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Automatic Doping of Polyaniline with Organic Electron Acceptors

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Complexes of polyaniline (PANI) with various organic π-electron acceptors such as benzoquinones were prepared by the automatic doping method. Relation of their electrical, electrochemical and spectroscopic properties to the strength in electron affinity of the acceptors were revealed.

Recently, doping reactions of organic π-conjugated polymers and their properties in the doped, electronically conducting state have been studied using a variety of inorganic ions as dopants. Automatic doping phenomena have been observed for PANI, when it is immersed in protonic acid(1) or nonaqueous electrolyte solutions.(2) On the other hand, only a few reports on the conducting polymers doped with organic electron acceptors are available,(3) although the charge-transfer (CT) complexation between the acceptors and aromatic molecules acting as donors has been widely known.(4) We report here automatic formation and characterization of the complexes of PANI with a series of organic electron acceptors. Optical, electrical and electrochemical properties of the complexes are discussed in terms of the strength in electron affinity of the acceptors.

We at first examined a possibility of automatic doping for some undoped π-conjugated polymers such as polypyrrole, PANI, polythiophene or poly(p-phenylene), with 7,7,8,8,-tetracyanoquinodimethane (TCNQ). Among these, polypyrrole and PANI exhibited an apparent color change immediately after immersing in a TCNQ solution in acetonitrile, indicating the automatic doping phenomena. This can be attributed to the lower ionization potentials of these two polymers than the others. We chose PANI as the polymer in this study of the automatic doping, because, compared with polypyrrole, the reduced (undoped) state of PANI is relatively stable and colorless (white), so that the complexation is visually observable. White PANI films with a perfect $\leftarrow C_6H_4\text{-}NH \rightarrow_n$ structure were obtained by electrochemical oxidation of aniline (0.5 mol dm^{-3}) in 2.75 mol dm^{-3} H_2SO_4 at a constant potential, 0.8 V vs. SCE, followed by electrochemical and chemical reduction as described before[5)] and drying at 80 °C under vacuum. These films were immersed in solutions of organic acceptors (10 mol dm^{-3}) in acetonitrile under an argon atmosphere for 1 week, immersing in pure acetonitrile for 1 day to remove excess acceptors, and drying at 80 °C under vacuum. Ten kinds of organic acceptors with redox potentials between +0.51 and -0.87 V vs. SCE, were used in this study (see Table 1, abbreviation of the acceptors are given in the table).

It was generally observed that white PANI put on a color more instantly on immersing in a solution of stronger acceptors. Figure 1 displays some examples of VIS-NIR spectra for the complexes prepared by the one-week treatment. Wavenumbers of the absorption peaks for these complexes can be roughly divided into four regions, (A) 440-450 nm, (B) 530-550 nm, (C) 625-655 nm, (D) 720-760 nm, and (E) 930-960 nm. The complexes of strong acceptors with $E^{0'} \geq -0.02$ V vs. SCE (e.g., TCNE and DDQ, see Figs. 1b and 1c) look greenish and their spectra have intense peaks due to the polaronic state in A and E regions.[2)] The complexes of medium acceptors such as BQ are bluish and give an intense peak in C region (Fig. 1d). The complexes of weak acceptors with $E^{0'} \leq -0.62$ V vs. SCE (e.g., NQ, see Fig. 1e) are palely colored and show no significant changes in their spectra from those of white PANI. Torrance et al. have reported the relationship between the CT band energy and the difference in redox potentials between donor and acceptor.[6)] This relationship, however, could not be clearly seen in the spectra described above, probably because the CT bands were hidden behind the intense absorptions of PANI.

Representative FT-IR spectra of the complexes are displayed in Fig. 2. Two characteristic bands appear at 1600 cm^{-1} and 1150 cm^{-1} depending on the strength of the acceptors. The 1600 cm^{-1} band assignable to $\nu(C{=}N)$ of $-HN^+{=}Q{=}NH^+-$ (Q: quinoid form)[7)] can be seen even for the complexes of weak acceptors, but the 1150 cm^{-1} band only for the complexes of strong acceptors. As the peak at 1150 cm^{-1} can be assigned to the electronic-like band caused by delocalization of electrons,[7)] the appearance of this band denotes an ionic nature of the complex.

Dopant concentration estimated from elemental analysis data for the complexes of DDQ, TCNE, TCNQ, and BQ is given in Table 1. The concentration is not straightforwardly related to the electron affinity of the acceptors; concentration of TCNQ doped in PANI is lower than that of a weaker acceptor, BQ. This result suggests that not only the electron affinity but

Table 1. Properties of PANI-organic acceptor complexes

Acceptor a)	$E^{0'}$(acceptor) / V vs. SCE	E_{RP} / V vs. Li/Li$^+$	Conductivity / S cm^{-1}	Acceptor content / wt%
DDQ	0.51	3.40	4.6×10^{-5}	14.3 (0.067) b)
TCNE	0.21	3.20	2.5×10^{-5}	10.2 (0.073)
TCNQ	0.17	3.20	5.6×10^{-4}	1.3 (0.0065)
Bromanil	-0.01	3.23	1.7×10^{-7}	—
Chloranil	-0.02	3.22	2.3×10^{-8}	—
DCBQ	-0.21	3.26	8.8×10^{-7}	—
BQ	-0.54	3.17	2.0×10^{-9}	2.9 (0.025)
TolBQ	-0.62	3.10	2.0×10^{-9}	—
NQ	-0.71	2.95	6.2×10^{-9}	—
TMeBQ	-0.87	3.03	2.1×10^{-9}	—

a) DDQ: 2,3-dichloro-5,6-dicyano-p-benzoquinone, TCNE: tetracyanoethylene, DCBQ: 2,6-dichloro-p-benzoquinone, BQ: p-benzoquinone, TolBQ: p-toluquinone, NQ: α-naphthoquinone: TMeBQ: tetramethyl-p-benzoquinone.

b) The mole ratio of acceptor/-C_6H_4NH- is given in the parenthesis.

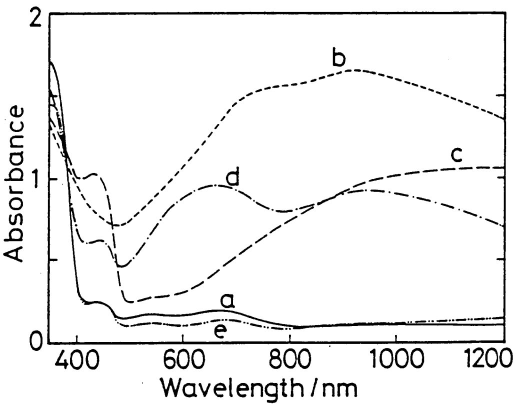

Fig. 1. Electronic spectra of PANI's undoped (a) and doped with DDQ (b), TCNQ (c), BQ (d) and NQ (e).

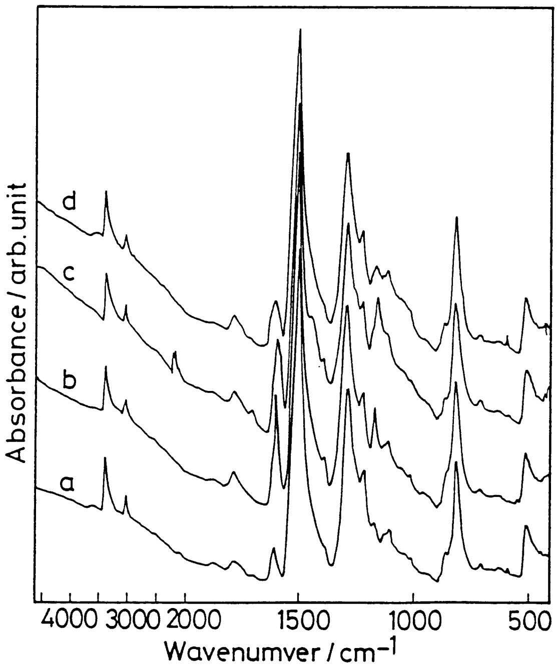

Fig. 2. Infrared spectra of PANI's undoped (a) and doped with BQ (b), TCNQ (c) and DDQ (d).

also the size of acceptors may affect the dopant concentrations.

Rest potentials of the complexes measured in 0.1 mol dm^{-3} Et_4NClO_4 / propylene carbonate + 1,2-dimethoxyethane, E_{RP}'s, are also listed in Table 1. E_{RP} of neutral PANI is 2.66 V vs. Li/Li$^+$ and shifts in the positive direction by doping of the acceptors. Roughly speaking, the E_{RP} value depends on the electron affinity of the acceptors. It is most positive (3.40 V vs. Li/Li$^+$) for the DDQ-doped PANI, almost constant (3.20 - 3.26 V) for PANI's doped with medium acceptors with $-0.21 \text{ V} \leq E^{0'} \leq +0.21$ V vs. SCE, and less positive (2.95-3.17 V) for PANI's with weaker acceptors.

Conductivity of PANI, which is less than 10^{-9} S cm^{-1} in the neutral form, increases up to 6×10^{-4} S cm^{-1} by acceptor doping as shown in Table 1. Although it is unavailing to compare quantitatively the conductivity values with electron affinity of the acceptors because of inconsistency in dopant concentration among the samples as described above, the table shows a tendency that stronger acceptors give higher conductivity. The result that the conductivity of PANI doped with 1.2 wt% TCNQ is markedly higher than that of PANI doped with 2.9 wt% BQ denotes the major contribution of electron affinity of the acceptor to the conductivity change.

The trends seen in the data of VIS-NIR and IR spectra, E_{RP} and conductivity with the strength in electron affinity of the acceptors can lead to a conclusion that the spontaneous reaction of PANI with organic acceptors are the donor-acceptor CT complexation, although CT bands have not been found clearly. The complexes of stronger acceptors have larger ionic-bond characteristics, resulting in a more effective formation of the polaronic state and higher conductivity.

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