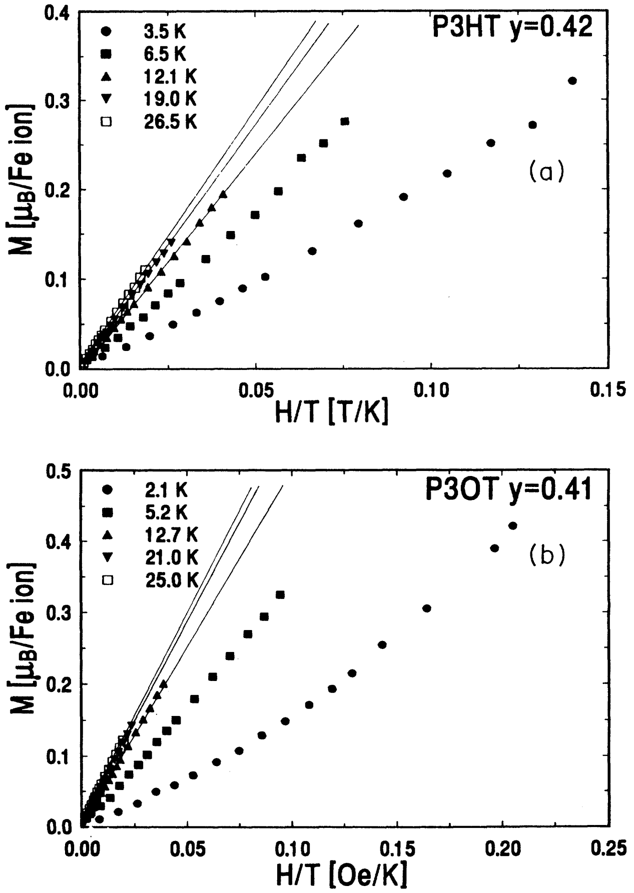

FIG. 3. (a) and (b) The magnetization vs H/T curves are shown for two $\mathrm{FeCl_4^-}$-doped samples: P3HT ($y=0.42$) and P3OT ($y=0.41$). Above 5 K the dependence of the magnetization upon T may be interpreted as the linear onset of the Brillouin function. For both samples the Brillouin function is not obeyed in the H/T runs of the magnetization at temperatures below about 5 K. For the highest temperature, the onset of the Brillouin function can be fitted with the following parameters: g factor equal to 2.00 and effective magnetic number $J=2.10$ (solid line).

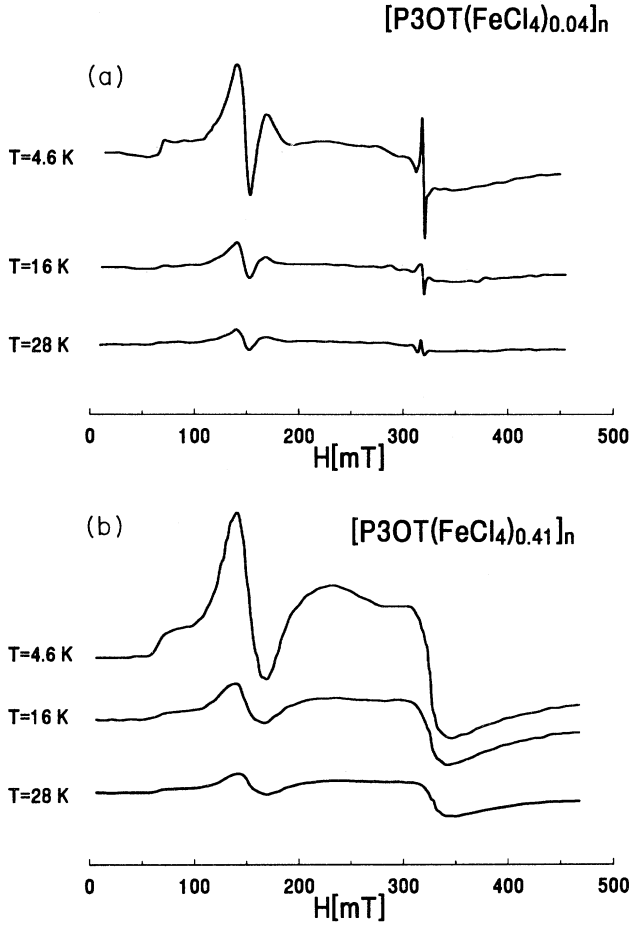

FIG. 4. ESR spectra for P3OT with low (a) and high (b) dopant concentrations, $y=0.04$ and $y=0.41$, respectively.

Figs. 4(a) and 4(b). Considerable differences between the ESR for lightly and highly doped P3OT samples are observed. Moreover, a decrease of the ESR intensity with increasing temperature can be seen. The latter phenomena may be rationalized by reduction of the cavity Q factor and disturbed distribution of the rf field, because of an increase of the conductivity with temperature and the skin currents which appear in the polymer films. Thus, as the ESR signal decreases with increasing temperature, the nonmetal-metal transition exemplified by increasing conductivity is observed. This transition and the effect of charge carriers localization was confirmed by electrical transport measurements at low temperatures.[22] For the sample with the low dopant concentration, three lines are observed in the spectrum, in contrast to the sample doped to a high doping level, where only two resonance lines are observed. First, consider the spectra of lightly doped samples. One can notice that a narrow line corresponding to a g value equal to 2.00 is seen. This line is intrinsic to the conjugated polymer backbone, and can be attributed to polarons localized to defects in the polymer chain. Disappearance of this resonance signal for samples with higher dopant concentration may be explained by assuming that the spinless bipolaron excitations are the favorable charge storage configuration, contrary to the case of the lightly doped sample. There also is a highly asymmetric line with $g=4.3$, which is an acceptable value for the high spin state of the ferric ion in the distorted tetrahedral ligand arrangement. This distortion suggests a strong interaction of the ferric complex with the polymer chain. Such strong interactions between impurity and polymer backbone were theoretically predicted for simple systems by Fredriksson and Stafström.[24] Moreover, anisotropy of the g factor is observed. Its nature, in compliance with magnetic results, suggests more complicated behavior of the ferric ion as the dopant of polythiophene matrix than of the polyacetylene matrix. Additionally, there is a broad line with $g=2$ attributed to the Fe^{3+} ion. The width of this line is approximately 40 mT (400 G) peak to peak. This line has been reported previously by Park *et al.*[25] and by Jones *et al.*[8] These factors did not change with temperature. Thus, the hypothesis of the change of electronic state with temperature can be ruled out in view of the ESR results.

To summarize, the results of magnetic measurements suggest that at low temperatures (below a temperature T_a) a short-range magnetic order exists. The temperature dependence of the susceptibility provides evidence for antiferromagneticlike interactions. The magnetization studies show that transition from a paramagnetic phase to an ordered phase occurs. The magnetization dependence on the H/T ratio for the lowest-measurement temperature is reminiscent of the effect of a short-range antiferromagnetically ordered phase. The fact that the effective magnetic moment is reduced because of distortion of the tetrachloroferrate complex supports the idea of very strong interaction between doping agent and polythiophene skeleton. Keeping in mind that guest ions are arranged in "channels" parallel to the polymer chain axes,[26] and the fact that wave functions of charge carrying species spread out over several monomers and overlap each other for high doping levels, the following conclusion can be drawn: The magnetic order is associated with exchange interactions between magnetic dopant agents mediated by localized (bi)polaronic states. Such a situation is more favorable for systems with a nondegenerate ground state, where only pairs of interacting charge carrying species can exist. Furthermore, because of this effect, the localization of charge carriers is observed. Because of the higher mobility of charge carriers at higher temperatures, above the T_a temperature doped polymers behave as paramagnetic materials.

ACKNOWLEDGMENTS

This work was financially supported by KBN Grants No. 3 0052 91 01/p1 and p3. We also thank Professor W. R. Salaneck for critically reading the manuscript. We thank Professor A. Oleś for interest in this work and Dr. A. Pacyna for important technical help and stimulating discussions. Fruitful discussions with Dr. B. Raynor and Dr. A. Bombik are greatly appreciated.

[1] R. L. Elsenbaumer, K. Y. Yen, and R. Oboodi, Synth. Met. **15**, 169 (1986).

[2] K. Y. Jen, G. G. Miller, and R. L. Elsenbaumer, J. Chem. Soc. D 17, 1346 (1986).

[3] M. Zagòrska and B. Krische, Polymer **31**, 1379 (1990).

[4] D. K. Campbell and A. R. Bishop, Phys. Rev. B **24**, 4859 (1981).

[5] S. A. Brazovskii and A. R. Kirova, Pisma Zh. Eksp. Teor. Fiz. **33**, 6 (1981) [JETP Lett. **33**, 4 (1981)].

[6] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[7] R. Lazzaroni, M. Lögdlund, S. Stafström, W. R. Salaneck, and J. L. Bredas, J. Chem. Phys. **93**, 4433 (1990).

[8] T. E. Jones, W. F. Butler, T. R. Ogden, D. M. Guttfredson, E. M. Gullikson, J. Chem. Phys. **88**, 3338 (1988).

[9] Z. Kucharski, H. Winkler, A. X. Trautwein, and C. Budrowski, in *Proceedings of the 1991 Conference on Electronic Properties of Polymers, Kirchberg, 1991,* edited by H. Kuzmany, M. Mehring, and S. Roth, Springer Series in Solid-State Sciences, Vol. 107 (Springer-Verlag, Berlin, Heidelberg, 1992), pp. 315–320.

[10] A. Proń, M. Zagórska, Z. Kucharski, M. Łukasiak, and J. Suwalski, Mater. Res. Bull. **17**, 1505 (1982).

[11] H. Sakai, Y. Maeda, T. Kobayashi, and H. Shirakawa, Bull. Chem. Soc. Jpn. **56**, 1616 (1983).

[12] K. Tamao, S. Kodama, J. Nakajima, and M. Kumada, Tetrahedron **38**, 3347 (1982).

[13] I. Kulszewicz-Bajer, A. Pawlicka, J. Plenkiewicz, and A. Proń, Synth. Met. **30**, 61 (1989).

[14] E. K. Sichel, M. F. Rubner, J. Georger, Jr., G. C. Papaefthymiou, S. Ofer, and R. B. Frankel, Phys. Rev. B **28**, 6589 (1983).

[15] A. Proń, Z. Kucharski, P. Bernier, I. Kulszewicz, M. Zagórska, J. Suwalski, and D. Billaud, Phys. Rev. B **31**, 4690 (1985).

[16] A. Proń, G. A. Fatseas, S. Krichene, S. Lefrant, F. Maurice, and G. Froyer, Phys. Rev. B **32**, 1839 (1985).

[17] S. Stafström and J. L. Bradas, Phys. Rev. B **38**, 4180 (1988).

[18] R. L. Carlin, *Magnetochemistry* (Springer-Verlag, Berlin, 1986), pp. 14–18.

[19] J. Chen, A. J. Heeger, and F. Wudl, Solid State Commun. **58**, 251 (1986).

[20] M. Kobayashi, J. Chen, T.-C. Chung, F. Moreas, A. J. Heeger, and F. Wudl, Synth. Met. **9**, 77 (1984).

[21] Lazzaroni *et al.*, in *Conjugated Polymeric Materials: Opportunity in Electronics, Optoelectronics and Molecular Electronics,* edited by J.-L. Bradas and R. R. Chance, NATO ASI Series E, Vol. 182 (Kluwer Academic, Dordrecht, 1990), pp. 149–169.

[22] F. Moreas, J. Chen, T.-C. Chung, and A. J. Heeger, Synth. Met. **11**, 271 (1985).

[23] P. Barta, S. Nizioł, M. Zagórska, and A. Proń, in Proceedings of the International Conference on Synthetic Metals [Synth. Met. (to be published)].

[24] C. Fredriksson and S. Stafström, Synth. Met. **44**, 65 (1991).

[25] Y. W. Park, J. C. Woo, K. H. Yoo, W. K. Hau, C. H. Choi, T. Kobayashi, and H. Shirakawa, Solid State Commun. **46**, 731 (1983).

[26] P. A. Heiney, J. E. Fischer, D. Djurado, J. Ma, D. Chen, M. J. Winokur, N. Coustel, P. Bernier, and F. E. Karasz, Phys. Rev. B **44**, 2507 (1991).