

Mechanism of Proton Doping in Polyaniline

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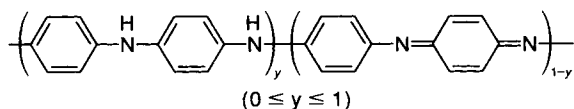
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SYNOPSIS

The protonation processes of polyaniline (PANI) were examined by means of both UV-visible and fluorescence spectra and *in situ* UV-visible and *in situ* electron spin resonance (ESR) spectra in order to understand the mechanism of proton doping in PANI. Results obtained from UV-visible and fluorescence spectra of PANI films indicate that the protonation processes take place on the imine segment of the polyemeraldine chain consistent with MacDiarmid's suggestions. It is noted that the protonation processes consist of chemical and diffusion processes. The doping processes at the initial stage are controlled by a chemical reaction, whereas the doping processes at the middle period are dominated by a diffusion process. *In situ* ESR spectra of PANI films have demonstrated that a polaron is formed after protonation processes, but a splitting process of bipolaron into polaron at the measured time region was not observed. For partial protonated PANI, moreover, the fact that variation of absorption value of the peak at 630 nm with doping time supported suggestions in which a parameter of the protonation state for the molecular structure of doped PANI should be considered. © 1995 John Wiley & Sons, Inc.

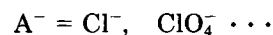
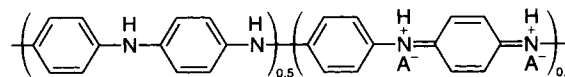
INTRODUCTION

Polyaniline (PANI) has attracted considerable attention because of its various structures, special doping mechanism, excellent environmental stability, and possible technical applications as electronic materials. Huang et al.¹ first proposed that the molecular structure of the base form of PANI has the general formula shown as



Hagiwara et al.² confirmed by the analysis of the ¹³C-NMR spectra that the chemical structure of the base form of PANI was found to be consistent with that proposed by Huang.¹ It has been demonstrated that the base form of PANI can be converted to its salt form by proton doping, in which the electron number on the polymer chain does not change after protonation. It seems that proton doping can take

place on the amine and the imine segment of the polyemeraldine chain. But, Huang et al.¹ first proposed that protonic doping only takes place on the imine segment of the polyemeraldine chain to form a bipolaron shown as



However, this is inconsistent with band structure calculated by Stafström et al.³ that rules out the presence of a bipolaron lattice in the emeraldine salt form, and is also inconsistent with magnetic properties.⁴ In order to explain the results of magnetic measurements, Epstein et al.^{4,5} and Wnek⁶ suggested that the transition from spinless bipolaron to a polaron metal has two steps. The first step is related to the instability of a bipolaron on a polyemeraldine chain with respect to the formation of two polarons. After that, MacDiarmid et al.⁷ proposed that the polaron is of semiquinone form. However, recently Jozefowicz et al.⁸ suggested that the polaron or semiquinone form is primarily resident in the ordered crystalline regions of the emeraldine salt,

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whereas the bipolaron form is primarily in the amorphous regions of the emeraldine salt. Moreover, Ray et al.⁹ recently reported that the protonation processes can take place on the amine segment of the polyemeraldine chain to form a $-\text{NH}_2^+$ group before protonation on the imine segment of the polyemeraldine chain. The protonation extent on the amine segment of the polyemeraldine chain depends on the acidity of solution. Therefore, extensive studies on the mechanism of proton doping in PANI are necessary.

In this study the protonation processes were examined by means of UV-visible spectra, fluorescence spectra, *in situ* UV-visible, and *in situ* electron spin resonance (ESR) spectra in order to understand the mechanism of proton doping in PANI.

EXPERIMENTAL

The emeraldine base form powder was synthesized chemically as reported by MacDiarmid et al.¹⁰ The free standing film of the base form and salt form of PANI were synthesized by methods reported previously.^{11,12} For UV-visible examination the thin film of the base form of PANI on a slide glass was made by a spinning coater at high temperature (60°C). The thickness of the film was about 50–100 nm. In order to obtain the film of the emeraldine salt form of PANI with a different protonation state the film of the emeraldine base form of PANI was dipped into a solution of HCl with varying acidity for about 30 s. It was then dried by a spin coater with a spin speed of 1670 irp/s at 60°C for about 1 min. The absorption spectra of the PANI film on the slide glass at wavelengths of 200–2000 nm were measured by a VU-3100 spectrophotometer. The sample of the base form of PANI for the fluorescence measurement is the same as the sample used for UV-visible spectra examination, but its salt form was proton-

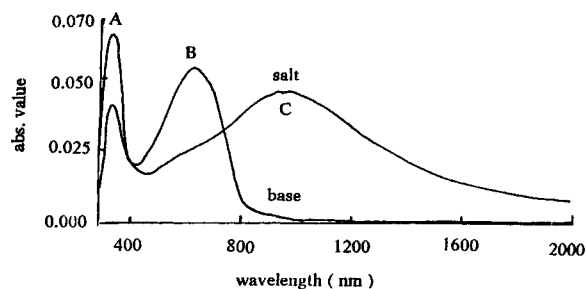


Figure 1 UV-visible absorption spectra of the emeraldine base and salt form of PANI films.

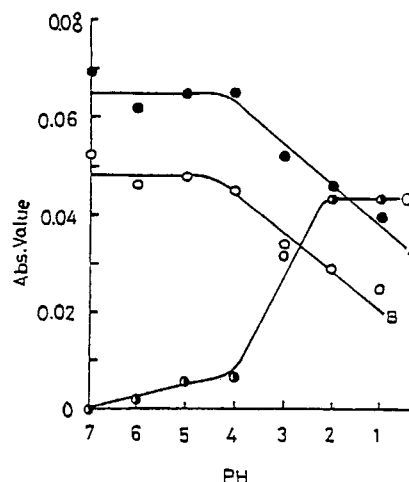


Figure 2 Variation of absorbance value of the peak at 325, 630, and 950 nm with the protonation state of PANI: (A) 325 nm; (B) 630 nm; and (C) 930 nm.

ated by HCl gas evaporated from concentrated HCl. The fluorescence spectra were performed by an MPF-4 fluorescence spectrometer (Hitachi). The *in situ* UV-visible spectra of the PANI film ($\sim 1 \mu\text{m}$ thick) with doping time at 400–900 nm was carried out by a Nanospecico spectrometer. For *in situ* ESR, spectra of PANI films were measured by an ER200D-SRC (Bruker).

RESULTS AND DISCUSSION

UV-Visible and Fluorescence Spectra

A typical UV-visible spectra of the emeraldine base and salt form of PANI films are shown in Figure 1. For the emeraldine base form of PANI, UV-visible spectra show two peaks at 325 and 630 nm, which are due to the excitation of the amine and imine segment on the polyemeraldine chain, respectively.^{3,13,14} These results indicate that the molecular structure for the emeraldine base form of PANI consists of an amine and imine segment on the polyemeraldine chain consistent with Huang's¹ suggestion on the molecular structure for the base form of PANI. For fully protonated PANI, the salt form, the peak at 630 nm disappeared except for an absorption at 325 nm, whereas a new peak at 950 nm occurred. Moreover, the position of the peak at 325 nm does not change with its protonation state although the absorption value of this peak decreases with its protonation state as shown in Figure 2 (A). These indicate that the protonation processes only take place on the imine segment of the polymer-

aldine chain, which is also consistent with Huang's suggestion.¹ The absorption value of the peak at 950 nm increases with an increase of the protonation state as shown in Figure 2(C). The new peak at 950 nm due to the polaron has been demonstrated.³⁻⁷ For partially protonated PANI (for example, pH = 6.2), the peak at 630 nm was also observed that indicates that the quinoid segment on the polyemeraldine chain is present in partially protonated PANI. However, its absorbance value decreases with an increased protonation state as shown in Figure 2(B). This again indicates that the protonation processes take place on the imine segment of the polyemeraldine chain. Moreover, this result suggests that a parameter of the protonation state, X , for molecular structure of doped PANI should be considered.¹¹

A typical fluorescence excitation and emission spectra of PANI film are shown in Figure 3. It is interesting to find that a peak at 380 nm in the excitation spectra of the emeraldine base form of PANI films was observed when an excited wavelength of 320 nm was used [see Fig. 3(a)]. Moreover, a peak at 320 nm in the emission spectra of the emeraldine base form of PANI film was observed when an emission wavelength of 380 nm was used (Fig. 3(b)). In fact, the excited wavelength used in the fluorescence spectra is shown in the $\pi - \pi^*$ transition observed in UV-visible spectra of PANI. Therefore, it is reasonable to believe that the peak at 380 nm in the excitation spectra corresponds to a transition of the excited electron at the π^* state backing to ground. For the emeraldine salt form of PANI, the excitation

and the emission spectra measured at the same conditions were the same as that of the emeraldine base form of PANI as shown in Figure 3. This result indicates that the protonation processes only take place on the imine segment of the polyemeraldine chain because the fluorescence spectra of the emeraldine salt form of PANI would be quite different from that of its base form if the protonation processes occurred on both the amine and imine segment of the polyemeraldine chain.

In Situ UV-Visible Spectra

It is found that the UV-visible spectra of PANI films for a given protonation state depend on the doping time. A typical variation of the absorption value of both peaks at 645 and 875 nm with doping time is shown in Figure 4. It shows that the absorption value of the peak at 645 nm decreases quickly with an increased doping time at the initial doping period, followed by a slow decrease. Finally it was independent of doping time after a critical doping time, which is called the balance state [Fig. 4(1a)]. If the doping level was increased, for example, if a pH of 1.89 was used, the same behavior was observed as shown in [Fig. 4(1b)]. On the other hand, a contrast phenomenon for the peak at 875 nm was observed as shown in Figure 4(2a) and 4(2b), respectively. These results suggest that the protonation processes of PANI film are controlled by the chemical reaction and diffusion processes. The chemical reaction means that the proton in the aqueous acidic solution

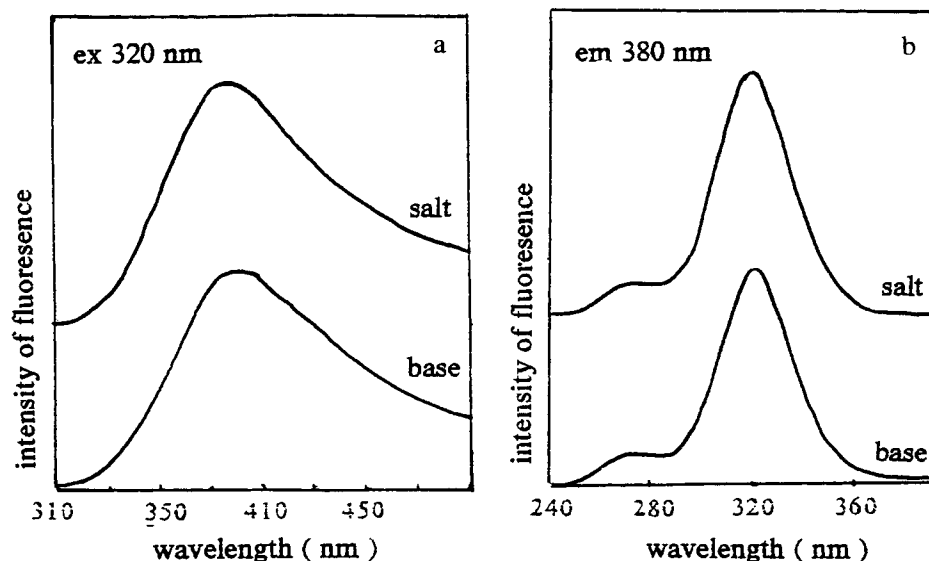


Figure 3 Fluorescence spectra of thin film of PANI: (a) excitation spectra and (b) emission spectra.

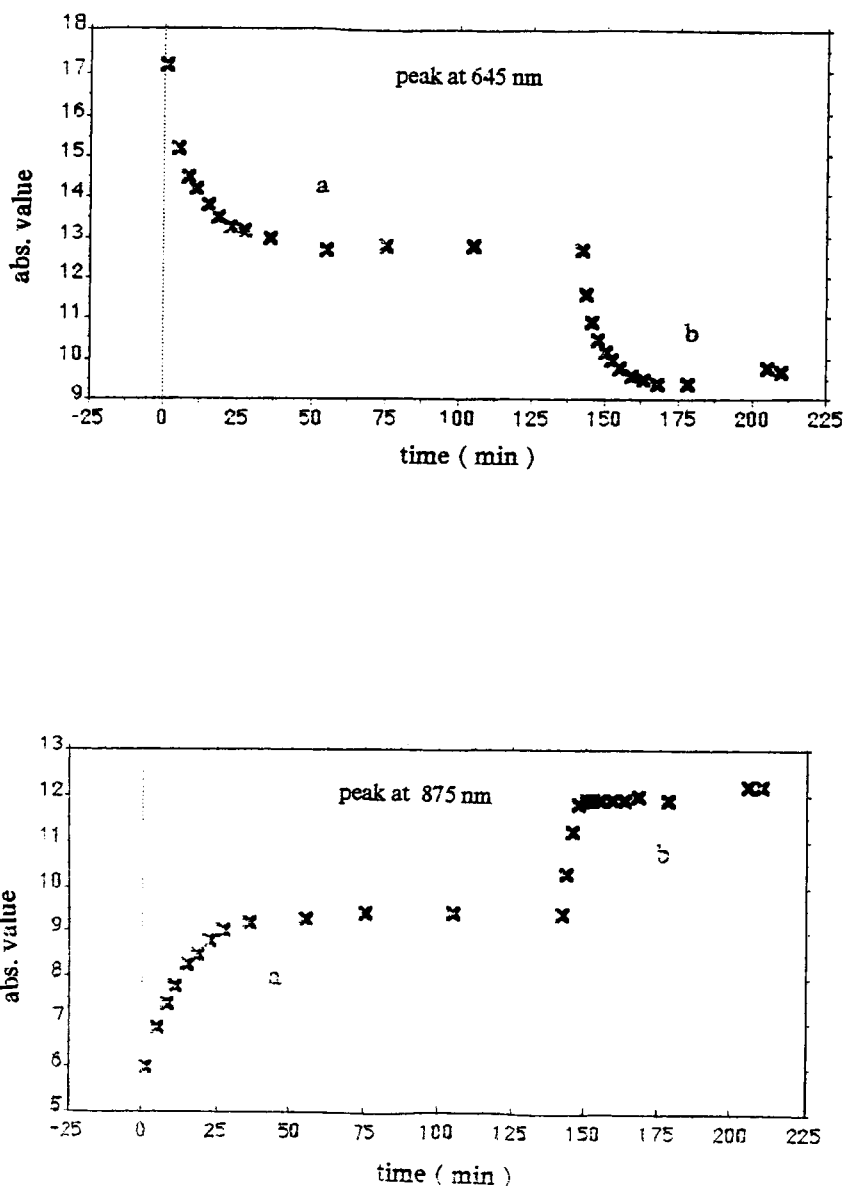


Figure 4 Variation of the absorption value of both peaks at 645 and 875 nm with doping time: (a) pH = 2.9 and (b) pH = 1.89.

react with the nitrogen atom on the imine segment of the polyemeraldine chain to form a semiquinone, that is a polaron; whereas, the diffusion processes correspond to diffusion of the proton (H^+) and counterion (for example, Cl^-) from an aqueous acidic solution into the film. The absorption value of the materials should obey the Lambert-Beer law as follows

$$A = \epsilon l C$$

where A is the absorption value of materials, ϵ is the molar absorption coefficient, l is the length of the

optical route, and C is the concentration of materials. It is expected that the relative quantity of materials for given thickness samples is determined by means of the absorption value of materials if no change in the molar absorption coefficient is assumed. Therefore, it is reasonable to show that the relative quantity of materials is controlled by its absorption value of materials. A typical variation of the absorption value of the peak at 645 and 875 nm with $t^{1/2}$ is shown in Figure 5. It is interesting to find that the absorbance value for both peaks at 645 and 875 nm only at the middle doping period is proportional to $t^{1/2}$, which suggests that the protonation processes

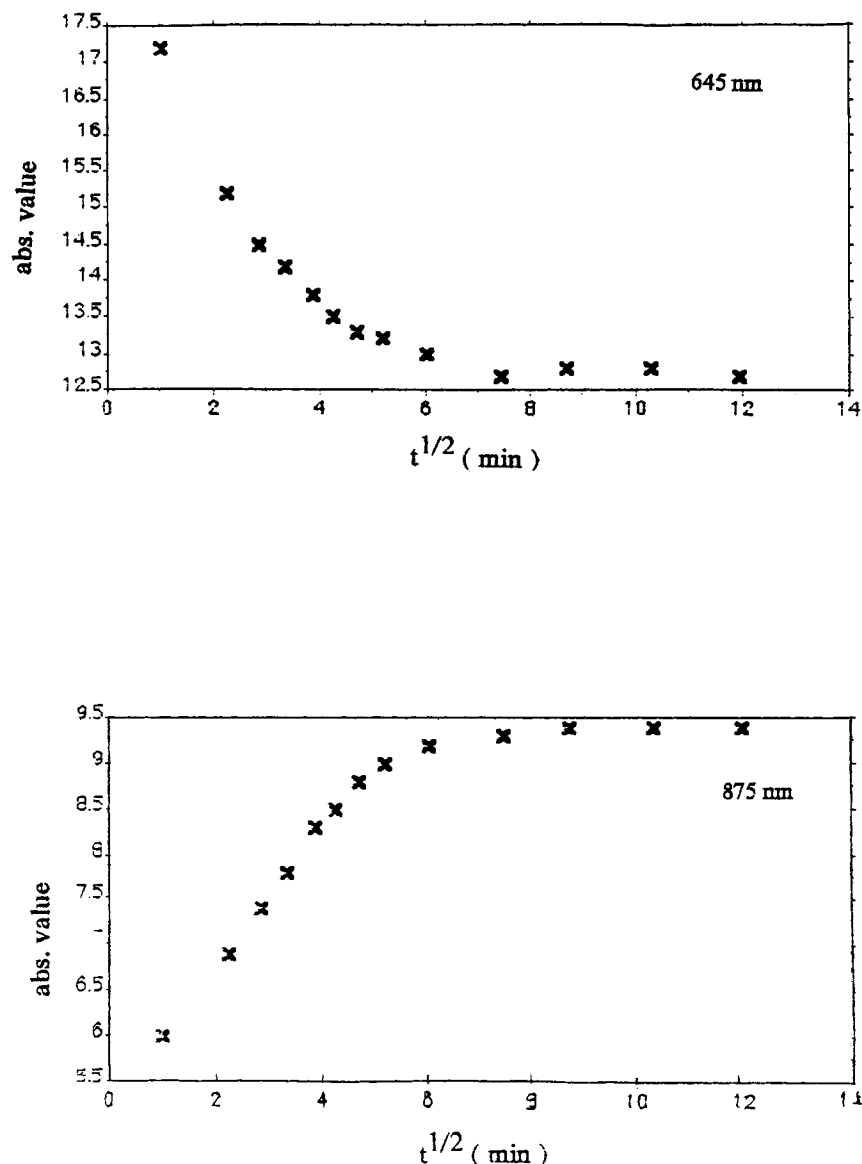


Figure 5 Variation of the absorbance value of the peak at 645 and 875 nm with $t^{1/2}$.

at the middle doping period are mainly controlled by diffusion processes. In addition, the velocity of the chemical reaction is faster than that of diffusion processes. Thus, it is reasonable to believe that the doping processes at the initial stage are dominated by a chemical reaction, whereas the doping processes at the middle doping period are controlled by diffusion processes. Further, the absorbance value for the peak at 645 and 875 nm is independent of the doping time when doping time is over the critical doping time (Fig. 4). This indicates that a balance state was achieved, which means the number of the protons in solution coming into film is equal to the

number of doped protons that get out of the film into solution. For partially protonated PANI film, the peak at 630 nm also could be observed, which is consistent with observations obtained by Wan.¹¹ This supported Wan's suggestion in which a parameter of the protonation state (X) for the molecular structure of doped PANI should be considered.¹¹

In Situ ESR Spectra

As discussed above, the protonation processes take place on the imine segment of the polyemeraldine chain. It is expected that either bipolarons

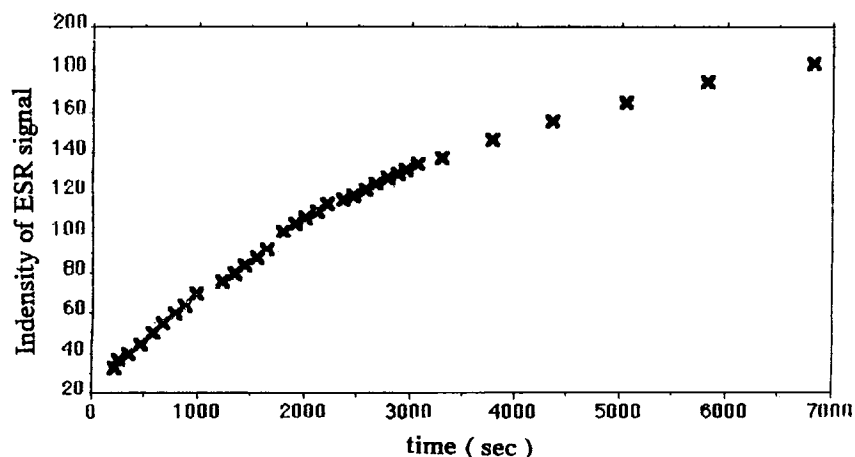
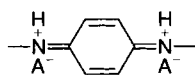
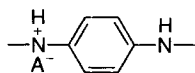


Figure 6 Relationship between the intensity of ESR signal and doping time.



or polarons



could occur. ESR is a good tool to distinguish between a polaron and bipolaron because the bipolaron being spinless. In order to explain the observed magnetic properties of PANI, researchers⁴⁻⁶ have suggested that spinless bipolarons could transfer into two polarons. Thus, it is expected that *in situ* ESR of PANI can give more information. A curve of the intensity of the ESR signal plotted to doping time is shown in Figure 6. As is known, the concentration of free radicals is proportional to the product of the square of the peak width and intensity of the ESR signal. In our experiments, the concentration of free radicals can be considered as the intensity of the ESR signal because the peak width remained unchanged with doping time. In Figure 6 an ESR signal at the beginning of the doping period (second scale) can be observed. The concentration of free radicals increases with an increase of doping time, which indicates that a polaron at the initial doping region was formed. If a bipolaron is formed at first, no ESR signal can be observed at the beginning of the doping period. Thus, this experiment indicates that a splitting process of a bipolaron into a polaron at a measured time period was not observed.

CONCLUSIONS

In summary, the protonation processes only take place on the imine segment of the polyemeraldine

chain. The protonation processes of PANI films consist of chemical reaction and diffusion processes. The chemical reaction processes mean that protons (H^+) in aqueous acidic solution react with the nitrogen atom on the imine segment of the polyemeraldine chain, and the protonation processes at initial stages are controlled by this chemical reaction. The diffusion processes mean that protons (H^+) and counterions (for example Cl^-) in aqueous acidic solution diffuse into a film of PANI, and a polaron is formed after the protonation processes. However, a splitting process of bipolaron into polaron proposed⁴⁻⁶ at observed time regions in this study was not observed. Moreover, the fact that variation of absorption spectra with doping time for partially protonated PANI support the suggestion proposed by Wan¹¹ in which the parameter of the protonation state (X) for the molecular structure of doped PANI should be considered.

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