METALLIC TEMPERATURE DEPENDENCE IN THE CONDUCTING POLYMER,
POLYANILINE: SPIN DYNAMICS STUDY BY ESR

Kenji Mizoguchi and Kiyoshi Kume
Department of Physics, Tokyo Metropolitan University, Minami-Osawa, Hachi-Oji, Tokyo, 192-03
JAPAN

(Received 14 December 1993, accepted for publication 19 January 1994 by H. Kamimura)

Microscopic spin and charge dynamics in polyaniline (PANI) are studied by ESR. Temperature dependence of the diffusion rates along a polymer chain $D_\parallel$ and across chains $D_\perp$ was determined for the emeraldine salt form with HCl. The main results are (a) $D_\parallel$ above 150 K follows metallic temperature dependence of $T^{-d}$ with $d=2-3$, (b) an abrupt change in $D_\parallel$ is found around 150 K, and (c) the anisotropy ratio $D_\parallel/D_\perp$ is larger than nearly $10^5$ around 150 K. These results lead us PANI being the highly one dimensional electronic system.

Although a great number of researches has been reported on many properties of conducting polymers interpreted as a so-called "metal", actual "metallic" temperature dependence of the electrical conductivity $\sigma$ can be scarcely reported [1]. Typically in polyacetylene doped with AsF$_6^-$, FeCl$_4^-$, ClO$_4^-$, $I_3^-$ and so on, "metallic" temperature dependence has been found only in the limited temperature range above 150-200 K [2,3], which were interpreted as a series and parallel network of semiconducting inter-metallic resistance and intra-metallic one. To investigate the conductivity within metallic region, several model fittings were applied to such data. However, all the model fittings with different "metallic" temperature dependencies $\sigma \approx T^{-1}$, $\sigma \approx T^{-2}$ and $\sigma \approx \exp(E_0/kT)$ could give a reasonable agreement with the experimental data [2,3]. Therefore, it is impossible to discriminate what is the intrinsic temperature dependence of $\sigma$ only with the conductivity measurement.

Up to now, the substantial suggestion to this point has been reported only by the voltage shorted compaction (VSC) method [4,5,6,7] for the doped polyacetylene as $\sigma \approx T^{-1}$ and $\sigma \approx T^{-2}$ depending on the species of dopants [5,6] and for the five membered ring polymers of polythiophene and poly(3methyli thiophene) [7] as $\sigma \approx T^{-1}$ and $\sigma \approx T^{-2}$. However, an evaluation of the VSC method has not been fixed so far. In the three-dimensional (3-D) metals, $\sigma \approx T^{-1}$ dependence is familiar, and $\sigma \approx T^{-2}$ was frequently observed in various low-dimensional metallic systems. An exponential-type dependence predicted by Kivelson and Heeger for highly one-dimensional metallic system [8], however, has never been definitely found experimentally not only in the polyacetylene, but also the five-membered ring polymers until now [9]. To understand the mechanism of the electrical conduction in the conducting polymers, it is important to study how the intrinsic conductivity behaves in these systems, especially with reliable microscopic techniques.

Spin dynamics study by Electron Spin Resonance (ESR) and $^1$H NMR through wide range of frequencies, is powerful tool to study microscopic behavior of charge carrier with spin as demonstrated on the neutral soliton dynamics in trans-polyacetylene [10,11], and the percolation transition in polyaniline with protonation [12]. In this letter, the first report of microscopic understanding of electrical conductivity along the chain will be demonstrated through a diffusion rate $D_\parallel$ which includes various features: abrupt change like a phase transition around 150 K, a metallic $T^{-d}$ (d$\geq$2) dependence of conductivity typical for low dimensional systems, and highly anisotropic behavior of spin and charge dynamics (polaron and/or Pauli spin). These features are clear evidence for the highly one-dimensional electronic structure in the powder polyaniline.

Emeraldine salt form (ES-I) of Polyaniline (PANI) has been prepared by a conventional tech-
neighboring chains. Here, an origin of $\Delta H_0$ is not clear, but probably a relaxation through oxygens in the sample as a contamination. Actually, ESR line width changed remarkably with the oxygen concentration in the sample [17].

Another interpretation than the above mentioned Q-1-D diffusion is interesting to consider. If
Fig. 2. The temperature dependence of the diffusion rates $D_h$ and $D_d$. At 150 K, abrupt change is found in $D_h$. Above 150 K, $D_h$ is of metallic and below 150 K it is of semiconducting. $D_d$ varies following the d.c. conductivity for the same sample down to 130 K, which implies that $D_d$ limits the electrical conduction. Below 130 K $D_d$ is governed by the other mechanism of cutoff than interchain hopping of the electron spin.

one has an isotropic 3-D coherent metal around room temperature as discussed by Wang et al. [18], the observed cutoff frequency $D_d$ could be attributed to some characteristic energy in "metal", for example, thermal energy ($k_BT$), Debye temperature or Fermi energy that needs to work as a reservoir of energy $h(\omega_{pe} - \omega_{ph})$ accompanying to a resonance transition. From $D_d \sim 10^{11}$ (rad/sec) at 300K one gets extremely small energy of $10^{-4}$ eV (-1K) which is unlikely small as a 3-D "metal".

It is well known that upon protonation the spin concentration $c$ in PANI increases more than two orders of magnitude, up to 5% per two rings at 300 K [17]. This fact supports that the observed ESR signal comes from polarons and/or Pauli spins produced by the protonation. Therefore, the electron spins observed by ESR carries not only spin, but also charge, i.e., the spin dynamics is equivalent to the charge dynamics: electronic transport. In such meaning Fig. 2 shows several interesting features; $D_h$ behaves being metallic and $D_d$ does semiconducting like that of $\sigma_{dc}$ above 150 K. Anisotropy ratio of the microscopic diffusion rates, $D_h$ and $D_d$ is extremely high; more than $10^5$ at 150 K and decreases down to $-10^3$ at 300 K. This result means that the on-chain conduction is of metallic, but interchain conduction is of hopping, that is, PANI powder is highly 1-D metal above ~150 K, but not 3-D metal. Note that a macroscopic measurement of anisotropy would be governed only by numbers of semiconducting inter-metallic junctions lying in two perpendicular current paths.

This statement does not contradict the observed Lorentzian line shape of ESR. By applying an analysis for Q-1-D spin chain by Hennessy et. al., one can estimate the line shape using a parameter $R=(\gamma/h)/(\omega^2)^{1/2}$, where $\gamma$ is the effective inter-chain coupling [18,19]. The second moment $m'=(\gamma/h)c\gamma_{h}^{2}S(\Sigma 1/r_{j}^{2})$ produced by the electronic dipolar interaction can be estimated as $8.9 \times 10^{17}$ (rad²/s²) for the ES-I structure [20] with $c=0.05$ (spins/two rings), $\gamma_{h}=1.76 \times 10^{7}$ (G⁻¹s⁻¹) and $S=1/2$. With the diffusion rates shown in Fig.2 and the relations $D_d=(\gamma/h)(\gamma/I)^{1/2}$ and $\gamma_I=\gamma_d/\sqrt{\pi}$, $R=12$ is obtained at 4.5K. $R=0$ means pure 1-D case and the line shape changes gradually to Lorentzian with increasing $R$. $R=12$ is known to give fairly well Lorentzian [18] as observed experimentally.

The present conclusion of the Q-1-D metallic state contradicts the 3-D metallic state concluded from the thermoelectric power $S$ and dielectric constant $\epsilon$ on the stretch aligned PANI-ES-II film [18]. Origin is not clear, but one possibility of this contradiction is a difference of crystal structure. Actually, the stretch aligned EB-II film has a different structure from the EB-I powder, and both of the protonated forms, ES-I and ES-II have also different structures [20]. In particular, the authors in ref.18 insisted only from the slopes of $S$ vs. $T$ that their conclusion of 3-D electronic structure for the aligned ES-II film could also be applicable to the ES-I powder, but the present conclusion strongly suggests a possible difference of the electronic structure between the ES-I powder and the aligned ES-II film. The spin dynamics study on the aligned ES-II film is in progress to investigate this contradiction in dimensionality of the electronic state.

Next interesting point is the metallic temperature variation of $D_h$ above 150 K. It can be fitted to power law $T^{-d}$ with $d=2-3$. This temperature variation for $D_h$ could be taken to be the same as that for the on-chain conductivity, since the on-chain diffusion rate $D_d$ can be converted to the electrical conductivity $\sigma$ with a relationship for the 1-D metals, $\sigma_{dc}=ne^2\tau/m = e^2N(E_F)D_d\epsilon^2$. Here, $n$ is the carrier concentration, $\tau$ the relaxation time of charge carrier, $m^*$ the electron effective mass,
the density of states at the Fermi energy per unit volume and \( c_\sigma = 9.5 \) \( (\text{A}) \) the unit length of chain axis. Then, if \( N(\varepsilon_F) = \text{const.} \), \( \sigma_{\delta} = D_\delta \sigma^\text{F} \) holds. In conventional 3-D metals, \( \sigma \propto T^{-1} \) around or at higher temperatures than Debye temperature \( T_D \) and \( \sigma \propto T^{-5} \) well below \( T_D \). If PANI is 3-D metal, \( \sigma \propto T^{-1} \) would be expected in the corresponding temperature range, since the Debye temperature in the conducting polymers is order of several hundreds of Kelvin [21]. This is not the case. In the 1- and 2-D organic metals, \( \sigma \propto T^{-2} \) has been often observed, but its mechanism was not definitely identified [22]. Anyway, the present temperature variation of \( D_\delta \) could be characteristic behavior in Q-1-D metal.

The metallic behavior of \( D_\delta \) above 150 K abruptly changes to weak semiconducting one. Below 150 K, \( 1/D_\delta \propto \log T \) approximately holds, but \( D_\delta \propto \log T \) does not. In 2-D weak localization case, conductivity should be enhanced by \( \log T \), but it is not the case. Below 80 K, one can also fit \( D_\delta \) to \( \sqrt{T} \) which is characteristic to disordered metal [23]. The coefficient of \( \sqrt{T} \), however, seems to be fairly larger than the "universal" value \( 6 \) \( (\Omega^{-1} \text{cm}^{-1} \text{K}^{-1/2}) [23] \). Then, one can not simply apply it. Fitting of \( D_\delta \) to another function \( \exp(bT) \) is also possible, but we have no physical idea to explain such dependence. The anomaly around 150 K has been reported by the Raman [24] and the thermoelectric power [18] (TEP) studies. Interestingly, a decrease of this temperature in the TEP was found with increasing crystallinity of the sample, which suggests a marked contribution of disorder to this phase change [18,27].

On the \( D_\delta \), the most pronounced point is a good coincidence of it with the d.c. conductivity \( \sigma \) above 130 K. Below 130 K, \( D_\delta \) stops to decrease steeply, which can be understood by the spin-spin interaction as a frequency cutoff, but not the interchain hopping [25]. These features are consistent with the previous report [26] which concluded that the temperature dependence of the d.c. conductivity is governed by the interchain hopping process \( D_\delta \), including the protonation dependence [26].

We summarize our main results as follows. We succeeded to analyze the microscopic spin and charge dynamics in PANI-HCl. The interchain hopping \( D_\delta \) governs the four terminal conductivity result and is semiconducting. On the other hand, the on-chain diffusion was metallic down to 150 K and appeared to follow the \( \sigma \propto T^{-d} \) (d=2) relation. It is worthy to estimate the microscopic conductivity \( \sigma_{\nu} \) from \( D_\nu \). However, in contrast to \( D_\delta \), it is hard to determine the absolute value of \( D_\nu \) with accuracy because of the several unknown parameters to be estimated; \( \Sigma, c(T), N(\varepsilon_F) \), and so on. Then we can estimate an order of intrachain conductivity \( \sigma_{\nu} \approx 1.5 \times 10^3 \) \( (\text{S/cm}) \) at 300 K, which is the same order as the estimated recently for PANI-CSA [27]. The mean free path \( t^* \) can also be estimated to be \( 0.5 \varepsilon_0 \) at 300 K and \( 5 \varepsilon_0 \) at 150 K [28]. These values of \( t^* \) indicate that PANI-HCl is on the border between metal and semiconductor.

Above 150 K it can be concluded that PANI-HCl is the highly anisotropic metal and \( D_\delta \) appeared to be of semiconductor, i.e., fairly weak but finite interchain coupling was suggested.

At the present stage, it is open what happens below 150 K in \( D_\nu \). Although \( 1/D_\nu \propto \log T \) or \( D_\nu \propto \sqrt{T} \) or \( D_\nu \propto \exp(bT) \) appeared to hold approximately in this temperature range, applicability of these formulae including its absolute value is not clear. Preliminary data of spin dynamics for the other pH samples suggest that this peak at 150 K tends to move to higher temperature with increasing pH value.

The present analysed conclusion is not consistent with that of NMR \( T_1 \). This would come from other sizable excess contributions than quasi-1D spin motion. A detailed discussion will be reported elsewhere [29].

As future reports it is interesting to study the spin dynamics of variety of PANI samples, crystal structure dependence of stretch aligned PANI and morphology dependence of PANI-CSA [27].

One of the authors (KM) would like to express his thanks to Dr. M. Nechtschein and Dr. J.-P. Travers for exciting and valuable discussions and providing the samples used in this work. This work is supported in part by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No.03640321).

REFERENCES


6. S. Masubuchi et al., to be published.
9. Although in Ref.6 the exponential temperature dependence has been assumed to explain a temperature dependence of resistivity measured by a conventional four-terminal method, it is simply one of the trial functions.
15. The hyperfine coupling has negligible contribution to the ESR line width, less than 1%, because of high electron spin concentration.
22. For example, A. Graja, Low-Dimensional Organic Conductors, (World Scientific, 1992).
28. Difference of $t'$ from that reported earlier mainly comes from the difference of $\Sigma_t$ used in the present paper.
29. F. Shimizu et al., to be published.