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THE EFFECT OF OXYGEN ON THE ESR LINEWIDTH IN POLYPYRROLE DOPED BY PF_6^-

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ESR linewidth (ΔH_{pp}) of as-grown polypyrrole, PPy–PF_6^-, was measured as a function of temperature under both helium and oxygen atmospheres to study an effect of oxygen on the ESR linewidth. Houzé and Nechtschein reported that an interaction between the charge carriers on a polymer backborn and paramagnetic spins of the oxygen molecules could cause an additional ESR broadening that is proportional or inversely proportional to the carrier diffusion rate $D_{\parallel}$ in the case of strong or weak interaction, respectively. The present experimental data demonstrate that only the ESR linewidth under oxygen atmosphere are not enough, but other information is indispensable to discriminate the above two cases. On the present PPy–PF_6^- case, supplemental data on d.c. conductivity, the ESR linewidth under helium atmosphere, VSC resistance, etc. make it possible to conclude mechanism of oxygen effect. © 1997 Elsevier Science Ltd

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Polypyrrole has been intensively investigated in this decade because of its stability in air and good electrical conductivity [1, 2]. In an early stage of investigation, it was understood that a bipolaron ground state was responsible for the conducting state, since sizable Pauli susceptibility was not observed definitely [3–6]. However, a recent advance in electrochemical synthesis of polypyrrole [7] made it possible to prepare a high quality self-standing film that led us to understand what is the intrinsic electronic properties in crystalline region [8–12]. Higher conductivity at 4.2 K [9, 13], definite Pauli-like susceptibility [8, 11, 14] consistent with a finite density of states at Fermi energy observed in photoelectron study [15] and Drude metallic response [8, 10] are evident indication of metallic electrons in this polymer. Nevertheless, it is still an open question what is the nature of the metallic state [16, 17].

So far, the intrinsic electrical resistivity within crystalline regions as a function of temperature is not known even in such a high quality film because of heterogeneous structure of the polymer. In this aspect, a microscopic technique to study the dynamics of charge carriers with spin are helpful, such as the frequency dependence of ESR linewidth that makes it possible to reveal interesting features for polyacetylene [2, 18–21], polyaniline [22–25], polythiophene [26–28] and polypyrrole [2, 28]. A voltage-shorted-compaction (VSC) study (it is better to represent this technique by a minimum separation of potential terminals (MSP) method) also gave interesting results consistent with ESR [9, 29, 30].

It has been well known that ESR linewidth broadens reproducibly under the atmosphere containing oxygen [3], which is suitable for an oxygen sensor [31]. Recently, a new method concerned with the dynamics of spin carriers was proposed by Houzé and Nechtschein making use of this effect, ascribable to an interaction between the spin carriers and the oxygens adsorbed on the conducting polymers [32]. Such an extra broadening of the ESR linewidth, represented by ΔH_{HN} in this work, was theoretically demonstrated to be proportional/inversely-proportional to the diffusion rate of the spin carriers in a *strong/weak* interaction regime. In this report, the usefulness of this technique will be examined for polypyrrole doped with PF_6^- ion. A point to be stressed is that without knowledge on the electronic states of the material, it is impossible to discriminate whether the actual cases are in the *strong* or *weak* interaction regime. In the present case, it can be concluded based on its metallic electronic states deduced from other experimental evidences that the interaction strength between the spin carriers and the oxygens is in the *strong* regime.

PPy–PF_6^- film was synthesized at −30°C for 20 h under argon atmosphere by an electrochemical technique with current density of 0.1 mA cm^{-2}. A glassy carbon was used as the working electrode and a Pt plate as the counter electrode. Electrical conductivity of two-fold stretched film with a four-terminal method is 550 S cm^{-1} at 300 K and is higher than 200 S cm^{-1} at 2 K as shown in Fig. 1. For an oxygen free sample, a film dried in a dynamic vacuum was sealed with helium gas of 400 torr for thermal contact in a 5 mmϕ quartz tube (hereafter abbreviated as *S*-He). Two other parts of the film were sealed in other quartz tubes with air of ambient pressure (*S*-Air) and with pure oxygen of about 10 torr (*S*-O) together with helium gas of 400 torr, respectively. ESR linewidth ΔH_{pp} was measured with a home-built spectrometer at frequencies between 40 and 24 000 MHz. All the spectra obtained in this work are well represented by Lorentzian lineshape. Thus the peak to peak ESR linewidth is determined by a least-square fit to Lorentzian lineshape, which allows a systematic and precise determination.

The temperature dependences of ESR linewidth are plotted for all the samples of *S*-He, *S*-Air and *S*-O in Fig. 2. The ESR linewidth increasing with temperature for the *S*-He is a characteristic feature found commonly in PPys doped with AsF_6^-, ClO_4^-, BF_4^-, TsO^- without oxygen [11]. On the other hand, the other samples with oxygen, *S*-Air and *S*-O, show a different behavior from *S*-He, that is, the linewidth shows a broad maximum around 15 K. This remarkable difference could be ascribed to an additional relaxation caused by interaction between a spin in the polymer backbone and one in the oxygen molecule adsorbed on the polymer. This additional relaxation rate is proportional to the frequency $C_B D_{\parallel}/l$ [33] of the interaction with oxygens for a contact time $t_W = l^2/D_{\parallel}$, multiplied by a transition probability p

$$\gamma \Delta H_{HN} = p C_B D_{\parallel}/l, \tag{1}$$

where C_B is the concentration of the relaxation centers (oxygens in the present case), $D_{\parallel}$ the diffusion rate along the polymer chain, γ the gyro-magnetic ratio of the electron spin, l the extension of the spin and p the transition probability given by

$$p = (16/27)(3Jt_W/2\hbar)^2/[1 + (3Jt_W/2\hbar)^2], \tag{2}$$

where J is the interaction energy [32].

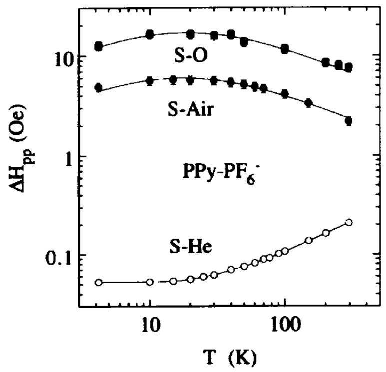

Fig. 2. The temperature dependence of ESR linewidth in *S*-He (open circles), *S*-Air (closed circles) and *S*-O (closed squares). The solid curves are guide for the eyes.

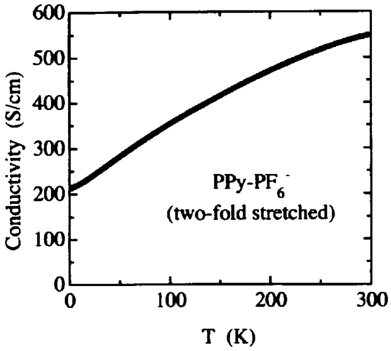

Fig. 1. The temperature dependence of the d.c. conductivity measured with a conventional four-terminal technique in the two-fold stretched PPy–PF_6^-.

ΔH_{HN} exhibits two different features in the two extreme conditions: (i) for the *weak coupling regime*, $3Jt_W/2\hbar = 3Jl^2/2\hbar D_{\parallel} \ll 1$, it is proportional to resistivity $\rho(T)$,

$$\Delta H_{HN} \propto (J/\hbar)^2/D_{\parallel} \propto \rho(T) \tag{3}$$

and (ii) for the *strong coupling regime*, $3Jt_W/2\hbar \gg 1$, it is inversely-proportional to resistivity $\rho(T)$, that is, proportional to conductivity $\sigma(T)$,

$$\Delta H_{HN} \propto D_{\parallel} \propto 1/\rho(T) = \sigma(T). \tag{4}$$

Thus, the contradictory conclusions can be attained with the same linewidth data, depending on the interaction strength, *weak or strong*. Here, it should be emphasized that based only on the linewidth data, one cannot conclude which regime the present systems belong to. To extract meaningful information from the linewidth data, other information on the electronic states is inevitable, such as metallic or semiconducting. Taking into account the several evidences for the metallic electronic states in the present system [8–11, 13–17], the observed temperature dependences for the samples *S*-Air and *S*-O in Fig. 2 can be interpreted as an indication of the *strong* regime for the interaction with oxygens, since at least at $T > 15$ K it behaves similarly to the metallic conductivity, as predicted by equation (4). The behavior at lower temperatures than 15 K will be discussed later. Here, note that the ESR linewidth picks up the information selected from the crystalline regions giving the Pauli susceptibility or the amorphous ones giving the Curie susceptibility, in the meaning that at least at higher temperatures than 50 K, the spin susceptibility determined by ESR–NMR technique is dominated by the Pauli susceptibility that represents the properties in the crystalline region [11].

The above conclusion is consistent with the linewidth in *S*-He in Fig. 2. The ESR linewidth increasing with temperature cannot be accounted for by a motional narrowing due to a thermally activated spin motion, but can be interpreted as typical of the Elliott (spin–phonon) relaxation mechanism due to the spin–orbit interaction that produces the Elliott broadening as [2, 34, 35],

$$\Delta H_{Ell}(T) \propto T_1^{-1} = \alpha(\lambda/\Delta E)^2/\tau = \alpha(\Delta g)^2/\tau \propto \rho(T), \quad (5)$$

where T_1^{-1} is the spin–lattice relaxation rate for electron spins, α the numerical constant, λ the spin–orbit coupling constant, ΔE the energy separation between bands, τ the relaxation time of electron momentum, Δg the *g*-shift and $\rho(T)$ the electrical resistivity. Equation (5) predicts that the Elliott broadening behaves correspondingly to the electrical resistivity. Thus, the temperature dependence of the linewidth in *S*-He suggests a metallic resistivity, consistent with the conclusion for *S*-Air and *S*-O. In the five-membered heterocyclic polymers, such as polypyrrole (PPy) and polythiophene (PT), it has been shown that the Elliott mechanism dominates the linewidth by virtue of the lack of "1-D" inversion symmetry in the heterocyclic molecules [2, 11, 36, 37].

If one assumes a hopping between localized states in the doped PPy, an alternative interpretation for ΔH_{pp} in *S*-He can be given: a hopping-induced relaxation via spin–orbit interaction dominates the linewidth, resulting in $\Delta H_{pp} \propto \sigma(T)$, as discussed in the amorphous semiconductors [38, 39]. If this were the case instead of the Elliott mechanism, the above conclusion would be reversed: the interaction with the oxygen spins is in the *weak* coupling regime, resulting in $\Delta H_{pp} \propto \rho(T)$ for the samples *S*-Air and *S*-O. This assumption of the hopping conduction is, however, inconsistent with the present observation of the four-terminal d.c. conductivity of 550 S cm^{-1} (Fig. 1) that requires the diffusion rate of 10^{15} rad s^{-1} based on the relation $\sigma = e^2N(E_F)D_\parallel c_\parallel^2$ with $\chi_p \approx 1.5 \times 10^{-5}$ emu/mol-ring, which is too large to assume the hopping conduction. Furthermore, the finite d.c. conductivity higher than 200 S cm^{-1} at 2 K could not be compatible with the hopping conduction between localized states.

To examine the above conclusion in *S*-Air and *S*-O, $1/\Delta H_{pp}$ is plotted in Fig. 3 together with ΔH_{pp} in *S*-He. This demonstrates that the temperature dependence of $1/\Delta H_{pp}$ in *S*-Air and *S*-O is quite similar to ΔH_{pp} in *S*-He at least above 50 K. Then, it is consistent with the conclusion that ΔH_{pp} in *S*-He is metallic in $\rho(T)$ and ΔH_{pp} in *S*-Air and *S*-O is metallic in $\sigma(T)$. Figure 3 suggests the intrinsic temperature dependence of electrical resistivity is described by $T^{1/2}$ above 50 K, which agrees with that observed in VSC resistance [2, 9, 11, 28]. It is worthy to note that these data sets show a definite deviation with each other below 50 K. The origin of this discrepancy between the samples without and with oxygen can be speculated as follows. One is a contribution of the Curie spins that are dominant below 50 K, giving rise to a remarkable broadening in addition to ΔH_{Ell} due to the Pauli spins. The other is a crossover of ΔH_{HN} from the *weak* to the *strong* regime at the peak temperature around 15 K demonstrated in Fig. 2, which could reduce ΔH_{pp} in *S*-Air and *S*-O. This point will be discussed in future, based on further investigations.

Let us make a rough evaluation on ΔH_{HN} at 300 K. Providing the minimum value of the microscopic conductivity within crystalline regions, $\sigma_{micro} = e^2N(E_F)D_\parallel c_\parallel^2$ to be $\sigma_{dc} = 5.5 \times 10^2$ S cm^{-1} and $c_\parallel = 3.9$ Å for PPy–PF_6^-, one gets the on-chain diffusion rate as $D_\parallel \geq 6 \times 10^{14}$ rad s^{-1} that is comparable to that of polythiophene–ClO_4^- [26, 27]. The relation $\Delta H_{HN} = pC_BD_\parallel/l\gamma$ with $l = 4$ gives $\Delta H_{HN}/pC_B \geq 5 \times 10^6$ Oe for PPy–PF_6^-.

In summary, an effect of oxygen on the ESR linewidth in polypyrrole–PF_6^- is examined. The temperature

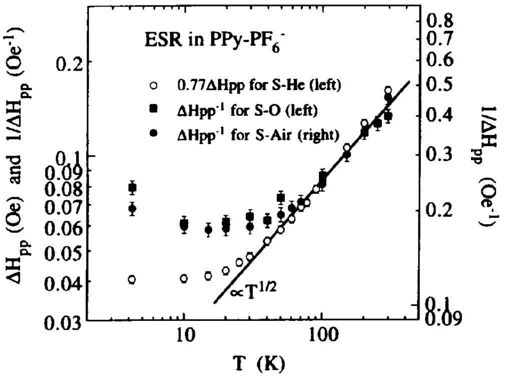

Fig. 3. The temperature dependence of ΔH_{pp} in *S*-He (open circles) is assigned to be Elliott (spin–phonon) relaxation mechanism that is proportional to the electrical resistivity $\rho(T)$. On the other hand, that of ΔH_{pp} in *S*-Air (closed circles) and *S*-O (closed squares) is assigned to be strong regime interaction with spins of the adsorbed oxygen molecules, which is proportional to the electrical conductivity. Hence, $1/\Delta H_{pp}$ for *S*-Air and *S*-O is proportional to ΔH_{pp} in *S*-He. Above 50 K, such a relation holds and suggests $\rho(T) \propto T^{1/2}$. The prefactor 0.77 is multiplied to ΔH_{pp} in *S*-He to superimpose the three data sets above 100 K.

dependence suggested that for the samples with oxygens the linewidth is inversely proportional to the linewidth of the samples without oxygens. Since the latter is known to be proportional to the electrical resistivity, such a relation could be interpreted with the relaxation arising from the interaction with oxygens in the *strong* coupling regime, $p \approx 0.6$. It is noteworthy that the linewidth with oxygens shows the maximum around 15 K, probably due to the crossover from the *weak* to the *strong* coupling regimes. The estimated linewidth normalized by the oxygen concentration C_B and the transition probability p following the model by Houzé and Nechtschein was rather large in comparison with that for PANI-HCl. Further investigation is in progress and will be published elsewhere.

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