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ESR studies on polarons in long oligothiophenes

Katsuichi Kanemoto* and Tatsuhisa Kato
Institute for Molecular Science, Nishigonaka 38, Myodaiji, Okazaki, 444-8585 Aichi, Japan

Yoshio Aso and Tetsuo Otsubo
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-hiroshima, 739-8527, Japan

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We have performed electron spin resonance (ESR) studies on long oligothiophenes (13 and 20 T) doped by iodine vapor. The oligomers gave anisotropic ESR spectra differing from ordinary cases in conjugated polymers. Our analyses by way of the Fourier transform of ESR spectra indicate that the cutoff event between parallel chains occurs at the same degree of frequency as the motion along a chain: 31.8 MHz at 50 K in 13 T. Above 150 K, we observed the signature of the cutoff motion between nonparallel chains (~5 MHz). We assert that polarons mainly move within aggregates consisting of parallel chains formed in the film.

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High conductivity exhibited by heavily doped conjugated polymers has remained attractive for technological applications since the first report on polyacetylene (PA) in 1977.[1] In most of the conjugated polymers, it is believed that polarons and/or bipolarons are generated by charge injection and work as charge carriers in the conductive phenomenon. Experimental signatures of polarons are commonly recognized as the presence of two electronic absorption peaks in an infrared range[2] and of paramagnetic spins. As to the latter, an electron spin resonance (ESR) spectroscopy is a straightforward way to acquiring detailed information on the paramagnetic spins, and hence lots of knowledge was derived from a variety of techniques based on ESR.[3] On the other hand, however, it is noted that difficulties are usually involved in the analysis of ESR signals for conjugated polymers due to the coexistence of several types of paramagnetic spins, as reported on *trans*-PA: ESR signals originating from diffusing and trapped solitons were suggested to coexist.[4]

Recently, conjugated oligomers have been widely studied because of their utility as a model of conjugated polymers as well as of their possibility of candidates for nanoscaled technology. Above all, oligothiophenes are one of the most progressive conjugated oligomers,[5] and sexithiophene (6-mer) was truly utilized for refined, optical researches.[6,7] Nevertheless, there is the question of whether such a length of oligomers is suited for a model of polymers, and indeed, it was observed for a series of oligothiophenes that electronic absorption peaks originated from the π-π^* transition shift to lower energy with an increase of its chain length up to the 20-mer, and further that the conductivity in heavily doped states is rapidly enhanced by the increase in chain length from 6-mer to 13-mer.[8] These findings indicate that oligomers with a length longer than at least 10-mer should be used for the model of conjugated polymers.

In this article, we report on the ESR investigation on 13-mer and 20-mer oligothiophenes in a heavily doped regime, which are suitable as models of π-conjugated polymers. We demonstrate that the use of these oligomers enables us to extract spectroscopic information excluding the inhomogeneity in chain length on heavily doped conjugated polymers, which has not ever been clarified with polymer samples. In addition, we utilize a pulsed ESR technique as well as a conventional continuous wave (CW) one. The former technique, giving ESR signals in a time domain, is available for examining the dynamics of observed electron spins[9,10] and for classifying the signals consisting of several paramagnetic species depending on their time dependences. Our approach with a variety of ESR techniques will present significant information on the nature of paramagnetic species, polarons, in heavily doped conjugated polymers.

Oligomer samples used were 13- and 20-mer α-linked oligothiophenes (hereafter, 13 and 20 T, respectively) with several octyl substituents at the β positions. Synthesizing procedures and some physical properties were reported previously.[8,11] We prepared ESR samples by exposing their casting films grown with CH_2Cl_2 to excess iodine vapor. In this stage, about 20% of thiophene rings were estimated to be doped by I_3^- ions through elemental analyses, and the conductivities were measured as 3.2–3.7 and 5.2–8.9 S cm^{-1} for 13 and 20 T, respectively.[8] CW and pulsed ESR measurements were performed for degassed samples ($<10^{-2}$ Torr) with an X band (9.6 GHz) Bruker ELEXES E680 spectrometer. In the pulsed ESR experiments, we typically used a 16 ns pulse for the $\pi/2$ rotation of the magnetization. Electron spin echoes were observed through the typical two-pulse sequence $\pi/2$-τ-π-τ.[12] An echo-detected (ED) ESR spectrum was measured via recording the maximum echo amplitude, with a phase cycling technique[13] in order to eliminate spurious responses due to surviving free induction decay (FID) signals. In all of the samples used, ESR signals were stable over several days, and we hardly detected ESR signals before doping, which assures that the origin of observed ESR signals is the species generated from doping with iodine vapor.

In Fig. 1, we present the CW ESR spectra of 13 and 20 T at representative temperatures (detailed temperature dependences will be published elsewhere). Both 13 and 20 T gave spectra with an apparent anisotropy at 50 K, typically of the case in g anisotropy.[14] In our knowledge, such anisotropic spectra have been scarcely reported on conjugated polymers, which is probably because the inhomogeneity in chain length reduces the spectral anisotropy. The presence of these g anisotropies indicates that the averaging effect does not oc-

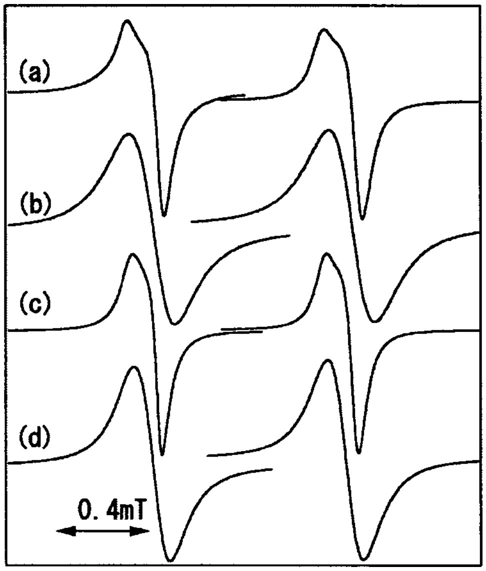

FIG. 1. ESR spectra for 13 and 20 T (left), and their simulated spectra using the Lorentzian line shape (right): (a) 13 T at 50 K, (b) 13 T at 200 K, (c) 20 T at 50 K, (d) 20 T at 200 K. Simulation data used were listed on Table I.

cur among the paramagnetic species with different directions of chain axes to a static magnetic field, and that each paramagnetic species exists, almost confined within an area parallel to the chain axes. The situation can happen for spins within a single chain or an aggregate consisting of a certain number of parallel chains.

At this temperature, an electron spin echo (ESE) was not detected in both 13 and 20 T. A spin echo is generally observed in the case that the resonance positions of individual components forming FID signals remain unaltered during a dephasing period and a refocusing one. In this sense, the absence of ESE is clear evidence that each spin component transfers over several areas giving different magnetic surroundings due to a hyperfine interaction, for instance. These mobile ESR signals are regarded as originating from polarons, and hence reflect the polaron dynamics. In the ESE experiment, the total of dephasing and refocusing periods (2τ) was more than 400 ns. Thus this experimental result signifies that the polarons in 13 and 20 T transfer along a chain or within an aggregate at the rate of at least 2.5 MHz.

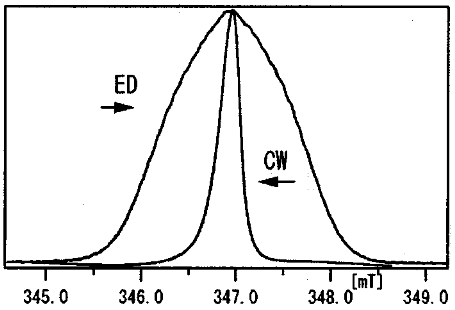

FIG. 2. The integrated CW ESR spectrum and the echo-detected (ED) ESR one for 13 T at 8 K.

Increasing the temperature above 50 K, any ESE signals were not detected in both samples. On the other hand, we could observe ESE signals for 13 T below 30 K, while 20 T still did not give ESE. In Fig. 2, we present ED ESR spectrum for 13 T at 8 K, together with the integrated CW spectrum at 8 K. The ED ESR spectrum is recognized as apparently broadened compared to the CW one: the square roots of the spectral second moment were 0.62 and 0.10 mT, respectively. This spectral broadening is caused by the quenching of motion of observed spins. The ESE signals were selectively detected from the total ESR signals by setting the parameter τ larger in order that the ESE signals may not be interfered with most of the FID signals giving no ESE. In practice, our estimate of the portion of ED signals to the FID ones was just about 2% and hence the ESE component is considered to be a small portion of the whole CW ESR signals. Therefore, we consider that the motion of polarons begins to stop in the low temperature range below 30 K, while most of the polarons are then sure to be still mobile.

For conjugated polymers, the electron spin dynamics including their dimensionality has been investigated in detail on the basis of the ESR line shape.[15] It should be noted, however, that the spectral anisotropy and the inhomogeneity in chain length inherent in ESR spectra of polymer samples have a possibility of giving a distortion in the line shape, regardless of the spin dynamics. Here we try to deduce the intrinsic information of line shape and examine the spin dynamics, by excluding the spectral anisotropy observed for our oligomer samples.

The spin dynamics has been studied on the basis of the time correlation function $G(t)$,[4,15,16] which is defined as the Fourier transform (FT) of the CW-ESR line shape $F(\omega)$. $G(t)$ generally varies depending on two parameters, the linewidth $\Delta\omega$ and the cutoff frequency out of a single chain ω_c, and it is proposed in the case of the motional narrowing that $G(t)$ should exhibit the time dependence of $\exp(-at^n)$ (a is an arbitrary parameter concerned with $\Delta\omega$): $n=\frac{3}{2}$ for one-dimensional (1D) motion ($\omega_c \ll \Delta\omega$) and $n=1$ for pseudo-1D motion ($\omega_c \gg \Delta\omega$) and 3D motion.[15] In our case, the 3D motion is not taken into consideration, because observed electron spins are presumed to move along a chain or within an aggregate.

Here we assume that oligomer chains in 13 and 20 T distribute in the films with a wholly random orientation, and that each oligomer sample exhibits an axially symmetric g factor originating from its molecular structure and has each identical line shape function $f(\omega)$, independently of the orientation to the static magnetic field. Then the relation

$$F(\omega)\propto\sum_{\theta} I(\theta)f[\omega-\omega(\theta)]\sin\theta \qquad (1)$$

is given, where θ is the orientation angle of an oligomer to the static field and $I(\theta)$ represents the sum of ESR intensity in the components making the angle θ and is proportional to the transition probability depending on the orientation as follows:[17]

$$I(\theta)\propto[\mathrm{Tr}\,\tilde{\mathbf{g}}\cdot\mathbf{g}-(\tilde{\mathbf{h}}\cdot\tilde{\mathbf{g}}\cdot\mathbf{g}\cdot\tilde{\mathbf{g}}\cdot\mathbf{g}\cdot\mathbf{h})/|\mathbf{g}\cdot\mathbf{h}|^2], \qquad (2)$$

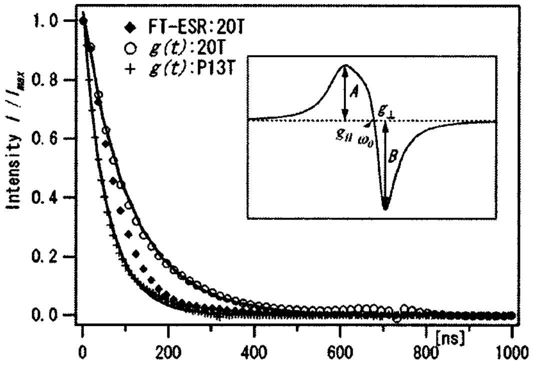

FIG. 3. The Fourier-transformed (FT) ESR for 20 T at 50 K and the correlation functions $g(t)$ after excluding the g anisotropy for 20 T at 50 K and P13T at 50 K. The inset represents ESR parameters used in the text.

where **g** and **h** represent a g tensor and a static field, respectively. Now, when we denote $g(t)$ for the FT of $f(\omega)$, the FT of $F(\omega)$ at ω_0 is given by

$$G(t)|_{\omega_0}=g(t)\sum_{\theta} CI(\theta)\sin\theta\cos[(\omega(\theta)-\omega_0)t], \quad (3)$$

where C is a proportionality factor. We can thus get $g(t)$ from the division of the Fourier-transformed (FT) CW spectrum by the sum part on the right side in Eq. (3). Here $g(t)$ is the correlation function excluding the spectral g-anisotropy, and directly related to the motion along a chain or within an aggregate.

In Fig. 3, we show the FT-ESR spectrum at ω_0 (in this case, almost the resonance center) for 20 T at 50 K and its $g(t)$ calculated from Eq. (3) using parameters defined in the inset. At this temperature, the motional narrowing effect is considered to give the main contribution to the electron spin dynamics for conjugated polymers.[10] The deference between the FT-ESR and the $g(t)$ demonstrates that the g anisotropy has a large influence on the spectral line shape and that its contribution should be essentially excluded for a line shape analysis. In Fig. 3, we further show with a solid curve the simulated result on $g(t)$ using the function of $\exp(-at^n)$. Best fitting was obtained with $n=0.97$ and $a=0.010\times10^{9n}/\mathrm{s}^{-n}$. The obtained n, quite close to 1, is strong evidence for pseudo-1D motion of observed spins. The cutoff event out of a single chain is thus suggested to occur with a much higher frequency than $\Delta\omega$($\sim$10 MHz). Therefore, taking into account the observed g anisotropy, it follows that electron spins, polarons, move pseudo-one-dimensionally with a rapid cutoff motion between parallel chains, thus signifying that polarons move mainly within an aggregate consisting of parallel chains.

Here the function $\exp(-at)$ corresponds to the Fourier transform of the Lorentzian line shape. We thus performed ESR simulations of the CW spectra for 13 and 20 T at 50 K using the Lorentzian line shape for $f(\omega)$ in Eq. (1). The result, shown in Fig. 1, demonstrates its validity of using the Lorentzian line shape. We show their simulation parameters in Table I. In the pseudo-1D motion, the ESR linewidth has been considered to correspond to $(\Delta\omega_0)^2/(D_\parallel\omega_c)^{1/2}$, where $\Delta\omega_0$ is the linewidth in the absence of motion and $D_\parallel$ is the diffusion frequency of the motion along a chain.[15] It is noted that, when we exclude the effect of g anisotropy from the spectrum, ω_c represents the cutoff frequency for the transfer between parallel chains. Since the spectral second moment is usually unchanged in the case of motional narrowing,[18] we can here substitute for $(\Delta\omega_0)^2$ the second moment obtained from the ED ESR at 8 K. Therefore, after subtracting the second moment due to g anisotropy ($1.6\times10^{-3}/\mathrm{mT}^2$), $(D_\parallel\omega_c)^{1/2}$, the averaged frequency within an aggregate, is estimated as 31.8 MHz for 13 T at 50 K, on the basis of the above mechanism. This value is surely consistent with the condition that an ESE was absent at 50 K (>2.5 MHz). Also, the condition of the pseudo-1D motion $\omega_c\gg\Delta\omega$ ($\sim$9.45 MHz) leads to $D_\parallel\ll 107$ MHz. This result signifies that the cutoff event between parallel chains occurs almost at the same frequency as the transfer along a chain.

TABLE I. Data for the simulation on ESR spectrum using the Lorentzian line shape under the assumption of axially g factor. ΔH_{PP} is the peak-to-peak linewidth in a differential ESR spectrum.

	$g_\parallel$	$g_\perp$	ΔH_{PP} mT
13 T 50 K	2.002 64	2.00174	0.062
200 K	2.002 32	2.00184	0.183
20 T 50 K	2002 60	2.00186	0.058
200 K	2.002 31	2.00184	0.135
P13T 50 K	2.002 81	2.00176	0.114
200 K	2.002 82	2.00157	0.207

Increasing the temperature above 50 K, CW ESR spectra broadened gradually in both 13 and 20 T as the examples at 200 K are shown in Fig. 1. The broadening effect with temperature is usually explained in terms of the Elliott mechanism,[19] known to be induced mainly by phonon scattering via the spin-orbit mixing. The mechanism is presumed to work for these oligomers, similarly to the case in conjugated polymers.[10,20] To be exact, this mechanism is considered to work effectively for the scattering perpendicular to one-dimensional chain,[21] and hence the broadening effect is consistent with the above result of higher cutoff motion at 50 K. In contrast, the spectral anisotropy in the g factor was observed to be reduced by increasing the temperature above 150 K for both samples. These behaviors are considered as resulting from the wandering of observed spins over nonparallel aggregates (or chains), not by a change in the electronic state. For clarifying the consideration, we prepared the 13 T sample diluted in the inactive polymer, poly(methyl methacrylate) (PMMA), with the mass ratio of 13 T/PMMA $=7.9\times10^{-3}$ (hereafter, abbreviated as P13T). We consider that with this sample, the transfer between nonparallel chains decreases at least by mixing the inactive polymer. CW ESR spectra for P13T and their simulation data using the Lorentzian line shape are shown in Fig. 4 and Table I, respectively. The spectrum at 200 K and its simulation data demonstrate that the g anisotropy is almost conserved even at the temperature, which is further ascertained by the comparison between 13 and P13 T of the anisotropy parameter A/B (defined on the inset in Fig. 3): 1.01 and 0.81 at 200 K,

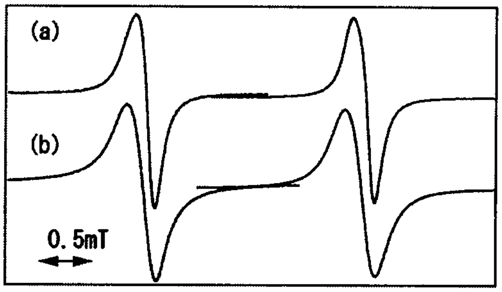

FIG. 4. ESR spectra for P13T (left), and their simulated spectra using the Lorentzian line shape (right): (a) at 50 K, (b) at 200 K. Simulation data used are listed on Table I.

respectively. Therefore it is confirmed that the spins of 13 and 20 T transfer among nonparallel chains in this temperature range. This behavior can be treated as the motional narrowing effect among the spins residing in nonparallel chains. In this case, its criterion, estimated with the g-anisotropic parameter $g_{\parallel}-g_{\perp}$, is ~5 MHz, which is a measure of the cutoff frequency between nonparallel chains in this temperature range.

At 50 K, the ESR spectrum of P13 T apparently broadened compared to 13 T. The spectral second moment is presumed not to change so much to account for the difference between them, because spin parameters such as a g factor and a hyperfine interaction are probably not much affected by the scale of aggregate. In this sense, the broadening effect must be brought by the difference in the spin dynamics. Then we calculated $g(t)$ for P13 T by substituting g parameters of 13 T for Eq. (3). The result is shown in Fig. 3. We further carried out the $g(t)$ simulation using the function of exp $(-at^n)$, leading to $n=0.94$ and $a=0.023\times10^{9n}/\mathrm{s}^{-n}$. The obtained n still suggests the pseudo-1D motion of observed spins, and hence that the cutoff event between parallel chains occurs at a higher frequency than $\Delta\omega$ (~17 MHz) even under the dilution with PMMA. In addition, we obtained $(D_{\parallel}\omega_c)^{1/2}=17.3$ MHz for P13 T by its spectral simulation with the Lorentzian and the use of the second moment of 13 T for $(\Delta\omega_0)^2/(D_{\parallel}\omega_c)^{1/2}$. When we assume that the $(D_{\parallel}\omega_c)^{1/2}$ difference between 13 T and P13 T is mainly attributed to the change in ω_c, the dilution with PMMA seems to diminish the cutoff event to the extent of about 30%.

As mentioned above, we could obtain several, physical pictures on the polaron dynamics of conjugated oligomers, which have not been clarified with polymer samples. Especially, the findings indicate that polarons move within the aggregates consisting of parallel chains, which probably leads to the formation of metallic islands. We further observed the signature of the transfer between nonparallel chains by increasing the temperature. These components of motion, hardly resolved with polymer samples, will be elements of consequence for a detailed investigation on the spin dynamics. Furthermore, the spin echoes, resulting from the quenching of motion in parts of the spins moving pseudo-one-dimensionally, will be utilized for obtaining static information concerning the nature of the wave function of polarons.

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*Present address: Department of Physics, Graduate School of Science, Osaka City University, Osaka 558-8585, Japan. Email address: kkane@sci.osaka-cu.ac.jp

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