

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

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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 σ 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 dependences $\sigma \propto T^{-1}$, $\propto T^{-2}$ and $\propto \exp(E_a/kT)$ could give a reasonable agreement with the experimental data [2,3]. Therefore, it is impossible to discriminate what is the *intrinsic temperature dependence of σ* 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 $\sigma \propto T^{-1}$ and $\propto T^{-2}$ depending on the species of dopants [5,6] and for the five membered ring polymers of polythiophene and poly(3methyl)thiophene [7] as $\sigma \propto T^{-1}$ and $\propto T^{-2}$. However, an evaluation of the VSC method has not been fixed so far. In the three-dimensional (3-D) metals, $\sigma \propto T^{-1}$ dependence is familiar, and $\sigma \propto T^{-2}$ was frequently observed in various low-di-

mensional 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 ^1H 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-

nique reported in the literature [13]. The obtained powder has been finally equilibrated with pH=0 hydrochloric acid. Carefully evacuated PANI powder was sealed into a quartz tube with helium gas for heat exchange. ESR line width was measured at frequencies from several tens MHz to 24 GHz by home built spectrometers except for X-band (JEOL RE-3XG). The obtained spectra were analysed by a least square fitting with Lorentzians to determine the line widths precisely down to mG. Electrical conductivity for the same sample was measured by conventional four terminal method.

Figure 1 shows the ESR line width as a function of inverse of square root frequency that is useful display for quasi-one-dimensional (Q-1-D) system because of the following reason. If the electron spin rapidly diffuses on the polymer chain with the diffusion rate $D_{||}$ (rad/sec) and hops to the neighboring chains with the rate D_{\perp} (rad/sec) for single direction, another electron feels dipolar local field modulated by the Q-1-D motion of each other. As a result, the spectral density $\phi(\omega)$ of this motion is given, at $\omega \ll D_{||}$, by [10,14]

$$\phi(\omega) = \frac{1}{\sqrt{4D_{||}D_{\perp}}} \sqrt{\frac{1 + \sqrt{1 + (\omega/2D_{\perp})^2}}{1 + (\omega/2D_{\perp})^2}}, \quad (1)$$

as a function of frequency ω . For the case of mutual diffusion of electron spins, $D_{||}$ should be replaced by $2D_{||}$. This equation has a simple form of $1/\sqrt{2\omega D_{||}}$ at $\omega \gg D_{\perp}$ and a constant value of $1/\sqrt{2D_{||}D_{\perp}}$ at $\omega \ll D_{\perp}$. The former form appears as a straight line in Fig.1, as is found actually.

The actual ESR line width $\Delta H_{pp} = 2T_2^{-1}/\sqrt{3}\gamma_e$ caused by the mechanism considered above is governed only by the pure electronic dipolar coupling [15] and can be described using the spectral density $\phi(\omega_0)$ at the Larmor frequency ω_0 by [10,16]

$$T_2^{-1} = c\gamma_e^4 \hbar^2 S(S+1) \Sigma_i [0.3\phi(0) + 0.5\phi(\omega_0) + 0.2\phi(2\omega_0)], \quad (2)$$

where γ_e is the electron gyromagnetic ratio, c the effective concentration of the electron spins, $\Sigma_i = \Sigma P_2(\cos\theta_{12})/r_1^3 r_2^3$ the lattice sum and the others have usual meanings. Analysis by eq.(2) indicated that the observed peak to peak line width $\Delta H_{pp}(\omega_0)$ is composed of two contributions; the one is $2T_2^{-1}(\omega_0)/\sqrt{3}\gamma_e$, depending on frequency following eq.(2) and the other is ΔH_0 being independent of frequency. Using $\Delta H_0 = 0.435$ (G) as an average for the data above 150 K because of large scattering for ΔH_0 derived by fitting, one can deduce the temperature dependence of $D_{||}$ and D_{\perp} as shown in Figure 2 with $\Sigma_i = 3.3 \times 10^{45}$ (cm⁻⁶) estimated for 100

neighboring chains. Here, an origin of ΔH_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

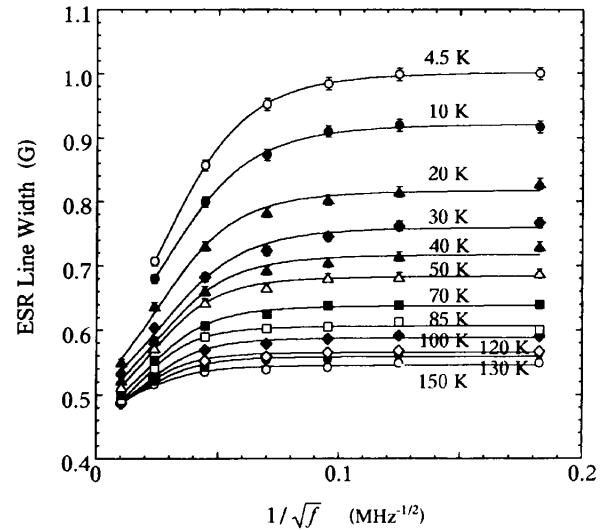
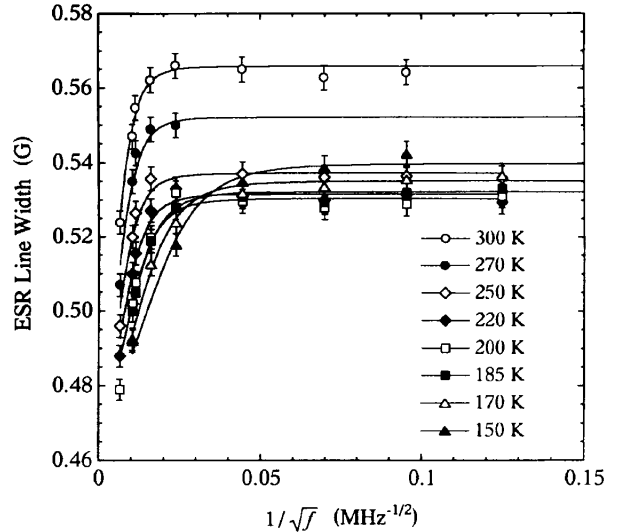


Fig. 1 The frequency dependence of ESR line width with an implicit parameter of temperature. Solid curves indicate the behavior expected from eq.(2) for quasi-one-dimensional diffusion. The slope of linear increase is proportional to $1/\sqrt{D_{||}}$ and the frequency where the line width levels off corresponds to D_{\perp} . Anomaly of the slope at 150 K can be found by noting that the slope increases with both increasing and decreasing the temperature from 150 K.

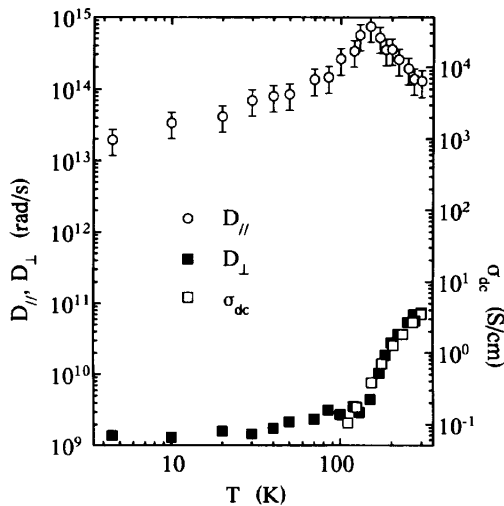


Fig. 2 The temperature dependence of the diffusion rates $D_{||}$ and D_{\perp} . At 150 K, abrupt change is found in $D_{||}$. Above 150 K, $D_{||}$ is of metallic and below 150 K it is of semiconducting. D_{\perp} varies following the d.c. conductivity for the same sample down to 130 K, which implies that D_{\perp} limits the electrical conduction. Below 130 K D_{\perp} 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_{\perp} could be attributed to some characteristic energy in "metal", for example, thermal energy ($k_B T$), Debye temperature or Fermi energy that needs to work as a reservoir of energy $\hbar(\omega_{be} - \omega_{bn})$ accompanying to a resonance transition. From $D_{\perp} \sim 10^{11}$ (rad/sec) at 300K one gets extremely small energy of 10^{-4} eV (~ 1 K!) 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; $D_{||}$ behaves being metallic and D_{\perp} does semiconducting like that of $\sigma_{d.c.}$ above 150 K. Anisotropy ratio of the microscopic diffusion rates, $D_{||}$ and D_{\perp} is extremely high; more than 10^5 at 150 K and decreases down to $\sim 10^3$ at 300 K. This result means that the on-chain conduction is of metallic, but interchain conduction is of hop-

ping, 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 $R = (J/\hbar) / \langle \omega^2 \rangle^{1/2}$, where J is the effective inter-chain coupling [18,19]. The second moment [16] $\langle \omega^2 \rangle = (3/5) c \gamma_e^4 \hbar^2 S(S+1) \sum (1/r_{jk}^6)$ produced by the electronic dipolar interaction can be estimated as 8.9×10^{17} (rad²/s²) for the ES-I structure [20] with $c = 0.05$ (spins/two rings), $\gamma_e = 1.76 \times 10^7$ (G⁻¹s⁻¹) and $S = 1/2$. With the diffusion rates shown in Fig.2 and the relations $D_{\perp} = (J/\hbar)(J'/J)^{1/3}$ and $(J/\hbar) = D_{||} / \sqrt{\pi}$, $R = 12$ 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 ϵ 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 $D_{||}$ above 150 K. It can be fitted to power law T^{-d} with $d = 2-3$. This temperature variation for $D_{||}$ could be taken to be the same as that for the on-chain conductivity, since the on-chain diffusion rate $D_{||}$ can be converted to the electrical conductivity with a relationship for the 1-D metals, $\sigma_{D_{||}} = n e^2 \tau / m^* = e^2 N(E_F) D_{||} c_{||}^2$. Here, n is the carrier concentration, τ the relaxation time of charge carrier, m^* the electron effective mass,

$N(E_F)$ the density of states at the Fermi energy per unit volume and $c_{||}=9.5$ (Å) the unit length of chain axis. Then, if $N(E_F)=\text{const.}$, $\sigma_{D_{||}} \propto D_{||} \propto T^{-2-3}$ 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 $D_{||}$ could be characteristic behavior in Q-1-D metal.

The metallic behavior of $D_{||}$ above 150 K abruptly changes to weak semiconducting one. Below 150 K, $1/D_{||} \propto \log T$ approximately holds, but $D_{||} \propto \log T$ 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 $D_{||}$ 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 $D_{||}$ 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_{\perp} , the most pronounced point is a good coincidence of it with the d.c. conductivity σ above 130 K. Below 130 K, D_{\perp} 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_{\perp} , including the protonation dependence [26].

We summarize our main result as follows. We succeeded to analyse the microscopic spin and

charge dynamics in PANI-HCl. The interchain hopping D_{\perp} 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 $\sigma \propto T^{-d}$ ($d \geq 2$) relation. It is worthy to estimate the microscopic conductivity $\sigma_{D_{||}}$ from $D_{||}$. However, in contrast to D_{\perp} , it is hard to determine the absolute value of $D_{||}$ with accuracy because of the several unknown parameters to be estimated; Σ_t , $c(T)$, $N(E_F)$, and so on. Then we can estimate an order of intrachain conductivity $\sigma_{D_{||}} \sim 1.5 \times 10^3$ (S/cm) at 300 K, which is the same order as the estimated recently for PANI-CSA [27]. The mean free path ℓ^* can also be estimated to be $0.5c_{||}$ at 300 K and $5c_{||}$ at 150 K [28]. These values of ℓ^* 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_{\perp} 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 $D_{||}$. Although $1/D_{||} \propto \log T$ or $D_{||} \propto \sqrt{T}$ or $D_{||} \propto \exp\{bT\}$ 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].

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REFERENCES

1. See, for example, Proc. of the Int. Conf. on Sci. & Tech. of Synth. Met. (ICSM'92), Göteborg, Sweden, 1992 [Synth. Met. 55-57, (1993)].
2. S. Masubuchi, S. Kazama, K. Mizoguchi, F. Shimizu, K. Kume, R. Matsushita and T. Matsuyama, Synth. Met. 57, 4866 (1993).

3. A.B. Kaiser and S.C. Graham, *Synth. Met.* **36**, 367 (1990) and references therein.
4. W. Meixiang, W. ping, C. Yong, Q. Renyan, W. Fosog, Z. Xiaojian and G. Zhi, *Solid State Commun.* **47**, 759 (1983).
5. S. Masubuchi, K. Mizoguchi, K. Mizuno and K. Kume, *Synth. Met.* **22**, 41 (1987).
6. S. Masubuchi et al., to be published.
7. S. Masubuchi, S. Kazama, K. Mizoguchi, H. Honda, K. Kume, R. Matsushita and T. Matsuyama, *Synth. Met.* **57**, 4962 (1993).
8. S. Kivelson and A.J. Heeger, *Synth. Met.* **22**, 371 (1988).
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.
10. K. Mizoguchi, *Makromol. Chem., Macromol. Symp.* **37**, 53 (1990) and references therein.
11. M. Nechtschein, F. Devreux, F. Genoud, M. Guglielmi and K. Holczer, *Phys. Rev. B* **27**, 61 (1983).
12. K. Mizoguchi, M. Nechtschein, J.-P. Travers and C. Menardo, *Phys. Rev. Lett.* **63**, 66 (1989).
13. A.G. MacDiarmid, J.C. Chiang, A.F. Richter and A.J. Epstein, *Synth. Met.* **18**, 285 (1987).
14. C.A. Sholl, *J. Phys. C* **14**, 447 (1981).
15. The hyperfine coupling has negligible contribution to the ESR line width, less than 1%, because of high electron spin concentration.
16. A. Abragam, *Principles of Nuclear Magnetism*, chapter 8 (Oxford University, Oxford, 1961).
17. M. Nechtschein, F. Genoud, C. Menardo, K. Mizoguchi, J.-P. Travers and B. Villeret, *Synth. Met.* **29**, E211 (1989).
18. (a) Z.H. Wang, E.M. Scherr, A.G. MacDiarmid and A.J. Epstein, *Phys. Rev. B* **45**, 4190 (1992), (b) Z.H. Wang, C. Li, E.M. Scherr, A.G. MacDiarmid and A.J. Epstein, *Phys. Rev. Lett.* **66**, 1745 (1991).
19. M.J. Hennessy, C.D. McElwee and P.M. Richards, *Phys. Rev. B* **7**, 930 (1973).
20. J.P. Pouget, M.E. Józefowicz, A.J. Epstein, X. Tang and A.G. MacDiarmid, *Macromolecules* **24**, 779 (1991).
21. D. Moses, A. Denenstein, A. Pron, A.J. Heeger and A.G. MacDiarmid, *Solid State Commun.* **36**, 219 (1980); N. Mermilliod et.al., *J. Physique* **41**, 1453 (1980).
22. For example, A. Graja, *Low-Dimensional Organic Conductors*, (World Scientific, 1992).
23. R.W. Cochrane and J.O. Strom-Olsen, *Phys. Rev. B* **29**, 1088 (1984).
24. H. Kuzmany, N.S. Sariciftci, H. Neugebauer and A. Neckel, *Phys. Rev. Lett.* **60**, 212 (1988).
25. C. Jeandey, J.P. Boucher, F. Ferrieu and M. Nechtschein, *Solid State Commun.* **23**, 673 (1977).
26. K. Mizoguchi, M. Nechtschein, J.-P. Travers, *Synth. Met.* **41-43**, 113 (1991).
27. M. Reghu, Y. Cao, D. Moses and A.J. Heeger, *Synth. Met.* **57**, 5020 (1993).
28. Difference of ℓ^* from that reported earlier mainly comes from the difference of Σ_{ℓ} used in the present paper.
29. F. Shimizu et.al., to be published.