Electronic states in conjugated polymers studied by electron spin resonance

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Abstract

Electron spin resonance (ESR) has been applied to fully-doped conjugated polymers. Two parameters deduced from ESR spectra, integrated intensity and line width, are analysed and we obtained information on the electronic states of various conducting polymers. The former gives us a spin susceptibility and the latter does dynamics of spin carriers through relaxation rates via several interaction paths, such as Elliott and spin diffusion mechanisms. The fully-doped conducting polymers usually show the Pauli-like, temperature-independent susceptibility with small Curie-one, called Curie-tail. We propose two different origins of the Curie-tail for conducting polymers corresponding to different categories, in terms of disorder. Spin dynamics studies through the ESR line width provide us microscopic transport properties and a suggestion that the polymers in category A, covering such as polyacetylene and polypyrrole, exhibit metallic transport properties down to 2 K. However, the other polymers in category B, such as poly-p-phenylenevinylene-H_2SO_4 and polyaniline-camphorsulfonicacid, fall into the localized non-metallic states at low temperatures where the Pauli susceptibility disappears.

Key words:
Electron spin resonance, Magnetic measurements, Transport measurements, Conjugated polymers

1. Introduction

Electronic states of conducting polymers have been thoroughly investigated for the last two decades by means of variety of techniques [1]. In this report, systematic interpretation of the data collected using electron spin resonance (ESR) technique will be demonstrated, focussing on the electronic states of fully-doped conducting polymers. Origins of the parameters for ESR spectra, integrated intensity and line width, are summarized in Table 1.

There is a consensus that the Pauli-like temperature independent susceptibility is observed in almost all fully doped conducting polymers with a proper level of crystallinity [2], which is an evidence for the finite density of states at the Fermi energy. In addition, it is common to observe Curie susceptibility at low temperatures, dubbed *Curie-tail* in this report. The origin of the Curie-tail has

not been unveiled, but we imagine that defects in the polymer would produce weak exchange-interacting, isolated spins which behave as the Curie-tail. This kind of Curie-tail would give a simple *"sum"* of the Pauli and the Curie susceptibilities. However, as Sariciftci, Heeger and Cao previously reported, another type of temperature dependence, *"crossover"* from the Curie to the Pauli type, has been found in polyaniline (PAni) doped with camphorsulfonicacid (CSA) [3]. Example of this *crossover* will be demonstrated in poly-p-phenylenevinylene (PPV) and is attributed to the Anderson localization, consistent with the present analysis of the ESR line width.

The ESR line width is known to arise from relaxation rates, resulted from several interactions with a lattice freedom; spin-phonon scattering through the spin-orbit interaction, so-called Elliott mechanism [4], electronic dipolar and/or hyperfine interaction modulated by spin dynamics [2,5], and exchange interaction with spins of adsorbed oxygen, proposed by Houze & Nechtschein [6]. These

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Table 1
Parameters analysed in this work.

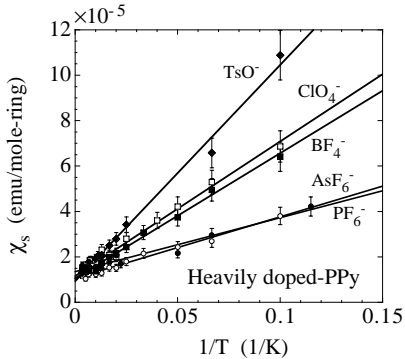|	**ESR**			
Parameter	• **Signal intensity**	• **Line width (relaxation rates)**		
Source	Spin susceptibility	Elliott mechanism	Spin diffusion	H-N mechanism
Phys. quantity	$N(E_F)$, Curie spin	$\propto \rho$	$D_\parallel, D_\perp$	$\propto \rho$ or σ
Key word	Polaron	λ_{S-O}	1D anisotropy	Effect of oxygen
Related polymers	Major polymers	PPP, PA, PPy, PT, PMeT	PAni, PPV, PT, (PA)	PPy, PAni

Fig. 1. The spin susceptibility versus $1/T$ for heavily doped PPy [7]. The solid lines represent the sum of χ_P and χ_C.

mechanisms are complementary to each other, to study dynamics of the charge carriers in the conducting polymers. Finally, it is stressed that the investigations with the relaxation rates can provide microscopic information of the charge carrier dynamics, compared with conventional transport measurements.

2. Results and discussion

2.1. Susceptibility

An example of the susceptibility in polypyrrole (PPy) doped with various dopant species [7] which obeys the sum of χ_P and χ_C is shown in Fig. 1. A similar behavior is also found in polyacetylene (PA), poly-p-phenylene (PPP), polythiophene (PT), doped with several acceptors, and PAni with HCl. Whereas some samples of PAni-CSA [3,8], PAni-DBSA, PPV-H$_2$SO$_4$ [9], and PA with potassium [10] show the crossover from χ_P to χ_C, as represented in Fig. 2.

A behavior of the sum in Fig. 1 suggests a weakness of coupling between the Pauli electrons and the localized spins, as schematically depicted in Fig. 3 (a). In PPy with varying dopant species, an inverse correlation between χ_P and χ_C was found [7], that is, the larger χ_P is, the smaller χ_C is. This is consistent with the sum model in Fig. 3 (a)
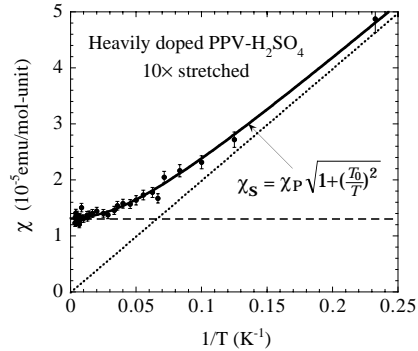

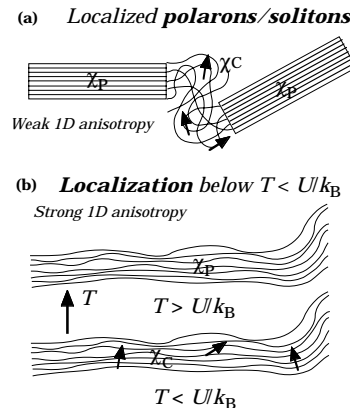Fig. 2. An example of the crossover from χ_P to χ_C [9].

Fig. 3. Two possible origins of the Curie-tail. (a) Coexistence of χ_P and χ_C in different crystallinity regions. (b) Crossover from χ_P to χ_C due to Anderson localization.

where χ_C increases in proportion to the volume of disordered part and χ_P does to that of crystalline part [7]. In the case of the Anderson localization (Fig. 3 (b)), such a correlation between χ_P and χ_C would not be expected, since χ_P at $T \geq U/k_B$ is approximately independent of the localization. Here, U is the on-site Coulomb energy at the localized sites. The crossover in χ is reproduced well by the solid curve in Fig. 2, which represents a phenomenological expression, $\chi = \chi_P \sqrt{1 + (T_0/T)^2}$, where $T_0 = C/\chi_P$ and C is the Curie constant at $T \leq T_0$. This expression means the disappearance of χ_P at temperatures below $T_0 \approx U/k_B$. Therefore, the crossover from χ_P to χ_C suggests

that the disordered sites are distributed over the whole sample which falls into the Anderson localization, giving rise to an insulating ground state as a whole, as represented in Fig. 3 (b). This kind of behavior seems to be favorably observed in loosely-stacked flexible-polymers with long interchain distances, such as PPV and PAni with large dopant molecules, resulting in a small stabilizing energy of crystallization. However, PPy is known to crystallize with the chains stacked densely without dopant molecules between the face-to-face stacked chains [11]. Therefore, the former polymers in category B, have lower stabilizing energy of crystallization, looser coupling between the chains and, as a result, higher one-dimensionality than the latter polymers in category A.

2.2. ESR line width

2.2.1. Elliott mechanism

In a system with free charge which carries a spin, one of relaxation mechanisms in ESR is the Elliott process caused by momentum scattering with spin-orbit coupling, λ [4]. Thus, the Elliott broadening requires atoms with larger atomic number, $z \propto \lambda$, in polymer backbone or in dopant molecule. Figure 4 summarizes the reported line widths, ΔH, for the alkali-PA's [12,13] and the acceptor-PPy, PT and PMeT [2,14]. This is strong evidence for the Elliott mechanism in these conducting polymers. It should be stressed that without this mechanism it is difficult to explain the observed ESR line width of PT which is larger by 20 times than that of PPy. The large difference of ΔH found between the alkali-PA's and the others in Fig. 4 reflects the difference of probability for charge carriers to hop to the responsible site with large z in a dopant and/or in a polymer chain. This suggests the wavefunction of charge carriers has less overlapping with that of the nitrogen atoms in PPy chains or the sulfar atoms in PT and PMeT chains, compared with that of the alkali dopants in PA.

It is well known that the Elliott broadening is proportional to the electrical resistivity, ρ, which is dominated by the momentum scattering with phonons and impurities [15]. Actually, the ESR line width is approximately proportional to T^2 in alkali-PA above 20 K [12,13], and to T^2 in PT, $T^{\frac{1}{2}}$ in PPy and T in PMeT down to 4 K, doped with various acceptor ions [14]. These observations are one of the evidences for metallic states in PPy, such as higher conductivity than 200 S/cm at 2 K [16], T-linear thermoelectric power as small as 10 μV/K at 280 K [17], metallic optical reflectance in IR over all temperature range [18], negative dielectric con-
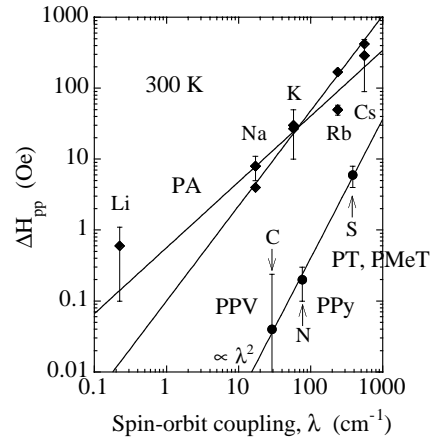

Fig. 4. The ESR line width vs. λ in conducting polymers.

stant typical of the metallic electronic states [19], metallic temperature dependence of electrical resistance by a Voltage-Shorted-Compaction (VSC) method [20], etc.

2.2.2. Spin dynamics

Spectral density of time-dependent local fields at a rapidly diffusing electron spin caused by other electron spins and/or nuclear spins in the polymer can be determined with the ESR relaxation rate (line width) [2,5]. The spectral density contains information on how the spins move within the polymer crystal; diffusion rates along the chains and across the chains. From a requirement of experimental limitation, this kind of analysis is applicable to conducting polymers with large dopant molecules, giving rise to fairly anisotropic electronic states, such as PAni-HCl [21], -CSA [8,22], -DBSA, and PPV-H_2SO_4 [9]. An example of such analysis on PAni-CSA is shown in Fig. 5. Note that PAni-CSA and PPV-H_2SO_4 (not shown) show a large anisotropy ratio, $D_{\parallel}/D_{\perp}$, and an insulating behavior at low temperatures, consistent with the NMR result [8]. This means the samples used ($\sigma \approx 10^2$ S/cm for PAni and higher for PPV at rt) have no metallic ground state, in agreement with the susceptibility showing the crossover from χ_P to χ_C, that is, disappearance of χ_P at low temperatures.

Let us comment on ^{13}C NMR relaxation data in ^{13}C-enriched PAni-CSA by Kolbert and coworkers [23]. They found a modified Korringa relation, $1/T_1 \propto T$ which was a familiar relationship as an evidence for a metallic state. Note that it is valid only for metals with a infinite mean-free-path l. However, for the typical 1D system near the border of metal-to-insulator transition, l would be comparable to the lattice constant. In this case, a diffusive relationship, $T_1^{-1} \propto T/\sqrt{D\omega}$, should be ap-
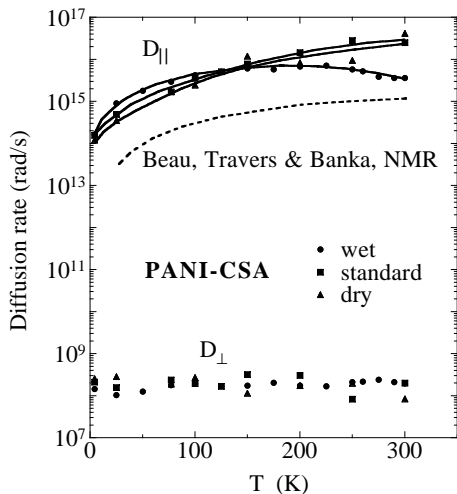
Fig. 5. Temperature dependence of the diffusion rates. Three symbols correspond to different m-cresor content. The solid curves are guide for the eyes. The broken curve shows NMR result by Beau *et al.* [8].

plied, except for $q=2k_F$ electron [24] and predicts $D(T)$=const. for the observed $1/T_1 \propto T$ relationship, which is consistent with the present analyses on the susceptibility and the ESR line width, along with ^{1}H NMR analysis [8].

3. Conclusion

The electronic states of the conducting polymers were investigated with ESR technique which could provide microscopic transport properties along with its anisotropy. Two limiting categories were found. In category A, the metallic electronic state in the densely crystallized region with χ_P over the whole investigated T-range coexists with χ_C of the localized polarons in the amorphous region. PPy's, PT's and PMeT's fall into this category, as confirmed by the Elliott broadening and susceptibility. Category B includes loosely crystallized polymers with larger dopant species. The looseness of chain packing induces a highly 1D electronic state and weak, but homogeneously distributed disorder through the whole sample which provokes Anderson localization at low temperatures; giving rise to a crossover from χ_P to χ_C. It will be difficult to make polymers of this type metallic because of a expected shallow minimum of cohesive energy. PPV and PAni fall into this category.

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