

method⁸⁻¹⁰ using EPN, DMPN, PNA and PNP.

$$\nu = \nu_0 + s\pi^* + a\alpha + b\beta \quad (10)$$

Kinetic procedures⁷. Rates of solvolysis for tert-butyl halides in these systems were measured at 35, 45 and 55 °C by conductivity method, and rate constants k_1^{obs} were determined by the Guggenheim equation.¹¹ Activation parameters were calculated as described in the previous report.¹²

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Electrochemical and Spectrophotometric Studies on Polyaniline and its Degradation

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A spectroelectrochemical study on the redox chemistry of polyaniline (PANI) was carried out by using indium-thin oxide (ITO) transparent electrode in aqueous acidic solutions. Three different PANI-derived species were observed depending on the potential. The most highly oxidized species having alternating benzenoid-quinoid structures degraded through hydrolysis reaction. The degradation products were confirmed to be *p*-benzoquinone (BQ) and *p*-diaminobenzene (PDAB) by spectrophotometry and potentiostatic experiments. Finally, a degradation mechanism is deduced from the observed behaviour.

Introduction

Recently interests in polyaniline (PANI) as a conducting polymer have been increasing rapidly.¹⁻¹² Possible applications of PANI include use in electrochromic² and microelectronic devices,³ in stabilizing photoelectrodes and protecting metals,⁴⁻⁶ in ion exchange⁷, and in organic batteries.^{8,9} However, there are few reports concerning the spectroscopic properties and the electrochemical degradation of PANI-film.¹⁰⁻¹²

Kobayashi *et al.*¹⁰ reported that *p*-benzoquinone (BQ) is a degradation product on the basis of spectral data taken through PANI-film. They also suggested that two redox reactions were involved in the electrochromic reaction of

PANI.¹⁰ Stilwell and Park¹¹ proposed a degradation scheme, based on their coulometric and spectrophotometric experiments. They suggested that the degradation process proceeds via hydrolysis of the oxidized species of PANI, pernigraniline, resulting in the production of *p*-benzoquinone. In another report¹² they assigned the spectra obtained from reduced PANI to π - π^* transition of the aromatic (benzene B band) structure, and those from oxidized PANI to the band of free electron carriers (delocalized radical cations).

In this paper spectroelectrochemical measurements using transparent indium-tin-oxide (ITO) electrode, and conventional cyclic voltammetric and spectrophotometric experiments are reported. The species of PANI appearing at various applied potentials were confirmed and the degrada-

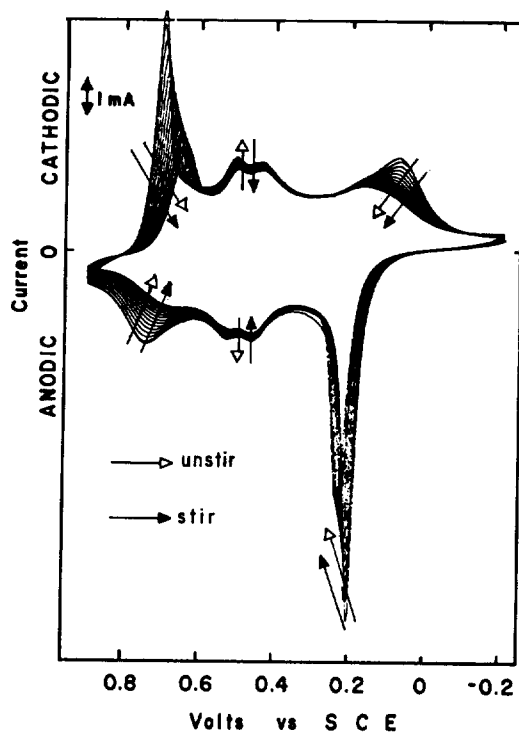


Figure 1. Cyclic voltammograms of polyaniline in 1.0M H_2SO_4 .

tion products were identified through these experiments.

Experimental

Aniline (Fluka) was used after purification by vacuum distillation.¹³ Distilled aniline was stored in the dark under the nitrogen atmosphere. Fluka's reagent grade benzoquinone (BQ), *p*-aminodiphenylamine (PADPA), and *p*-diaminobenzene (PDAB) were recrystallized from ethanol. Reagent grade sulfuric acid was used as supporting electrolyte without further purification. All electrolyte solutions were prepared from doubly deionized water whose conductivity was less than $10^{-7} \Omega^{-1} \text{cm}^{-1}$.

The electrochemical measurements were carried out with a Princeton Applied Research (PAR) model 273 Potentiostat/Galvanostat and a PAR model 377A Coulometric Cell System. The electrochemical cell used was a three-compartment pyrex glass cell. The working electrode compartment was separated by a fine porosity glass-frit from the counter electrode. The reference electrode was a saturated calomel electrode incased in a bridge tube which made contact with the test solution by means of a fine porosity frit-tip place near the working electrode, and all potential data given here are referred to the saturated calomel electrode (SCE). All the experiments were performed in nitrogen atmosphere at room temperature.

The PANI-films were grown by potential sweeping between -0.2 and 0.9 V vs. SCE at 100 mV/sec in $1.0 \text{ M } H_2SO_4$ solution with the aniline concentration of 0.10 M . Pt-wire and ITO electrodes were used as the working electrodes for conventional CV and spectroelectrochemical measurements, respectively. The UV/VIS spectra were taken with JASCO UVDEC-610 spectrophotometer.

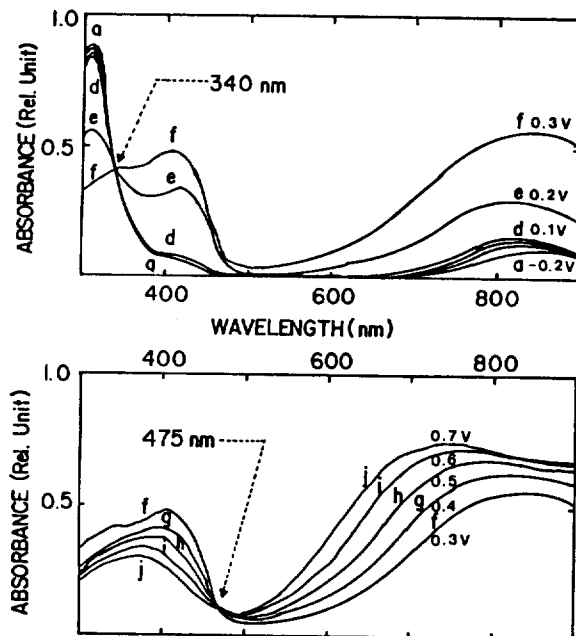


Figure 2. Visible spectra of polyaniline film coated on ITO electrode at -0.2 (a), 0.1 (b), 0.0 (c), 0.1 (d), 0.2 (e), 0.3 (f), 0.4 (g), 0.5 (h), 0.6 (i), and 0.7 V (j).

Results and Discussion

Cyclic Voltammetry. Figure 1 illustrates representative cyclic voltammograms of polyaniline (PANI)-film in $1.0 \text{ M } H_2SO_4$ solution. The cyclic voltammetric (CV) peaks in the potential range of 0 – 0.2 V and 0.6 – 0.8 V , that had been previously reported¹⁴ to arise from redox reactions of PANI-film, were observed to decrease gradually in both stirred and unstirred solutions as shown in Figure 1. This gradual decrease of peaks indicates that the film degrades during the potential sweeping. Observations of such gradual changes of CV's for PANI films have also been reported by others.^{2,3,11} However, the CV peaks at 0.4 – 0.6 V in a quiescent solution increased, rather than decreased. On the other hand, when the solution was stirred, the CV peaks decreased with increasing number of the potential sweep cycles. This fact implies that the peaks at 0.4 – 0.6 V are due to redox reactions of the degradation product, namely, *p*-benzoquinone (BQ). BQ having its standard electrode potential of about 0.5 V for BQ/HQ, has been previously confirmed as a major degradation product¹¹. (See spectrophotometry section below).

Spectroelectrochemistry. Shown in Figures 2(a–f) and 2(f–j) are the spectra obtained from PANI-coated ITO electrode at various potentials corresponding to degrees of oxidation ranging from the fully reduced (yellow) to the fully oxidized (blue) states. In Figure 2(a–f), the peak at about 310 nm decreases with increasing positive potential while the one at 410 nm increases. In Figure 2(f–j), the peak at 410 nm decreases while the one at 750 – 800 nm increases with increasing potential. Furthermore, the spectra of 2(a–f) and those of 2(f–j) exhibit an isosbestic point at 340 nm and 475 nm , respectively. This indicates that at least three species having different absorption maxima take part in the course of the PANI oxidation. The spectra of PANI-film changing with the potential in a similar manner have also been noted

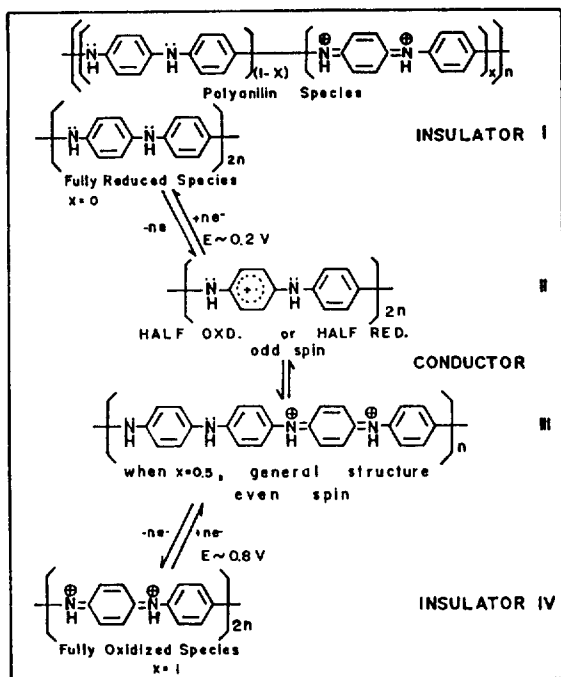


Figure 3. Structural model and redox scheme of polyaniline.

by other investigators.^{10,12,15,16}

According to the results of Figures 1 and 2(a-f), the spectra having a well-defined absorption maximum (λ_{max}) at 310 nm in the potential region between -0.2 and 0.1 V are representative of the fully reduced insulating state of PANI, which is called leucoemeraldine. A second species (with λ_{max} of 410 nm) derived from oxidation of the fully reduced PANI was observed under the potential 0.1 to 0.3 V as shown in Figures 2(e) and 2(f). When more positive potentials up to 0.7 V are applied to the PANI-ITO electrode, this species transforms further into another having its maximum absorbance at 750 – 800 nm, and there is a well defined isosbestic point at 475 nm. However, judging from the similarity between the spectra *f* and *j* and from the fact that the oxidation peak between 0.3 and 0.6 V in Figure 1 is very small, the species corresponding to the spectrum *j* is considered to have a oxidation state that is close to the species corresponding to the spectrum *f*. Thus, the two λ_{max} measured at 410 nm and 750 – 800 nm are considered to represent partially oxidized conducting species, II and III of Figure 3, respectively.

The above assignments of the various species are consistent with the in-situ conductivity³ and the in-situ ESR behaviour¹⁷ of PANI. Paul, Ricco and Wrighton³ concluded that PANI equilibrated under the potential of 0.2 – 0.6 V has the highest conductivity. Glarum and Marshall¹⁷ reported that the ESR-data of PANI shows a large peak corresponding to maximum spin density at 0.2 V, the peak becomes extinct between 0.3 and 0.6 V, and reappears up to about half intensity of the maximum at 0.75 V. Based on the above facts, the chain structures shown in Figure 3 are proposed as the structures of PANI at various potential ranges. The chemical structures for PANI in Figure 3 are conceptually consistent with the conduction model of polaron/bipolaron (familiar to chemist as radical/diradical) that is universally accepted at the present time.¹⁸⁻²⁰ MacDiarmid and coworkers¹⁸⁻²⁰ proposed that emeraldine salt prepared chemically contains

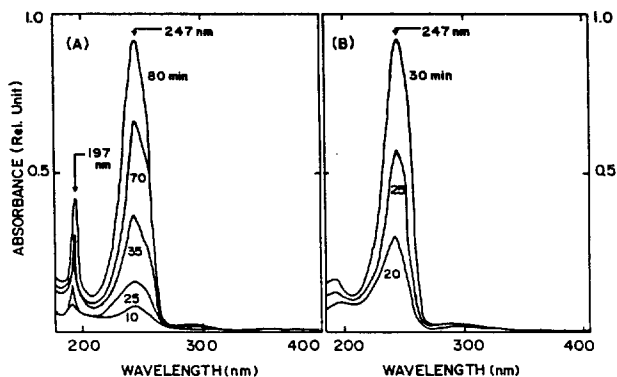


Figure 4. UV/VIS spectra of the 0.1 M H_2SO_4 solutions in which polyaniline film was electrolyzed at 0.65 V (A) and 0.8 V (B).

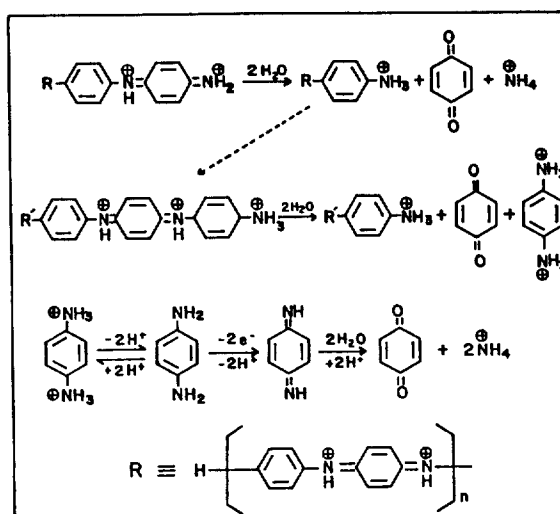


Figure 5. Scheme for degradation of polyaniline in aqueous acidic solutions.

localized bipolarons centered on the quinoid rings (equivalent to the even spin structure of Figure 3), and transforms into metallic polaron lattice (equivalent to the odd spin structure of Figure 3) by an internal redox reaction and coulombic repulsion between polarons. Conducting PANI prepared electrochemically, which might be thought to contain delocalized radicals, can be preferentially transformed into quinoid structure via the disproportionation reaction under proper potential as in Figure 3.

Spectrophotometry. In order to investigate whether degradation product is soluble, we ran spectrophotometric experiments. After a PANI film was grown by 30 potential-sweep cycles on a Pt-wire, the PANI-film was rinsed with a stream of 1.0 M H_2SO_4 and the solution in the cell was replaced with 1.0 M H_2SO_4 . The geometric area of Pt electrode was 0.3 cm². Potentiostatic electrolysis was performed in the mini-cell constructed of two quartz-curvettes of spectrophotometer. The potential was stepped and held at desired potential until the current was steady. The UV spectra of the electrolyzed solutions were recorded for each applied potential.

Typical results taken from the solutions with the applied potential of 0.60 and 0.85 V, are shown in Figures 4(A) and 4(B), respectively. The second spectrum peak [Figure 4(B)]

having its maximum absorbance at 247 nm is the same as that of authentic BQ, as was confirmed by other investigators.^{10,11} However, the first peak [Figure 4(A)], which has not been noted by others,^{10,11} having maximum at 197 nm, is close to that of authentic PDAB or aniline samples in acidic solutions. When the film potential was 0.65V, both spectrum of BQ and a spectra that can be assigned either to PDAB or aniline were observed as shown in Figure 4(A). When the potential was below 0.5V no absorption peak was observed. Absorption peaks of the electrolyzed solutions increased with time during electrolysis, as shown in Figure 4. This indicates that the degradation products become soluble through hydrolysis reaction of the oxidized PANI or its degradation products.

We conclude from these observations that not only BQ is a major soluble degradation product as has already been confirmed,^{10,11} but either PDAB or aniline is also produced as a result of degradation. If PDAB is formed it is further oxidized at high enough potentials and is turned into BQ by a hydrolysis reaction. However, at lower potential PDAB may survive. On the other hand, if aniline is regenerated in the degradation process, at higher potential PADPA should have been obtained by oxidation of aniline. A spectrum resembling that of PADPA was not observed from any of the electrolyzed solutions. We can, thus, assign the absorption peak at 197 nm to protonated PDAB.

The scheme in Figure 5 is proposed as a probable degradation mechanism of PANI in aqueous acidic solutions, on the premises that: (I) fully-oxidized PANI has alternating benzenoid-quinoid structures; (II) the quinoid is at the end of PANI-chain; and (III) hydrolysis occurs favorably at the end group. The pKa's of oxidized PANI²¹ and protonated PDAB²² were reported to be about 2.5 and 3.3, respectively. Therefore, in 1.0M H₂SO₄ solution protonated species of PANI and PDAB are probably dominant over the unprotonated ones.

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