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Electrical conductivities and electron spin resonance spectra of polyaniline salts with different counteranions

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SUMMARY

Electrical conductivities and ESR spectra were obtained for polyaniline salts that contained different counter anions. The electrical properties were markedly different from one salt to another, although the concentrations of counteranions were almost identical. The ESR spectra showed that different types of unpaired electrons were created upon protonation. There was a close correlation between the charge-transport property and the nature of unpaired electrons created upon protonation.

INTRODUCTION

The charge-transport properties of conducting polymers are sensitively dependent on the nature of dopants. The doping of polyaniline is performed by the treatment of the corresponding polymer base with appropriate acids; the protonation of the polymer base with an acid results in the formation of bipolarons that are diamagnetic, and successively some bipolarons are converted to polarons that are paramagnetic (1). The magnetic properties are, therefore, expected to have some correlation with the charge-transport properties. This is the subject of the extensive magnetic studies of polyanilines (2,3). In the present work, we have studied the charge-transport properties and the electron spin resonance (ESR) spectra of polyanilines treated with different acids. The results have shown that the nucleophilicity as well as the acid strength is an important factor for functioning as a good dopant, and that the nature of unpaired-electrons created upon protonation is strongly dependent on the nature of acids used.

EXPERIMENTAL

Polyaniline perchlorate was prepared by the method reported in our previous papers (4,5): to aniline (0.62 g) in acetonitrile (20 ml) was added dropwise an acetonitrile solution (20 ml) containing $Cu(ClO_4)_2 \cdot 6H_2O$ (5.0 g) with stirring under a nitrogen atmosphere at ambient temperature. Precipitate formed was collected on a fritted glass filter, washed with acetonitrile and dried in vacuum. The product was washed again with acetonitrile in a Soxhlet extractor to eliminate possible contaminants and oligomer components; it was confirmed by ESR that the resulting material was not contaminated by paramagnetic copper species. Polyaniline base was obtained by treating the perchlorate with 4 M NH_3 for 4 h. The polyaniline base thus obtained was used as a starting material for protonation with different acids. The protonation was carried out by using 4 M acids for 4 h to obtain the corresponding polymer salts each having the highest dopant concentration. The anion concentrations were determined by elemental analyses as shown in Table 1. The C, H, N and halogen analyses were performed by Huffman Laboratories, Golden, CO., USA.

The electrical conductivities were determined by van der Pauw's four-probe method on compressed pellets at temperatures between 80 and 300 K. The ESR spectra were obtained with a Varian E3 spectrometer for oxygen-free and oxygen-adsorbing states of each material. An oxygen-free sample was sealed in a quartz tube after pumped in vacuum for 4 h. An oxygen-adsorbing sample was equilibrated with atmospheric oxygen. Mn^{2+}/MgO was used as a calibrant for the *g* value. For the determination of relative ESR signal intensities, the spectra were recorded in an identical spectrum condition, and the integrated intensities were calculated by referring to the Mn^{2+}/MgO signal recorded simultaneously.

Results and Discussion

The as-prepared polyaniline perchlorate had an anion concentration of 0.4 for each aniline unit, and its electrical and ESR properties were agreed with those reported previously (4,6): $\sigma = 4$ S cm^{-1}, $g = 2.003$, and $W = 0.3$ G. A polymer base obtained from this perchlorate was used as the starting material for the protonations, because this polymer base had been reported to have a very small quantity of chain defects (6). In the present study, concentrated acids were used for the protonations to obtain each salt that had the maximum dopant level. The quantities of the counter anions involved were determined by elemental analyses as shown in Table 1. The electrical conductivities of all salts followed the semiconducting relation, $\sigma = \sigma_\infty \exp(-E/kT)$, at high temperatures as shown in Fig. 1; the activation energies *E* are collected in Table 1 together with the room-temperature powder conductivities. At low temperatures, the

Table 1. Electrical conductivities σ/S cm^{-1} at 300 K, activation energies *E*/eV for electrical conduction at high temperatures, ESR signal intensities *I* and ESR peak-to-peak widths *W*/G of different polyaniline salts, $[(-C_6H_4NH-)A_m \cdot nH_2O]_x$.

dopant A	composition *m*	 *n*	σ	*E*	*I*[a]	*W* O_2-free	 O_2-ad
ClO_4[b]	0.4	0.4	4	0.038	100	0.3	2
base	0	0.4	$<10^{-6}$	--	1	8.5	8.5
ClO_4	0.4	0.6	2	0.037	80	0.3	3
Cl	0.5	0.5	2	0.050	120	0.4	3.5
Br	0.4	0.4	0.03	0.08	90	3.5	5
I	0.35	0.2	0.001	0.14	30	9	8
CF_3CO_2	0.3	0.6	0.1	0.11	30	0.2	3
CH_3CO_2	0.2	0.1	$<10^{-6}$	--	3	10	9

[a] Referring to the intensity of the polymer base.

[b] As-prepared polymer that was used for the preparation of the polymer base (ref. 4 and 6).

observed σ *vs.* T curves deviated from the semiconducting relation, and was well explained by the hopping model, $\sigma = (A/T)^{1/2}\exp[-(B/T)^{1/4}]$.

The perchlorate and the chloride are the most electroconductive among the salts studied. In contrast, the bromide and the iodide are poorly conductive, although their anion concentrations are almost identical with those of the chloride and the perchlorate. In the X-ray photoelectron spectrum (XPS) of a polyaniline chloride, a 2*p*-electron peak of neutral Cl species was observed in addition to the corresponding peak of Cl^- ions (7,8). On the basis of this observation, it has been deduced that a part of the chlorine atoms are bonded to carbon atoms in the aromatic rings; the concentration of the chlorine

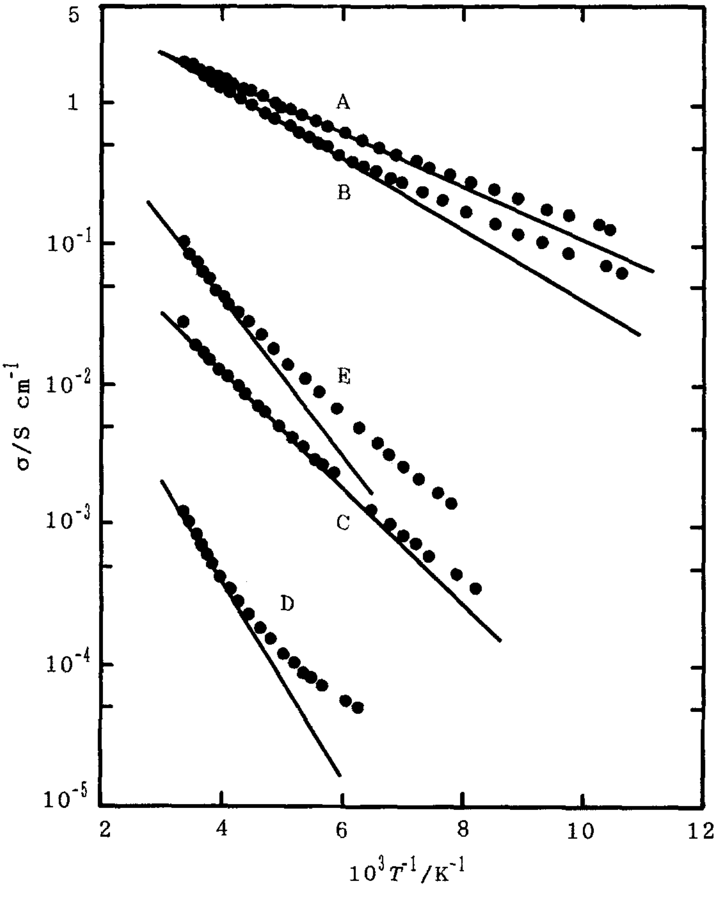

Fig. 1. Temperature dependence of electrical conductivities σ of polyaniline salts: A, perchlorate; B, chloride; C, bromide; D, iodide; E, trifluoroacetate. The straight lines show the semiconducting relations $\sigma = \sigma_\infty\exp(-E/kT)$ with the activation energies collected in Table 1.

atoms that function as dopants (or contribute to charge transport) is lower than the total Cl concentration that was determined by elemental analyses (7,8). In contrast, the XPS of the perchlorate showed a single Cl peak attributed to ClO_4^- (9). This difference between the chloride and the perchlorate is due to the difference between the nucleophilicities of the two counter anions. The substitution of Br and I in aromatic rings is expected to occur more readily than that of Cl. The quantities of Br^- and I ions that function as dopants are much less than the total halogen contents. For this reason, the low conductivities were observed for the bromide and the iodide, the total anion concentrations of which were almost identical with those of the perchlorate and the chloride. The dopant levels of the trifluoroacetate and of the acetate are almost identical with each other. Their electrical conductivities are, however, quite different. Acetato anions are hardly substituted into the aromatic rings, and hence the dopant level is expected to be identical with the anion content determined by the elemental analysis. The conductivity of the acetate was, however, as low as that of the polymer base. The acid strength of acetic acid is too weak to perform a protonation followed by the formation of polarons and/or bipolarons, in contrast to trifluoroacetic acid.

In our previous papers (6,10,11), we have reported that the ESR signal of the perchlorate is exchange-narrowed with a peak-to-peak width W of 0.3 G at room temperature, whereas the signal of the polymer base has a W of 8 G without showing an exchange narrowing. The signal intensity of the former is a factor of 100 stronger than that of the latter. When the perchlorate adsorbs oxygen, the linewidth W markedly increases up to 3 G, although the signal intensity and the g value are practically unchanged. In contrast, the ESR signal of the polymer base is not influenced by adsorption of oxygen. The ESR signal of polymer base has been explained to be due to unpaired electrons localized on defects of polymer chains, whereas the paramagnetism of the perchlorate is explained by polaron spins that are highly mobile. The mobility of the polarons is expected to be strongly influenced by oxygen adsorption. Thus, the oxygen-adsorption effects on ESR spectra are significantly different between the two electrically different polymers, and hence the observation of the oxygen-adsorption effects is useful to distinguish the paramagnetic species formed upon protonation (*i.e.*, polaron spins or defect spins). When the polymer base was treated with perchloric acid, the resulting perchlorate showed ESR properties identical with those of the as-prepared perchlorate. The chloride and the trifluoroacetate showed very narrow ESR signals, and the oxygen-adsorption effect resembled that of the perchlorate. On the other hand, the nature of ESR spectra observed for the acetate and the iodide closely resembles that of the polymer base, although the signal intensities were significantly larger than that of the polymer base. This suggests that the increase of the ESR signal upon protonation with these acids is due to the formation of additional defect spins; the number of polaron spins formed upon the treatment is very small. This is consistent with their electrical properties.

In conclusion, the selection of appropriate counter anions is important for doping polymers; a strong acid with a low nucleophilicity such as perchloric acid is appropriate for protonation of polyaniline base. The observation of the ESR spectra of the resulting polyaniline, including oxygen-adsorption effect, is useful to characterize unpaired electrons created by protonation, and is closely related to the charge-transport properties.

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References

1. Geniès E M, Boyle A, Lapkowski M, Tsintavis C (1990) Synth Met 36: 139, and references therein.
2. Proc Int Conf Sci Technol Synth Met, June 26-July 2, 1988, Santa Fe, NM, USA: Synth Met (1989) 29.
3. Proc Int Conf Sci Technol Synth Met, Sept. 2-7, 1990, Tübingen, FRG: Synth Met (1991) 41.
4. Inoue M, Navarro R E, Inoue M B (1989) Synth Met 30: 199.
5. Inoue M, Brown F, Muñoz I C, Muñoz F O (1991) Polym Bull accepted.
6. Iida M, Asaji T, Inoue M, Grijalva H, Inoue M B, Nakamura D (1991) Bull Chem Soc Jpn 64: 1509.
7. Kang E T, Neoh K G, Khor S H, Tan K L, Tan B T G (1989) J Chem Soc Chem Commun: 696.
8. Kang E T, Neoh K G, Tan T G, Khor S H, Tan K L (1990) Macromol 23: 2918.
9. Inoue M B, Nebesny K W, Fernando Q, Inoue M (1991) J Mater Chem 1: 213.
10. Inoue M, Grijalva H, Inoue M B, Iida M, Asaji T, Ikeda R, Nakamura D (1991) Synth Met 41: 679.
11. Iida M, Asaji T, Ikeda R, Inoue M B, Inoue M, Nakamura D, J Mater Chem, submitted.

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