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# MOLECULAR AND ELECTRONIC STRUCTURES OF DOPED POLYANILINE

J. TANAKA and N. MASHITA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, Japan

K. MIZOGUCHI AND K. KUME

Department of Physics, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo, Japan

## ABSTRRACT

The molecular and electronic structures of polyaniline are studied by measuring the reflection spectra in the infrared to visible regions, the Raman spectra and the magnetic susceptibility. The structure of the polymer changes during the discharge process and the molecular structure model at several oxidation stage is presented , which is composed of p-benzoquinonediimine and phenyl or anilino rings.

## INTRODUCTION

Polyaniline has attracted a lot of attention because of its high electrical conductivity , stability and electrochemical utility. The aqueous electrochemistry of polyaniline has been studied from various aspects, however, a relatively few studies have been appeared which concerned with the structural changes occurring in the redox process. MacDiarmid and his coworkers [1] proposed several model structures for the reduced and oxidized forms of polyaniline and its protonated forms but accurate molecular structures for each redox state are not clarified as yet. We have studied the structure of polyaniline polymerized on electrode in aqueous solution by the reflection spectra in the infrared and visible regions and Raman spectra. The magnetic susceptibility is also measured for wide temperature range and it indicates a

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term of Pauli paramagnetism, which is in accord with the result of Epstein et al.[2] The molecular structure of the polymer changes during the discharge process; this conformational change is found by Raman spectra as well as by infrared spectra. The model structures of polyaniline at several oxidation levels are proposed which are composed of a chain of p-benzoquinonediimine and phenyl rings. A theoretical consideration on the electronic structure of the metallic state will be presented based on this molecular structure.

## EXPERIMENTAL

Polyaniline was prepared by electrochemical synthesis [3] on a glassy carbon electrode from 0.67 M aniline in aqueous $HBF_4$ solution (13%). It shows dark green color. The synthesized material on the electrode was washed with water for 10 to 24 hours. The reaction proceeds with dedoping of $BF_4^-$ ion. The level of doping was monitored by analyzing the $BF_4^-$ ion by a colorimetry using methylene blue as colouring reagent.[4]

## RESULTS and DISCUSSIONS

The freshly prepared material contains $(C_6H_5N)_2^+BF_4^-$ unit which is so-called emeraldine salt with 50% dopant. The pressed pellet of fresh material shows electrical conductivity of 36 S/cm. The electrical conductivity decreases by washing with water to 3.7 S/cm at 24% doping level and 0.15 $S/cm^{-1}$ at 15%. The change from a metallic state to insulator occurs by reducing the oxidized film just by washing with water on the electrode.

In order to find the structural change occurring in the redox reaction, the reflection spectra at several dopant concentration are measured as shown in Fig.1. The film with the highest doping level in aqueous solution (50%) exhibits a high reflectance in the far-infrared region showing formation of free carrier. By decreasing the dopant content, the reflectance in the far infrared region is diminished. The reflection spectra becomes a typical of semiconductor or insulator below 25% doping level. The absorption spectra calculated by a Kramers-Kronig transformation of reflectance are shown in Fig.2.

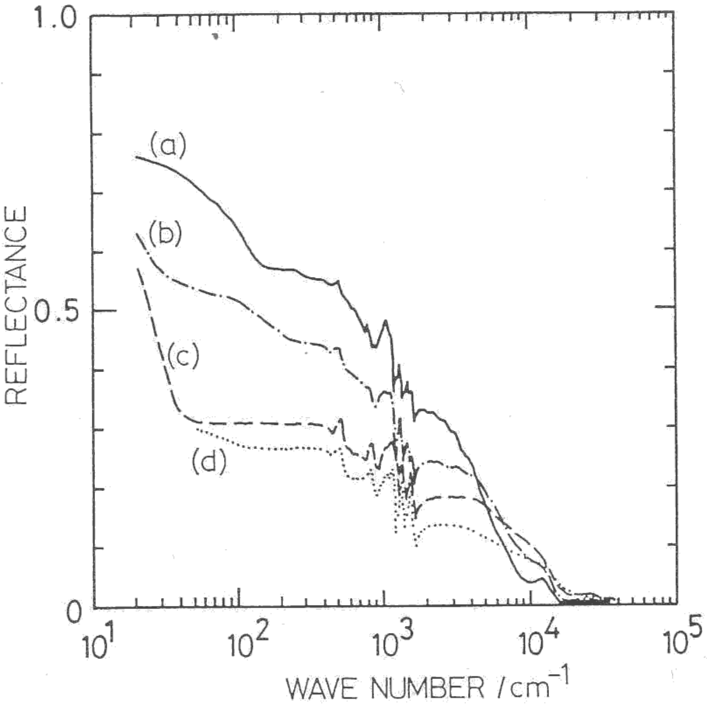

Fig.1 Reflection Spectra of the Pressed Pellets of Doped Polyaniline

(a) 54% doping (36 S/cm) (b) 24% (3.7 S/cm) (c) 17% (0.7 S/cm)

(d) 15% (0.1 S/cm)

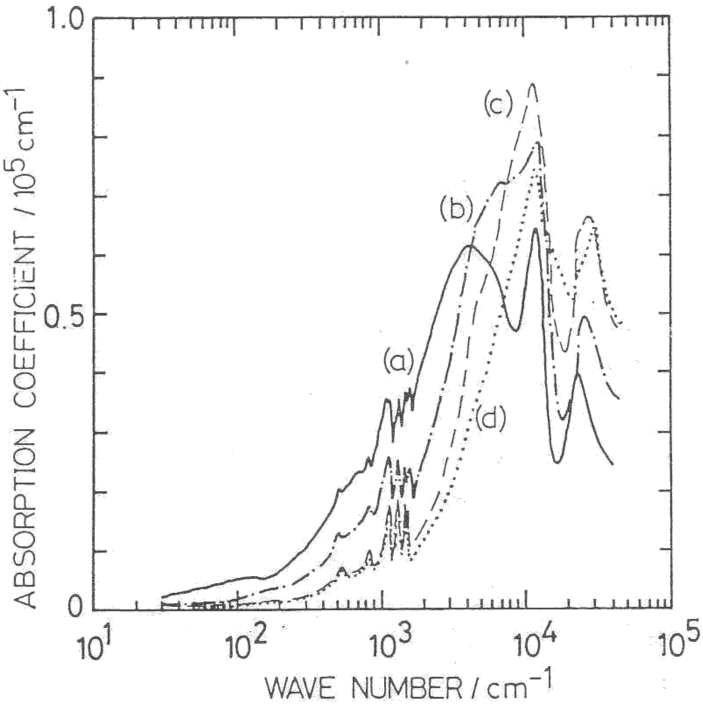

Fig.2 Absorption Spectra Obtained by Kramers-Kronig Transformation

(a) 54% doping (36 S/cm) (b) 24% (3.7 S/cm) (c) 17% (0.7 S/cm)

(d) 15% (0.1 S/cm)

The free carrier absorption appears only for 50 - 25% doped film at 10 - 5000 $cm^{-1}$ region with a broad shape. The absorption spectra at 400 - 30000 $cm^{-1}$ show several peaks which are characteristic of the chromophores of anilino and the p-benzoquinonediimine cation radical and the interaction between them. The absorpiton peaks in the visisble and near infrared region are in good agreement with the absorption spectra directly measured with as grown thin film polymerized on Nesa glass; the peaks are found at 12000 and 25000 $cm^{-1}$. The MO calculation by the Pariser-Parr- Pople method is performed on the model unit shown in Fig.3 to find assignments of these excitations. From the calculated excitation energies and transition moments (Fig.4), the band at 10000 $cm^{-1}$ can be assigned to the intramolecular charge transfer from the anilino group to the benzoquinone-diimine group and the band at 25000 $cm^{-1}$ is due to the long axis polarized transition of the anilino group. Another broad peak is found at 5000 $cm^{-1}$ region only for the heaily doped film; this band may be explained by the exciton type splitting of the charge transfer transition occurring in the anilino group inserted between the two benzoquinonediimine cation groups (Fig.4). The phenylene-p-benzoquinonediimine radical is a unit of a polaron lattice which shows a metallic property as will be discussed later.

Several vibrational peaks are found at 490, 800,1130-1200, 1300, 1520 and 1610 $cm^{-1}$ which are in agreement with the infrared absorption spectra measured by a transmission method. The 1520 $cm^{-1}$ band shifts to higher frequency with decreasing the dopant concentration which has been assigned to the CH bending/CN stretching coupled mode of the p-benzoquinonediimine and anilino groups.[5]

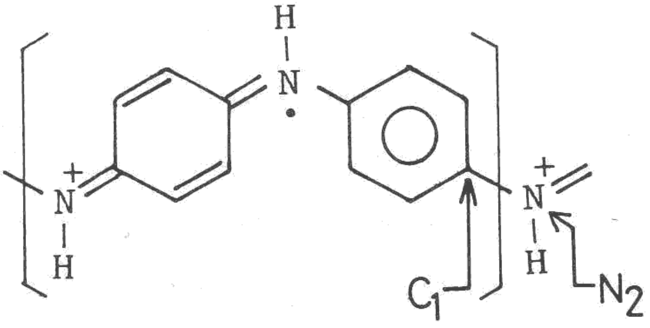

Fig.3 A Model Unit of 50% Doped Polyaniline

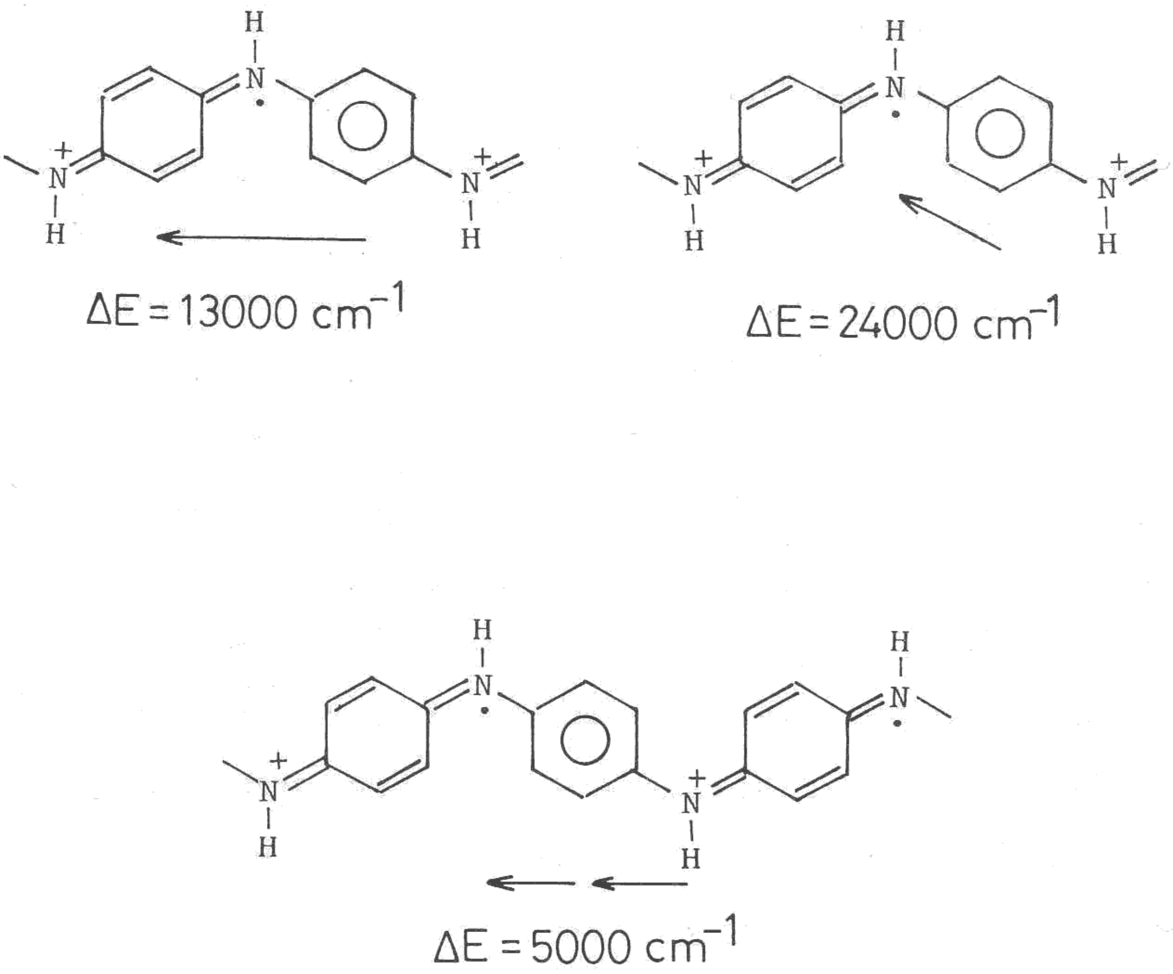

Fig.4 Transition Moments to the Electronic Excited States

Raman spectra (Fig.5) of films of various doping levels show several peaks and the assignments for these bands are given by Furukawa et al.[6] We found a drastic change of the Raman spectra accompanying with dedoping. The Raman bands of 50 % doped film show prominent peaks characteristic of benzenoid (1670 cm$^{-1}$) and quinoidal (1490 and 1340 cm$^{-1}$ ) forms, while that of 34% doping level exhibit only the band of the benzenoid form. The film with 24% doping gives both quinoidal and benzenoid forms. An appearance of Pauli paramagnetism was reported by Epstein et al.[2] above 33 % doping level, accordingly, the unpaired electron might be formed in the structure above this doping level. However, at 33% doping level, the polyaniline chain includes only the benzenoid structure, namely no p-benzoquinonediimine ring. Based on this result the structural changes associated with dedoping of polyaniline film are considered as shown in Fig.6. The first form has a metallic character and the third form is insulator and they may correspond to the oxidation stages found in cyclic voltametry[1] in aqueous solution around the first peak at 0.4 to 0.0 V to S.C.E., respectively. The change of the weight of polyaniline film during the discharge has been studied by Okabayashi et al.[7] which is consistent with the scheme of Fig.6 . Sasaki et al.[8] and Glarum et al.[9] reported the spin concentration measured by ESR was increased at 0.1 V to S.C.E., which is in accordance with the result of electrochemical potential spectroscopy [10] and the present Raman spectra.

## CONDITION of METALLIC STATE

Basic structural requirement for an appearance of metallic state of the polymer is that the chain contains a repetition unit with a mobile carrier. Another important condition for the metal is the presence of effective elecron transfer (exchange) interaction between these unit groups. A metallic condition is satisfied in the 50% doped polyaniline by the electron delocalization along the $>C=N^+H-C<$ bonds. The interaction between these unit is guaranteed by the coplanar structure of the two rings, and is found in the optical spectra as an inter-ring charge transfer band. Epstein and his coworkers [11] presented a model of polaron which is composed of emeraldine salt with one unpaired

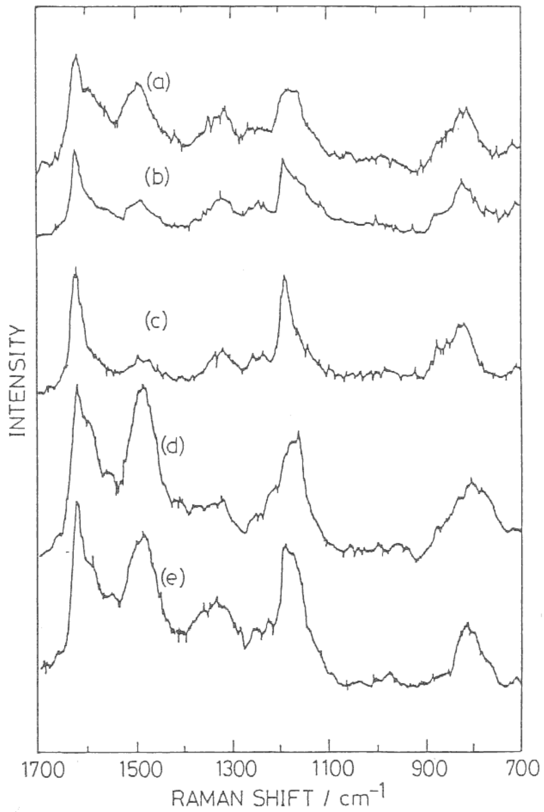

Fig.5 Raman Spectra of Doped Polyaniline (a) 50% (b) 43% (c) 34% (d) 24% (e) 20% doping

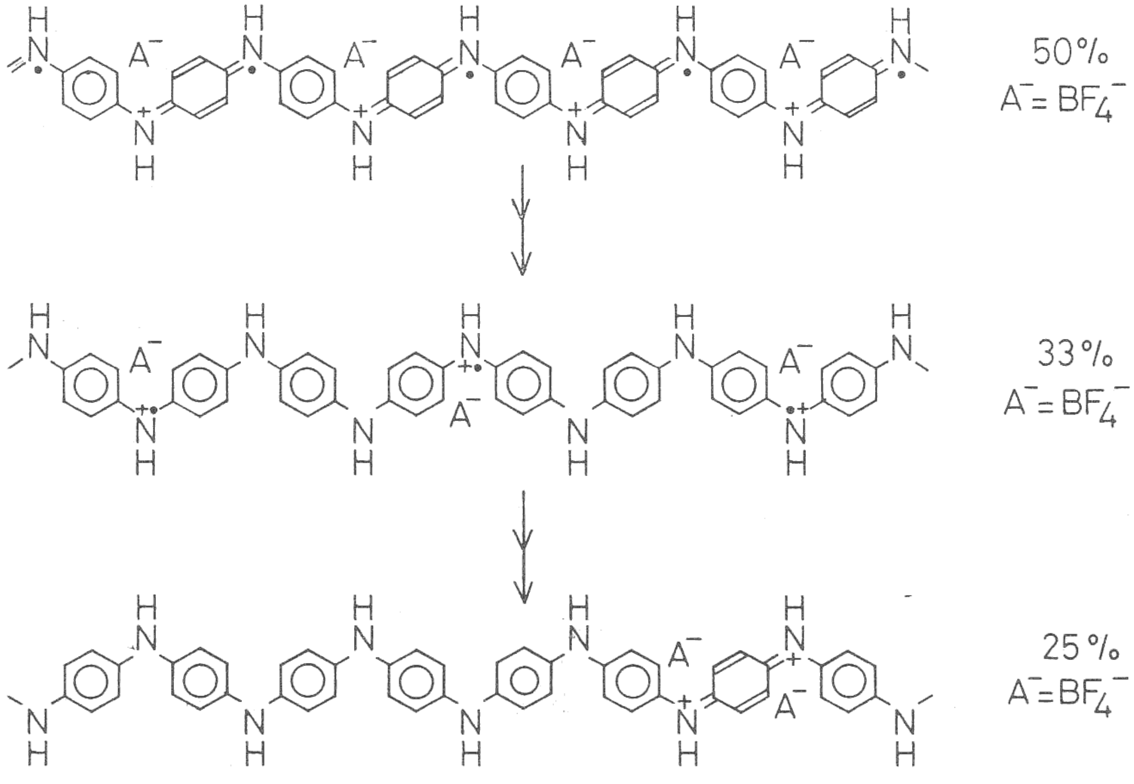

Fig.6 A Scheme of Structural Change Associated with Dedoping of Polyaniline

electron for the two anilino groups. Furukawa et al.[6] showed by the resonance Raman spectra that the emeraldine salt is composed of chromophores of different skeletal conformations. Moreover our Raman data and the magnetic susceptibility of Epstein et al. showed that the radical chain composed of only the anilino rings actually exists for 33 % doping level. However, both the p-benzoquinone-diimime and the phenyl rings are included at 50% doping level. Accordingly, the metallic property is ascribed to the chain consisting of p-phenylene-p-benzoquinonediimine unit(50%) and that of three anilino groups(33%) as shown in Fig.6. Both repeating units have one unpaired electron for each unit.

The electron transfer interaction along these chain is represented by the tranfer integral of the HOMO in the position connecting these units; that is given by the atomic orbital coeffcients in the HOMO of model unit (Fig.3), $c(C_1) \times c(N_2)$ times $\beta(C-N)$, the resonance integral between these atomic orbitals. The temperature dependence of magnetic susceptibility of 54% doped film is illustrated in Fig.7, where the Curie and Pauli terms are separated on the basis of their temperature dependences. The temperature independent Pauli term is $\chi(\mathrm{Pauli}) = 7.0 \times 10^{-5}$ e.m.u./two anilino group, which is in good agreement with the result of Epstein et al.[2] The density of states near $E_F$ is estimated from this value at 2.1/ unit.eV. By using the one-dimensional tight binding model, it is given by $D(E_F) = 1/\pi ta$, where a is a periodic lattice length, t is a transfer integral. We found t = 0.15 eV by using the experimental value. The transfer integral can be estimated by $t = c(C_1)c(N_2)\beta$ and it is -0.13 eV in agreement with experiment by assuming the resonance integral $\beta(C-N) = -1.4$ eV. Following this estimate the band width will be as narrow as 4t = 0.6 eV.

Zuo et al.[11] and Park et al.[10] discussed the sign of thermoelectric power of 50% doped polyaniline to be n-type. It can be explained on this polaron model that the carrier is the electron thermally activated over $E_F$ at the nearly half-filled one dimensional band. For the less doped film the conduction

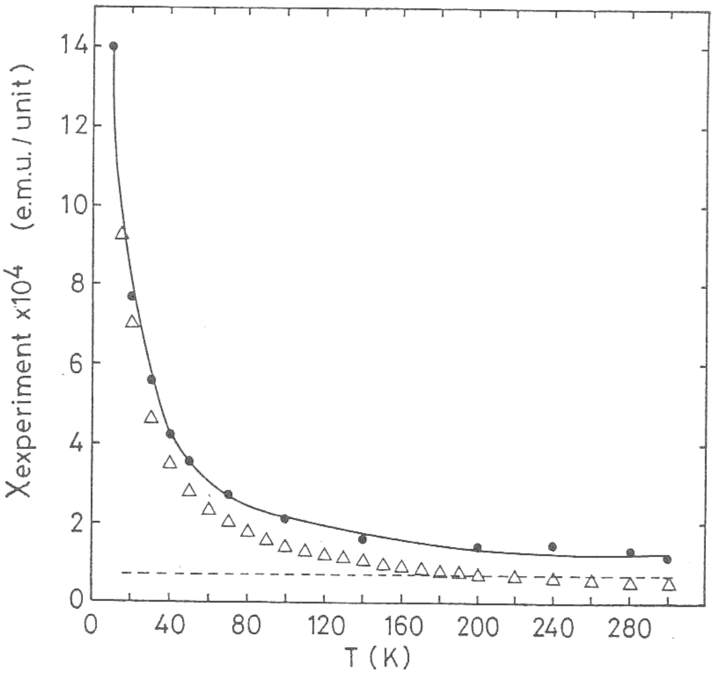

Fig.7 Temperature Dependence of Magnetic Susceptibility.

(—●—●—●—) Observed Values, ( △ △ △ ) Curie term, (------) Pauli term.

mechanism may be quite different because the polaron is absent and a crossover of thermoelectric power to p-type or semiconductor type must be explained by other mechanism.

The finding of the free carrier reflectance in the far infrared region and the presence of Pauli paramagnetism, and linearly temperature dependent Seebeck coefficient may be sufficient evidences for the metallic state of the polyaniline. Moreover, the temperature dependence of the electrical conductivity [11] may be reasonably explained by the one-dimensional hopping model, which may be a typical conduction mechanism in conducting polymer.

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