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Electron Spin Resonance Study of Intrinsic Paramagnetism of Soluble Polyaniline Perchlorates

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An ESR study was carried out on two polyaniline perchlorates prepared by different chemical methods: Soluble perchlorate I prepared by the use of copper(II) perchlorate as an oxidative coupling agent, and perchlorate II (corresponding to polyemeraldine perchlorate) obtained by treating a polymer base with perchloric acid. The ESR signal intensity of perchlorate I shows a thermally activated temperature dependence at temperatures between 95 and 300 K. The ESR signal intensity of perchlorate II was temperature-independent. When this polymer adsorbed oxygen, the ESR signal showed a thermally activated paramagnetism resembling that of perchlorate I. These paramagnetic properties can be explained by polaron spins that are antiferromagnetically coupled with each other, and are different from the Pauli-type paramagnetism. This suggests that the charge-transport cannot be explained by the migration of paramagnetic polarons along a polymer chain alone.

The charge transport of polyaniline is sensitively dependent on the protonation of the polymer chains,[1,2] and the protonation results in a significant enhancement of paramagnetism.[1-3] The relation between the charge transport and the magnetic properties is the important subject of the conducting polyaniline. Usually electroconducting polymers contain a significant number of unpaired electrons due to defects of polymer chains. The susceptibility of these defect spins is strongly temperature-dependent. This makes it difficult to study the intrinsic paramagnetism, which is expected to be weakly temperature-dependent. Recently, we have reported that a polymerization of aniline by the use of copper(II) perchlorate as an oxidative coupling agent yields a polyaniline perchlorate that has a doping level of ca. 0.4 per polymer unit and is soluble in dimethyl sulfoxide (DMSO).[4] The solubility is expected to be due to a low degree of chain defect and/or cross linking of polymer chains. Therefore, the new polyaniline perchlorate is a good material for studying the intrinsic magnetism of conducting polyaniline. Preliminarily we have reported that the electron spin resonance (ESR) signal intensity of this perchlorate shows a thermally activated temperature dependence differing from the Pauli-type paramagnetism.[5] The present paper is the full report of the ESR study.

Experimental

Perchlorate I in Table 1 was prepared by the method reported in our previous paper:[4] Freshly distilled aniline was polymerized by the use of copper(II) perchlorate as an oxidative coupling agent in acetonitrile. The resulting powder material was washed with acetonitrile in a Soxhlet extractor to eliminate possible oligomer components and copper perchlorate. The obtained polymer did not show an ESR signal attributable to Cu(II) species. A polymer base was obtained by treating the perchlorate with 4.5 M NH_3 solution for 20 h. By treating this polymer base with 3 M perchloric acid for 3 h, perchlorate II was obtained. The compositions determined by elemental analyses for the three polymers are shown in Table 1 together with the room-temperature conductivity. The elemental analyses were performed by Huffman Laboratories, Golden, CO., U.S.A.

Table 1. ESR Data Observed for Polyanilines at Room Temperature: g Value and Molar Magnetic Susceptibility χ (in emu mol^{-1}) per $-C_6H_4NH_y-$ Unit and Peak-to-Peak Width W in Oxygen-Free and Oxygen-Adsorbing States

Polyaniline	σ/S cm^{-1}	g	$10^6\chi$	W/G	
				O_2-free	O_2-ads
Perchlorate I[a]	1.3	2.0027	40	0.28	2.0
Polymer base[b]	10^{-10}	2.0036	0.3	8.5	8.5
Perchlorate II[c]	1.8	2.0027	45	0.42	1.5

a) As-prepared perchlorate: $[(-C_6H_4NH-)(ClO_4)_{0.4}\cdot 0.4H_2O]_n$. b) Base: $[(-C_6H_4NH-C_6H_4NH-)_{1-x}(-C_6H_4N=C_6H_4=N-)_x\cdot 0.4H_2O]_n$ ($x\approx 0.6$). c) Perchlorate prepared from the base: $[(-C_6H_4NH-)(ClO_4)_{0.4}\cdot 0.6H_2O]_n$.

The ESR spectra were obtained with the aid of a JEOL SCXA ESR spectrometer. The sample temperature was controlled by flowing a cold nitrogen gas between 95—300 K. Mn^{2+}/MgO and DPPH were used as references. The ESR spectra were recorded on the two conditions for each material: 1) The oxygen-free samples were sealed with He gas in a quartz tube after kept in dynamic vacuum for 3—4 h, and 2) the oxygen-adsorbing samples were sealed in a cell with He gas after equilibrated with atmospheric oxygen. Each observed derivative curve was digitized and doubly integrated: The error of the integration was ca. 20%. The magnetic susceptibility was calculated by referring to the signal intensity of Mn^{2+}/MgO powder used as a marker, the susceptibility of which was calibrated with DPPH. The molar susceptibility was calculated for each $-C_6H_4NH_y-$ unit. The electrical conductivity was determined on the compressed pellets of the powder materials by van der Pauw's four-probe method.

Results

Electrical Conductivities. The room-temperature conductivities are shown in Table 1. The two perchlorates show a semiconductive property with an activation energy of 0.04 eV at high temperatures, and the temperature dependence throughout the temperature range investigated (80—300 K) is explained by the variable-range hopping model (Figs. 1 and 2):6)

$$\sigma = (T_0/T)^{1/2}\exp[-(A/kT)^{1/4}] \qquad (1)$$

The parameters obtained were: T_0=4.2×10^{11} K and A/k=3.2×10^6 K for perchlorate I, and T_0=5.5×10^{12} K and A/k=4.5×10^6 K for perchlorate II. No significant difference is appreciable for the charge-transport properties of the two perchlorates.

ESR of Perchlorate I (As-Prepared Perchlorate). The ESR spectrum of perchlorate I showed a symmetric signal with a g value of 2.0027 and a peak-to-peak width W of 0.28 G (G=10^{-4} T). The g value was temperature-independent. In contrast, the W was temperature-dependent as shown in Fig. 3: It showed a maximum at 185 K. The magnetic susceptibility calculated from the signal intensity at 297 K was 0.3×10^{-6} emu g^{-1}, which gave a molar magnetic susceptibility of 40×10^{-6} emu mol^{-1} for each aniline unit. Figure 4 shows the temperature dependence of the relative signal intensity I_r=$I(T\,\mathrm{K})/I(297\,\mathrm{K})$, which is proportional to the magnetic susceptibility. The I_r gradually decreased with decreasing temperature, differing from that reported for polyemeraldine salts3) prepared by the use of ammonium peroxodisulfate, $(NH_4)_2S_2O_8$, as an oxidative coupling agent.

When the perchlorate was exposed to air, the peak-to-peak width increased (W=2.0 G at 297 K), and showed a strong temperature-dependence (Fig. 3). The ESR relaxation is markedly influenced by the adsorption of oxygen molecules. On the other hand, the integrated signal intensity was unchanged by oxygen adsorption.

ESR of Polymer Base. The treatment of perchlorate I with an alkaline solution yielded an insulating polymer base $[(-C_6H_4\text{-}NH\text{-}C_6H_4\text{-}NH\text{-})_{1-x}(-C_6H_4\text{-}N{=}C_6H_4{=}N\text{-})_x]_n$

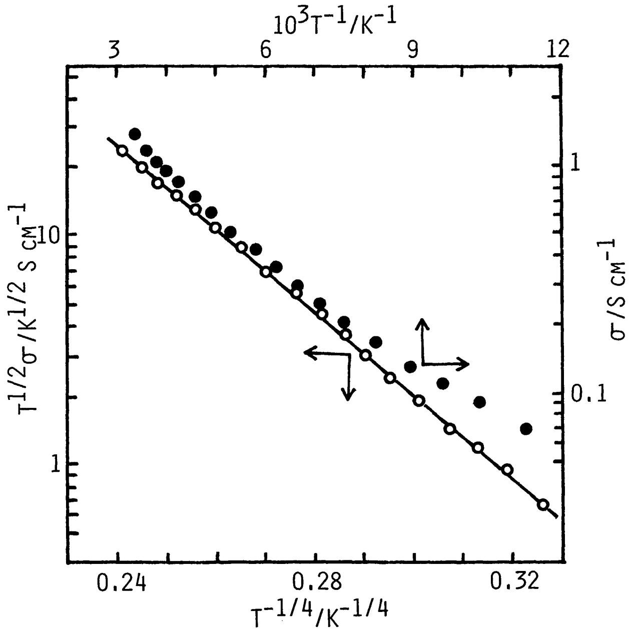

Fig. 1. Electrical conductivity σ of the as-prepared polyaniline (perchlorate I). The solid line shows the hopping model.

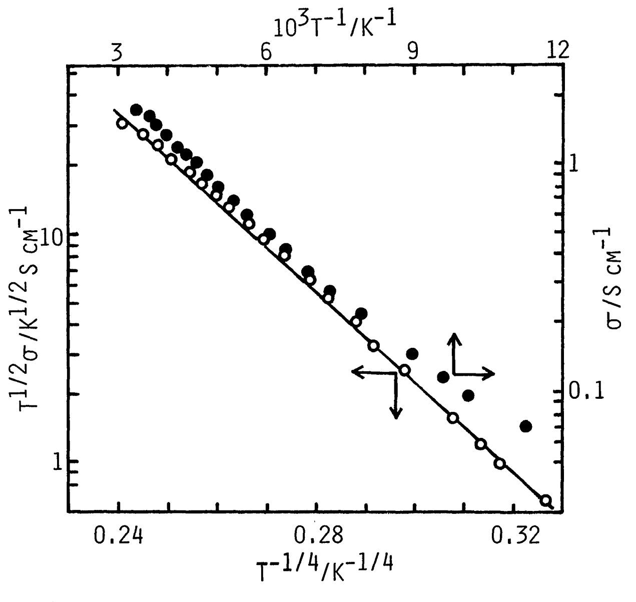

Fig. 2. Electrical conductivity σ of perchlorate II obtained by the protonation of polyemeraldine base. The solid line shows the hopping model.

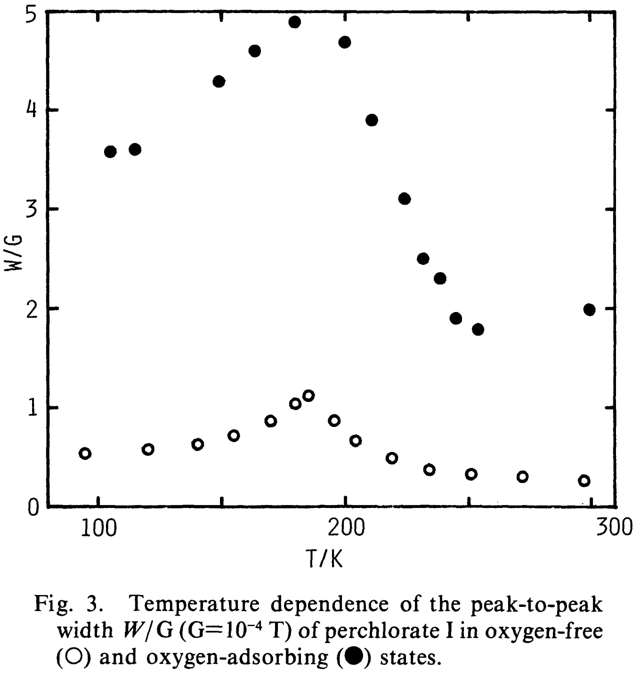

Fig. 3. Temperature dependence of the peak-to-peak width W/G (G=10^{-4} T) of perchlorate I in oxygen-free (○) and oxygen-adsorbing (●) states.

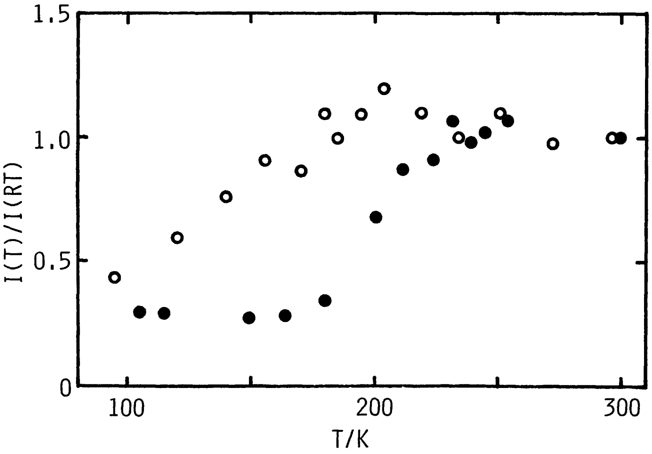

Fig. 4. Temperature dependence of the relative signal intensity $I(T\ \mathrm{K})/I(\mathrm{Room\ Temp})$ of perchlorate I in oxygen-free (○) and oxygen-adsorbing (●) states.

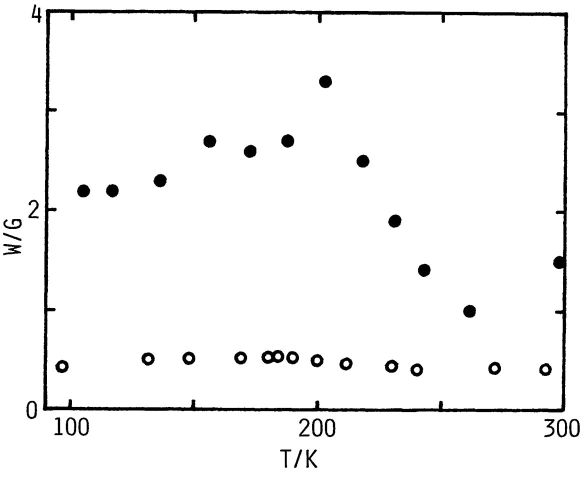

Fig. 5. Temperature dependence of the peak-to-peak width W/G ($\mathrm{G}=10^{-4}$ T) of perchlorate II in oxygen-free (○) and oxygen-adsorbing (●) states.

with $x\approx0.6$; the composition is practically identical with that of polyemeraldine base. The polymer base showed a broad ESR signal with a g value of 2.0036 and a peak-to-peak width W of 8.5 G at 297 K. These ESR parameters were temperature-independent throughout the temperature range investigated. The magnetic susceptibility was 3×10^{-9} emu g^{-1}: This gave a molar susceptibility of 3×10^{-7} emu mol^{-1} for each $\text{-}C_6H_4NH_y\text{-}$ unit. The signal intensity $I_r=I(T\ \mathrm{K})/I(297\ \mathrm{K})$ obeyed the Curie–Weiss law $I_r=C/(T-\theta)$ with $\theta=-21$ K throughout the temperature range investigated (95—300 K). These magnetic properties were not substantially influenced by adsorption of oxygen: g=2.0036, W=8.5 G at 297 K, and $\theta=-14$ K for the oxygen-adsorbing polymer. The Curie constant C was calculated to be 9×10^{-5} emu K mol^{-1} for each ring by referring to the room temperature susceptibility. A spin system containing one unpaired electron on each site has the Curie constant 0.375 emu K mol^{-1}. The ratio $C/0.375$ gave a spin density of 2×10^{-4} per $\text{-}C_6H_4NH_y\text{-}$ unit. This spin density is much smaller than that reported for polyemeraldine base prepared by the conventional method.[3] The polymer obtained by the use of the new oxidant contains a very small number of chain defects.

ESR of Perchlorate II (Perchlorate Obtained from Polymer Base). When the polymer base was treated with perchloric acid, the ESR signal narrowed (W= 0.42 G and g=2.0027 at 293 K), and the signal intensity increased by a factor of 100. The susceptibility of this perchlorate was equal to that of the as-prepared polymer (perchlorate I) within the experimental error (Table 1). Figures 5 and 6 show the peak-to-peak width W and the signal intensity I_r, respectively, as functions of temperature. The I_r showed a very weak temperature-dependence. Upon adsorbing oxygen, the signal broadened markedly (Fig. 5), whereas the integrated signal intensity at room temperature was unchanged. The I_r of the oxygen-adsorbing sample showed a thermally activated temperature dependence (Fig. 6), in contrast to the oxygen-free sample.

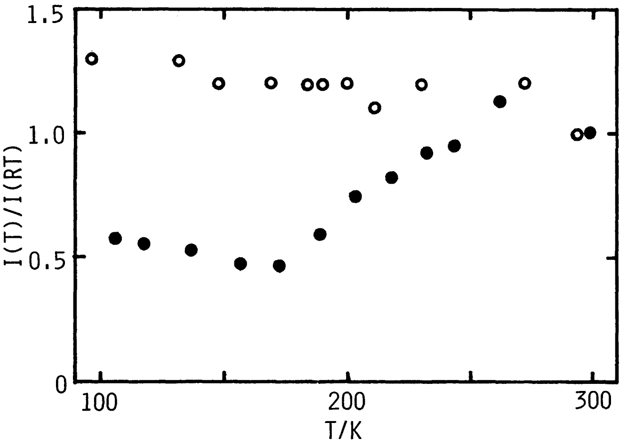

Fig. 6. Temperature dependence of the relative signal intensity $I(T\ \mathrm{K})/I(\mathrm{Room\ Temp})$ of perchlorate II in oxygen-free (○) and oxygen-adsorbing (●) states.

Discussion

The solution electronic spectrum of the as-prepared polymer (perchlorate I) shows that the charge carriers are paramagnetic polarons rather than diamagnetic bipolarons.[4] The intrinsic magnetism of the polarons is expected to be observed for the polymer. The nature of the ESR spectra is markedly influenced by oxygen adsorption. The similar oxygen-adsorption effect has been extensively studied for polyacetylene, and it has been interpreted by the coexistence of mobile spins and trapped spins, although the ESR signals of the two different spin species have not been observed individually.[7] The ESR peak-to-peak width W of perchlorate I markedly increases upon oxygen adsorption. The oxygen-adsorbing polymer shows a clear maximum of

W at ca. 185 K. Around this temperature, the differential scanning calorimetry showed no appreciable thermal anomaly; usually, a sudden change of ESR relaxation accompanies a phase transition. Therefore, it is probable that additional spin sites are formed by oxygen adsorption, as proposed for polyacetylene: The temperature dependence of W can be explained by the presence of two spin species, line-widths of which exhibit different temperature dependence. The more important experimental result is that the temperature dependence of the signal intensity observed for the polymer is different from that reported for polyemeraldine salts. The signal intensity of the latter polymer increases with decreasing temperature, but it deviates from the Curie–Weiss law. This magnetic behavior has been explained by the superposition of a strong Curie-type paramagnetism and a weak temperature-independent paramagnetism.[1–3,8] In contrast, the signal intensity of polyaniline perchlorate I decreases with decreasing temperature. Obviously, at least one of the two possible spin species in perchlorate I shows a thermally activated temperature dependence, although their ESR signals cannot be distinguished from each other. This magnetic property is not explained by the Pauli-type paramagnetism. In polyaniline, the molecular planes of the neighboring $-C_6H_4NH-$ groups are twisted with one another due to a steric effect,[2,9] and hence the electronic band formed by the π-electron overlap is not expected to be wide enough to show the Pauli paramagnetism. A thermally activated paramagnetism similar to that of the perchlorate has been reported for a variety of paramagnetic compounds that have a strong antiferromagnetic interaction via superexchange interaction mechanism.[10] This type of magnetic interaction is operative between unpaired electrons that reside on the conjugated system of a polymer chain.[11] A conceivable interaction mechanism for polyaniline is schematically shown in Fig. 7: A polaron spin that resides on a positively charged nitrogen atom induces a spin polarization of a π electron on the adjacent carbon atom, and this spin polarization is induced in succession until another unpaired electron is encountered on a nitrogen atom. Consequently, the two unpaired electrons are antiferromagnetically coupled with each other. This antiferromagnetic interaction may occur among a number of polaron spins existing on a polymer chain. The ground level of this spin system is singlet and the paramagnetism is induced by a thermal activation.

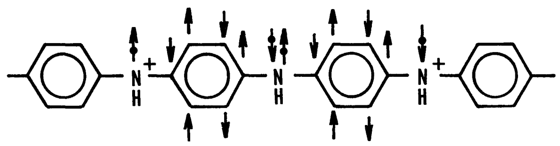

Fig. 7. Superexchange interaction operative between two polaron spins in a polyaniline chain. An unpaired electron on a positively charged nitrogen atom causes the spin polarization of a π electron on the adjacent carbon atom. The spin polarization is induced in succession until another unpaired electron is encountered. Consequently, the two unpaired electrons are coupled antiferromagnetically.

In the course of the treatment of a polymer base with acid, protonation is expected to occur in preference at the quinone-imine nitrogen and to yield bipolarons that have no unpaired electron. The magnetic susceptibility of the resulting polymer salt, however, is a factor of 100 larger than that of the parent polymer base. On the basis of this observation, Ginder et al.[8] have proposed that a bipolaron produced by protonation is converted to two polarons by an internal redox reaction and the resulting polarons migrate successively so as to reduce the Coulomb repulsion. This mechanism well explains the origin of the paramagnetism induced by protonation. On the other hand, the X-ray photoelectron spectra (XPS) of polyemeraldine salts exhibit a weak nitrogen 1s peak attributable to bipolarons in addition to a strong polaron peak.[12–14] The solution electronic spectrum and the XPS of polyaniline perchlorate II have evidenced that a small number of bipolarons coexist with polarons in the polymer chains, whereas perchlorate I contains no significant number of bipolarons.[4,14] This is an important structural difference between perchlorates I and II. A bipolaron that is diamagnetic may be thermally excited to two neighboring paramagnetic polarons. When these two states are in a thermal equilibrium, a thermally activated magnetism is expected to be observed. The interconversion between a bipolaron state and a two-polaron state is, however, accompanied by a polymer conformation rearrangement,[4] which requires a large activation energy. In a normal temperature range, therefore, the thermal activation of a bipolaron to two polarons in solid state is hardly observed in the susceptibility vs. temperature curve. On the other hand, the superexchange interaction is readily influenced by the electronic state of intervenient atoms between interacting polarons. In this manner, bipolarons that coexist with polarons in perchlorate II may result in the difference between the magnetic properties of the two perchlorates in oxygen-free states. In oxygen-adsorbing states, the two perchlorates show an identical temperature dependence of signal intensity. Since the oxygen-adsorbing materials show a stronger temperature dependence than that of the corresponding oxygen-free materials, the oxygen-adsorption enhances the magnetic interaction between polarons, so that the effect of the structural difference is smeared out.

The charge-transport of polyaniline has been explained by the hopping of paramagnetic polarons along the polymer chains. The present study has shown that the polyaniline chains do not show the Pauli-type paramagnetism. Two explanations are conceivable: 1) Hopping polarons responsible for charge-transport do not show the Pauli-type paramagnetism, and 2) there is no direct relation between the two physical properties. The second case is consistent with a recent theoretical calculation of doped polyaniline, which has indicated that large spin densities are distributed on nitrogen atoms whereas large net-charge densities exist on phenyl rings.⁹⁾ These results suggest that the charge transport in polyaniline cannot be explained by paramagnetic polaron migration along a polymer chain alone. An additional effect contributes to the charge transport. For example, a charge transfer between phenyl rings that face to each other in proximity may be one of the important contributing factors.

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