Optical properties of polyaniline

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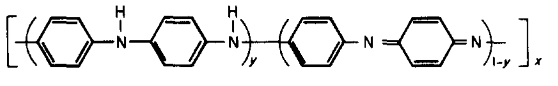
Optical absorption has been used to study polyaniline at various levels of oxidation and protonation. The conversion of leucoemeraldine base to its salt accounts for the blue shift of the $\pi-\pi^*$ absorption from 3.94 to 4.17 eV. The emeraldine base has an absorption peak at 2.1 eV due to the localized benzenoid HOMO (highest occupied molecular orbital) to quinoid LUMO (lowest unoccupied molecular orbital) excitation. Protonation of the emeraldine base causes a lattice distortion of polyaniline to form a polaronic lattice structure, which accounts for the shift of the 2.1 eV absorption to 1.5 eV. Further protonation of emeraldine salt causes the breakdown of the polaronic lattice to a confined bipolaron lattice. When the acid strength of the solution is very high (96% H_2SO_4), most of the amine nitrogens are protonated. Characteristic absorptions of isolated quinoid imine units ($\sim$2.5 eV) and benzene units ($\sim$4.8 eV) have been found. The evolution of band structure corresponding to the optical-absorption change during the protonation of polyaniline at each specific oxidation state is studied by gradually changing the acid strength of the solution to which the polymer is subjected. We have also studied the optical-absorption change at one fixed acid strength by slowly oxidizing leucoemeraldine to emeraldine then to pernigraniline by electrochemical and chemical means. Detailed information has been obtained on the band structure changes in relation to lattice structure interconversions during the transitions between various oxidation and protonation states.

(Keywords: polyaniline; conducting polymer; optical; emeraldine; oxidation; protonation)

INTRODUCTION

The structure of polyaniline has only recently been clearly elucidated[1–4]. The non-conducting form of this polymer



can, in principle, exist in a continuum of oxidation states ranging from completely reduced leucoemeraldine ($y = 1$) to completely oxidized pernigraniline ($y = 0$). The conductivity of this material is a function of both the degree of oxidation and the degree of protonation[2,5]. The emeraldine ($y = 0.5$) oxidation state of polyaniline exhibits the highest level of conductivity upon protonation, reaching a value of $5\ \mathrm{S\,cm^{-1}}$. Stafstrom *et al.*[6] proposed a polaronic lattice structure for this highly conducting state, which agrees with theoretical band-structure calculations, optical properties and Pauli susceptibility.

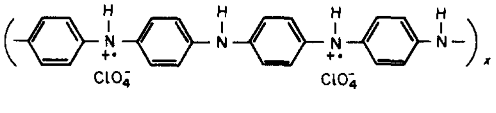
The structural change of polyaniline in corresponding to the change of pH and redox potential has been illustrated in the literature before[2–4] using electrochemical methods. In this paper, we present the optical properties of polyaniline at different oxidation and protonation states, in order to gain more understanding of the chemical reactions that occur and the materials that are formed during the variation of redox potential and pH. The results appear to agree very well with the data obtained from electrochemical studies and to be consistent with the structure proposed previously.

The effects of changing the oxidation level and the protonation level on the electronic structure of polyaniline have been among the most important issues; the resulting spectral changes have been extensively investigated in recent years, and a number of papers have been published[1,3,6–16]. Our early studies on this subject appear to be unknown to workers in the field[17]. For example, we showed that polyaniline could be dissolved in concentrated sulfuric acid, and the polymer did not show any degradation, as evidenced by its spectrum, if the dissolution process was maintained in the cold condition[18]. A similar approach was later adopted by other workers. In this paper, we will provide a broad picture of the electronic structure of polyaniline in various conditions. We believe that this paper contains a lot of new information that has not been seen in the open literature. Although similar work has been done before, the unique nature of the work presented here can help to increase the understanding of this subject.

EXPERIMENTAL

$\pi-\pi^*$ transition in reduced polyaniline (leucoemeraldine)

Spectra of leucoemeraldine at various degrees of protonation. A green, free-standing film of emeraldine hydroperchlorate[19]



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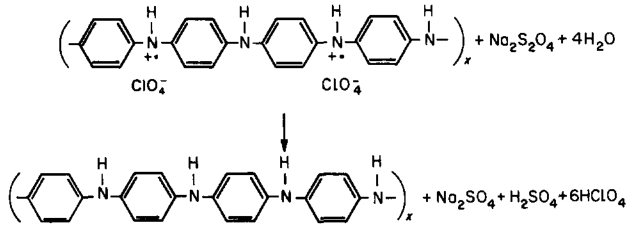
(10 mm × 30 mm × ~0.01 mm) was placed on a quartz plate (8 mm × 50 mm × 1.5 mm) so that it covered approximately one-half of the slide. The film was then wetted with 1 N aqueous HCl so that it adhered to the quartz surface. The film was then permitted to partly dry in the air for ~1 h. A very thin layer of 'five minute' epoxy cement was placed around the edge of the film so that the edges were firmly attached to the quartz. The main body of the film adhered firmly and smoothly to the quartz when it was wet. The assembly was then placed in a quartz cell (4 mm × 10 mm × 60 mm).

A sodium dithionite ($Na_2S_2O_4$) solution (pH ≈6), prepared by dissolving ~1 g of $Na_2S_2O_4$ in ~20 ml of distilled water, was then added to the cell so that it completely covered the top of the film. Within a few seconds the film changed from dark transparent green to a very pale transparent yellow, indicating that it had been reduced to the leucoemeraldine oxidation state:



From our earlier studies we have shown that the emeraldine hydrochloride is completely deprotonated at pH 6–7, hence it is assumed that the leucoemeraldine base is produced by this treatment. The sodium dithionite solution was removed by tilting the cell and placing a piece of absorbent tissue paper at the entrance to the cell. The tissue immediately absorbed the solution and emptied the cell.

A solution of HCl with pH 3.0 was then placed in the cell and was removed using tissue paper as described above. This washing procedure was repeated twice more and the HCl solution with pH 3.0 was then placed in the cell for optical studies. The top of the cell was covered tightly with several layers of semiadhesive 'Parafilm' in order to exclude air and prevent oxidation of the leucoemeraldine to the emeraldine. If the total time taken for the removal of the sodium dithionite and for the washing etc. did not exceed ~1 min, air oxidation of the leucoemeraldine film was negligible, as could be seen by the absence of any green tint caused by the formation of the emeraldine salt.

Spectra were obtained at room temperature using a Beckman DU-8 u.v.–visible spectrophotometer. In all studies, a spectrum of the aqueous solution was first obtained using the same cell containing a piece of blank quartz slide in order to confirm that there was no absorption due to the cell or its contents. Spectra were obtained at room temperature by first storing in the computer of the spectrophotometer the spectrum of air (no cell present) followed by the recording of the spectrum during ~15 min.

The spectrum recorded on the chart paper had the air blank automatically subtracted. The spectrum was then checked by recording it again in order to ensure that no immediate decomposition of the film had occurred during the recording of the first spectrum. After the spectrum had been obtained, the HCl solution was removed by tissue paper as described above and, as a precautionary measure, the cell was re-treated with sodium dithionite solution and then washed with HCl solution of pH 2.0, as described above. The cell was finally filled with the solution and a spectrum was recorded. This procedure was repeated with solutions of pH 1.0, −0.2 (1 N HCl), −1.05 (3 N HCl) and −2.12 (6 N HCl). (The 'pH values' given for solutions more acidic than pH 1.0 are actually Hammett acidity functions (H_0) which reflect the proton donating ability of highly acidic solutions more accurately than pH[20,21]. In dilute solutions the Hammett function and pH are identical.)

A series of spectra using a different piece of free-standing film were recorded using aqueous solutions of H_2SO_4 at pH 2.0, 1.0, 0.13 (1.0 N H_2SO_4), −1.12 (5.0 N H_2SO_4) and −2.06 (9.0 N H_2SO_4). The second spectrum recorded at each concentration was identical to the first spectrum recorded at that concentration. The spectrum of the leucoemeraldine base was recorded at pH 13.0 (0.1 N NaOH) using the same piece of film used for the studies in H_2SO_4 and employing the same procedure described above.

Spectrum of leucoemeraldine during air oxidation. A leucoemeraldine film in 1.0×10^{-2} N H_2SO_4 on a quartz plate (synthesized using sodium dithionite as described above) in the spectroscopic cell was exposed to laboratory air for ~10 h by removing the Parafilm protective wrapping from the top of the cell. The leucoemeraldine film became light green during this time, indicating that some oxidation had occurred. The spectrum was then measured using the procedure described above.

Change in spectrum of leucoemeraldine during electrochemical oxidation

Electrochemical potential versus *electric charge study.* Emeraldine hydrotetrafluoroborate film was electrochemically deposited on a piece of Pt foil (1 cm^2) using a constant potential method[22] at 0.75 V for ~3 h. After rinsing the film with 0.1 M $Pb(BF_4)_2$ + 0.5 M HBF_4 solution for ~1–2 min the assembly was transferred to a small vial containing 20 ml of 0.1 M $Pb(BF_4)_2$ + 0.5 M HBF_4 solution. Two pieces of Pb ribbon (6 mm × 70 mm) were placed in the solution as counter and reference electrodes. The Pb ribbon surface was scraped with a knife before being placed in the solution.

The emeraldine hydrotetrafluoroborate film was reduced at 0.2 V (*versus* Pb) for ~2–3 h to the corresponding leucoemeraldine. A constant current of 10 μA cm^{-2} was then applied between the working electrode (Pt foil containing polyaniline film on the surface) and the counter electrode. The distance between the two electrodes was ~1 cm. The potential was recorded *versus* the Pb reference electrode so as to controllably oxidize the slightly protonated leucoemeraldine base to a maximum potential of 1.0 V (*versus* Pb), i.e. to the approximate oxidation state of nigraniline. This oxidation process took ~17 h. The potential was continuously recorded and is given in *Figure 1*.

Spectra of electrochemically oxidized polyaniline. The top of a piece of conducting glass (8 mm × 50 mm × 1.5 mm) (with indium oxide coating) was connected to an alligator clip. The contact between the clip and the conducting glass was secured with a coating layer of Electrodag. A piece of Pt foil (12.5 mm × 12.5 mm) was

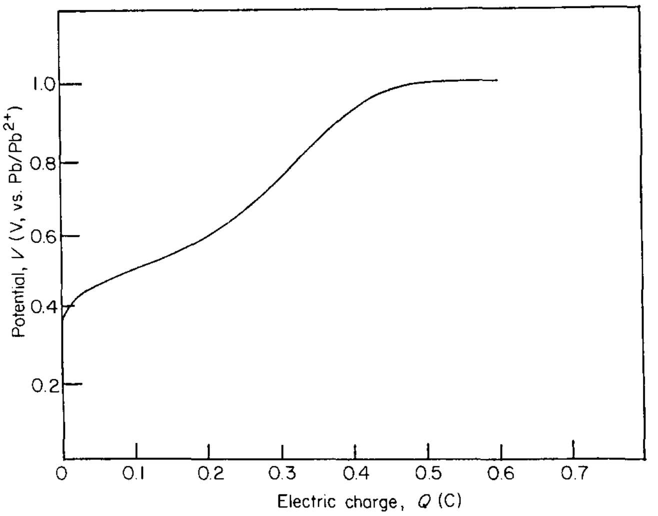


Figure 1 Plot of potential (V) *versus* electric charge (Q) for the slow electrochemical oxidation of leucoemeraldine at 10 μA cm^{-2} in 0.1 M $Pb(BF_4)_2$ + 0.5 M HBF_4 solution

used as a counter electrode. The conducting glass was used as the working electrode. The electrolyte solution was 0.1 M $Pb(BF_4)_2$ + 0.5 M HBF_4. The two electrodes were ~1 cm apart with the conducting side of the glass facing the Pt foil. The film of emeraldine hydrofluoroborate was synthesized on the conducting glass using the constant applied potential method (0.75 V). The time used for growing the film was ~180 min. The glass electrode was then rinsed with 0.1 M $Pb(BF_4)_2$ + 0.5 M HBF_4 solution for ~2–3 min. An electrochemical cell was constructed as shown in *Figure 2.* A Pt wire was wound tightly around the indented part of the conducting glass. A piece of Pb ribbon was scraped with a knife to clean the surface, then the upper part was surrounded by Teflon tape to prevent its contacting the Pt wire or the conducting glass.

The conducting glass and Pb ribbon were inserted into a rectangular cell (4 mm × 10 mm × 60 mm). A solution containing 0.1 M $Pb(BF_4)_2$ + 0.5 M HBF_4 was added to the cell to a level such that the polyaniline was completely covered. Some Teflon tape was inserted into the entrance of the cell to seal the cell and to fix the electrodes firmly in place, then 'five minute' epoxy cement was placed over the tape. The Teflon tape on the top of the cell prevented the epoxy cement from flowing into the cell. All of the above manipulations were carried out in an argon-filled glove bag to prevent air from entering the cell. The polymer was reduced at a constant applied potential of 0.20 V *versus* Pb during ~16 h.

The first spectrum was taken immediately after disconnecting the cell from the power source, using a DU-8 u.v.-visible Beckman spectrophotometer which covers the spectral range 850–350 nm. The spectrum was recorded in the same way as described before, except that a similar cell containing a piece of conducting glass and 0.1 M $Pb(BF_4)_2$ + 0.5 M HBF_4 solution was used as a blank. Two hours after the spectrum had been recorded it was observed that the potential of the polyaniline had increased to 0.40 V *versus* Pb. This might have been caused by a trace amount of oxygen remaining in the solution, which would be expected to oxidize the film. A spectrum was taken of this film using a Cary 14 spectrophotometer to extend the spectral range between 350 nm (3.54 eV) and 1250 nm (~1.0 eV).

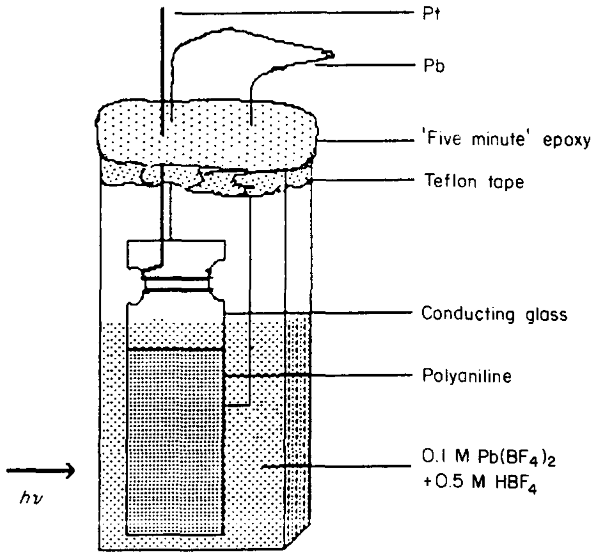
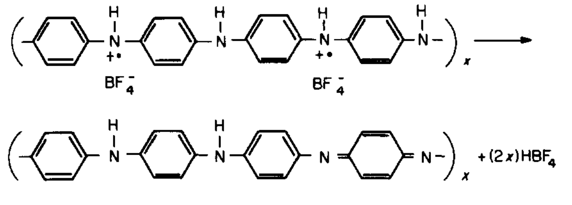


Figure 2 Electrochemical cell used in the step-wise electrochemical oxidation of leucoemeraldine in 0.1 M $Pb(BF_4)_2$ + 0.5 M HBF_4 solution

A constant potential of 0.50 V *versus* Pb was then applied between the polyaniline electrode and the Pb electrode. After 3 h the cell was disconnected from the power source and was allowed to rest for 1 h. The voltage had dropped to 0.46 V *versus* Pb. The spectrum of this material was recorded as that used for the first spectrum. Additional spectra were taken after a 3–4 h constant potential oxidation of the polyaniline followed by a stand period of ~1 h. The potentials (*versus* Pb) applied and the potentials (*versus* Pb) that were recorded after the 1 h stand period (given in parentheses) were 0.60 V (0.57 V), 0.90 V (0.86 V) and 1.00 V (0.93 V). A constant potential oxidation during ~16 h was carried out at 0.70 V *versus* Pb (0.70 V *versus* Pb) and at 0.80 V *versus* Pb (0.80 V *versus* Pb). All spectra except the first three were recorded both with a Cary 14 and DU-8 u.v.-visible spectrophotometer to check that the spectra were identical. The spectra given in *Figure 3* are those recorded on the Cary 14 spectrophotometer.

Change in spectrum during protonic acid doping of emeraldine base

On conducting glass substrate. A film of emeraldine hydrotetrafluoroborate (8 mm × 30 mm) was electrochemically deposited on a piece of conducting glass (8 mm × 50 mm; In/Sn oxide coating) as described above; the time for polymerization was ~3 h. The final potential to which the film was subjected was ~0.50–0.70 V *versus* SCE. The resulting assembly was then rinsed briefly for ~1 min in distilled water and placed in 500 ml of distilled water for ~16 h. No attempt was made to exclude air from any of these procedures. This treatment should result in complete deprotonation of the emeraldine salt to yield the corresponding emeraldine base, namely:



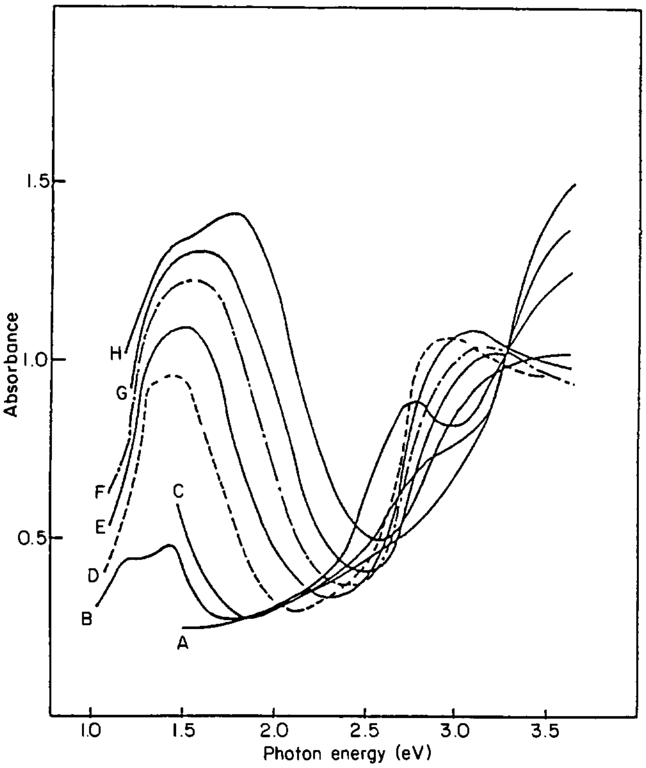


Figure 3 Absorption spectra of different oxidation states of polyaniline. The voltages given are the open circuit potentials characteristic of polyaniline in different oxidation states: A, 0.20 V; B, 0.40 V; C, 0.46 V; D, 0.57 V; E, 0.70 V; F, 0.80 V; G, 0.86 V; H, 0.93 V

The piece of conducting glass on which the film adhered firmly was placed in the same cell as described for the leucoemeraldine and distilled water (pH ≈ 5–6) was added; the spectrum was recorded as described for the leucoemeraldine. The conducting glass/film assembly was placed in 300 ml of 1.0×10^{-4} N HCl for ~16 h. A spectrum was then recorded. The film was washed and the cell was refilled with HCl solutions having molarities of 2.0×10^{-4} (3 h), 4.0×10^{-4} (4.5 h), 6.0×10^{-4} (2 h), 8.0×10^{-4} (16 h) and 1.0×10^{-3} (2 h). The figures in parentheses correspond to the equilibrium times in acid before spectra were recorded.

On quartz substrate. A green, free-standing film of emeraldine hydroperchlorate was attached to a quartz substrate as described for the leucoemeraldine. The film on quartz was first rinsed with 0.1 M KOH and was then placed in 0.1 M KOH for 30 min. The film was transferred to a quartz cell (4 mm × 10 mm × 60 mm) which contained 0.1 M KOH. The spectrum was recorded as described for the leucoemeraldine on a Perkin-Elmer Hitachi model 330 spectrophotometer. The solution was removed. The film was washed with water twice and then with 1 M HCl twice. Finally, after placing fresh 1 M HCl in the cell, the spectra were recorded.

Emeraldine salt

Spectrum of emeraldine salt in aqueous solutions of 80% acetic acid. The emeraldine base form of polyaniline powder[2] was put in 80% acetic acid. The solution was stirred for 10 min then the powder and solution were filtered through a funnel containing a filter paper. The filtered green solution was then transferred to a quartz cell (4 mm × 10 mm × 60 mm) and spectra were taken as described for the leucoemeraldine. A portion of the solution was then diluted to half the original concentration by adding an equal amount of 80% acetic acid to the solution prepared from the solid emeraldine base. Repeating the same procedure four times yielded concentrations of 1/2, 1/4, 1/8 and 1/16 of the original concentration. Spectra were taken of each of these solutions and 80% acetic acid solution.

Comparison of spectra of emeraldine salt as a solid and in solution. A piece of free-standing emeraldine $\cdot 2HClO_4$ attached to a quartz plate was prepared electrochemically. The film was allowed to dry in air, and the spectrum was recorded in air. The spectrum of a solution of chemically made emeraldine base in 80% aqueous acetic acid was obtained as described above.

Spectrum of emeraldine base in concentrated sulfuric acid. A 20 mg sample of chemically made emeraldine hydrochloride was put in 200 ml of 96% H_2SO_4. The solution was then stirred until no solid could be seen. The colour of the solution was brown–black. Then 30 ml portions of this solution in 96% H_2SO_4 were diluted by adding 3.66, 7.14, 11.04, 15.45 and 20.49 ml of H_2O respectively to make 90%, 85%, 80%, 75% and 70% concentrated H_2SO_4. These solutions were prepared in an ice bath to keep them cool. Then the spectra were recorded as described for the leucoemeraldine in quartz cells (no blank in reference beam).

Slow oxidation of emeraldine base in 80% acetic acid. Emeraldine base was dissolved in acetic acid. A capillary was used to transfer a very tiny amount of ammonium persulfate aqueous solution to the quartz cell. The solution was stirred using the capillary tube. A spectrum was then recorded. This procedure was repeated until the solution became purple.

RESULTS AND DISCUSSION

π–π^* transition in reduced polyaniline (leucoemeraldine)

The spectral range obtainable with the Beckman DU-8 u.v.–visible spectrophotometer is ~1.5 to ~5.6 eV (850–220 nm). The spectra were identical in the pH range 2–13, both in HCl and H_2SO_4. However, on changing the normality of the H_2SO_4 solution from 10^{-2} to 9.0 N, a small but significant blue shift from 315 nm to 298 nm was observed, as can be seen in *Figure 4*. This shift was reversible. On changing the normality back to 10^{-2} N the peak maximum was 315 nm. The extent of protonation is not known at any pH.

When the leucoemeraldine film in 10^{-2} N H_2SO_4 was exposed to air for ~10 h, during which time it turned to a light green colour, its spectrum changed from that given in *Figure 4* to that given in *Figure 5*. The main effects noted were that the maximum at 315 nm in *Figure 4* shifted slightly to 327 nm in *Figure 5* and that a new peak appeared at 424 nm in *Figure 5*. Also in *Figure 5* a new absorption appeared to be growing at a value greater than 850 nm.

Since polyaniline contains benzene rings, the discussion will be built up from the benzene π–π^* transition. Benzene exhibits two absorption bands around 180 nm and 200 nm and a weak absorption band around 260 nm (~4.8 eV). All three bands are associated with the π

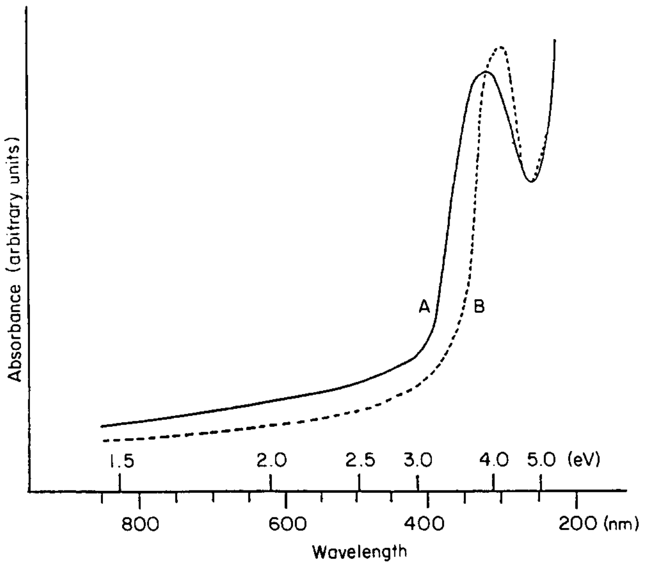


Figure 4 The absorption spectra of A, leucoemeraldine base and B, leucoemeraldine salt

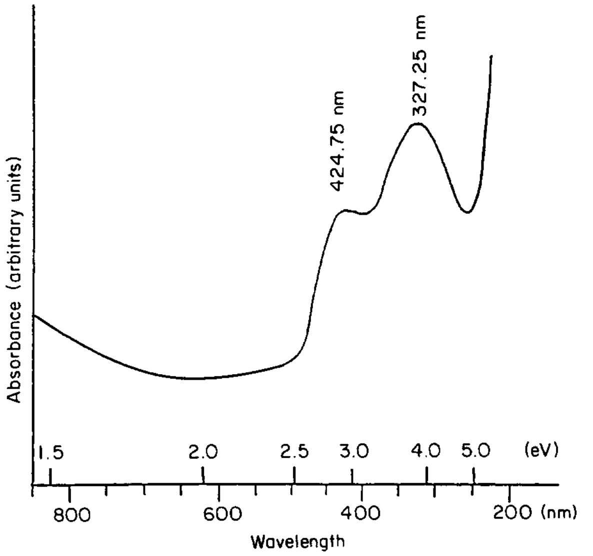


Figure 5 Absorption spectrum of the polymer obtained by oxidation of leucoemeraldine base by air in 10^{-2} N H_2SO_4

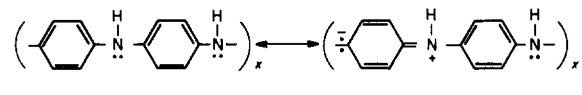
electron system of benzene. The two intense bands may be ascribed to transitions to dipolar excited states, while the weak 260 nm band is ascribed as the forbidden transition to a homopolar excited state. The 260 nm ($\sim$4.8 eV) band possesses fine structure and is intense in substituted benzenes.

Substitution of benzene with polar groups containing unshared electrons (auxochromes, like OH or NH_2), shifts the absorption bands to longer wavelengths and also intensifies them. The effect of auxochromes on the benzene bands is explained in terms of the interaction of unshared electrons with the benzene nucleus. Braude calls this interaction π–p conjugation[23]. The phenyl derivatives of the nitrogen show progressive red shifts in the 260 nm band, which shifts to longer values with an increase in the number of phenyl groups. For example, aniline, diphenylamine and triphenylamine exhibit bands at 280, 285 and 297 nm, respectively. Such a variation in a series of compounds is a measure of the resonance interaction of the phenyl groups with the central atom[24].

U.v. spectra of some oligoanilines have been studied by Honzl and Tlustakova[25]. In the case of polyaniline, Zach[26] investigated the band structure of an infinite linear polyaniline using the HCO approximation. According to his calculation λ_{max} of polyaniline was 327 nm ($E = 3.79$ eV). Most of the band gap studies of conducting polymers were carried out by using valence effect Hamiltonian (VEH) calculations. By assuming the torsional angle of 30° between adjacent phenyl rings, Boudreaux *et al.*[27] obtained a band gap of $\sim$3.8 eV for leucoemeraldine. When a torsional angle of 0° was adopted, a band gap of $\sim$3.6 eV on the polymer was obtained. These theoretical results are fairly close to the experimental findings. Recently, Kobayashi *et al.*[28] reported the π–π^* transition at 305 nm (4.07 eV) for the reduced polyaniline (leucoemeraldine). Our study shows that the leucoemeraldine base form (pH $\geqslant$ 2) has an absorption maximum at 315 nm ($\sim$3.94 eV) (*Figure 4*).

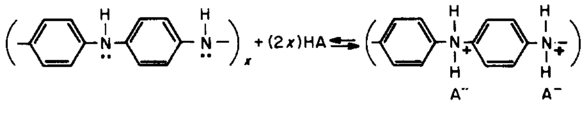
In general, well reduced forms of polyaromatic systems have the first absorption band assigned to the π–π^* transition. For example, 3.2 eV for polypyrrole[29] and 2.6 eV (band edge 2.0 eV) for polythiophene[30]. Actually, from VEH calculations and X-ray photoelectron spectroscopy data, the first two or three bands are contributed from π–π^* transitions in these polyaromatic systems (PPP, PPS[31], PPy[32], etc.). In the case of polyphenylene sulfide, Bredas *et al.*[31] pointed out that the lowest band was mainly a contribution from $3p_z$ sulfur and $2p_z$ carbon orbitals (where z is the direction perpendicular to the plane containing the sulfur atoms). This band has a bonding character between the p_z orbitals on sulfur atoms and sulfur connected to carbon atoms. The second band is flat and gives rise to a very high peak in the density of states due to the very small contributions coming from the sulfur atoms as well as from the carbon atoms bonded to sulfur. Similarly, the two highest occupied bands for leucoemeraldine were composed of delocalized π orbitals from the rings with a strong admixture of nitrogen p_z orbitals based on Boudreaux's VEH results[27].

Based on the above discussion, the π–π^* transition at 3.94 eV of leucoemeraldine base is the transition associated with π electrons of the benzene ring delocalized on nitrogen atoms. Possible resonance forms are:



Thus, we would expect that protonation of the lone pair electrons on the nitrogen would hinder this conjugation and would shift the absorption band to a value greater than 3.94 eV. This effect is similar to the protonation of aniline monomer. It has been found that the anilinium ion shows very similar u.v. spectra to benzene[33], because the π electrons are localized in the benzene ring. The 280 nm (4.43 eV) band in aniline shifts to 260 nm (4.77 eV) in the $C_6H_5NH_3^+$ ion[33].

Huang *et al.*[2] have shown that leucoemeraldine base starts to become protonated at pH $\lesssim -0.2$, i.e. $>$1 N HCl. The electrochemical data indicate that somewhere between pH 0.3 and pH -0.2 extensive protonation is expected to occur, namely:



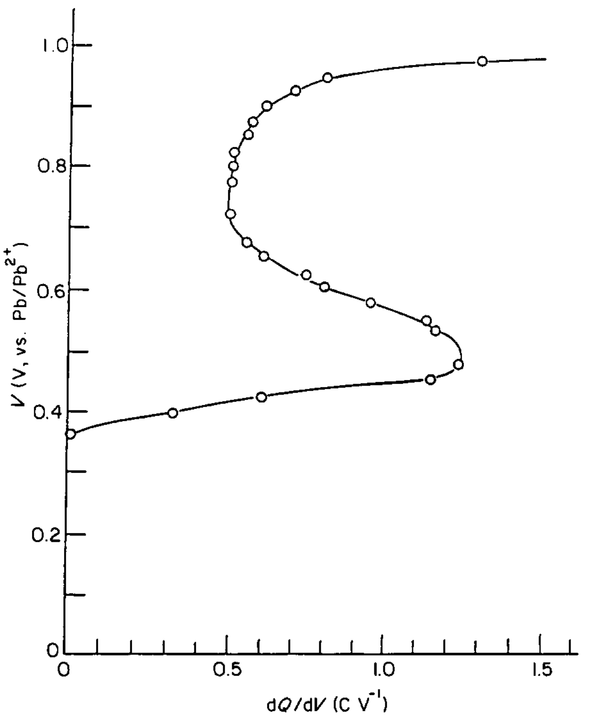


Figure 6 Graph of potential, V, *versus* dQ/dV obtained by replotting the data given in *Figure 1*

Thus very little protonation is expected at pH 2. Hence, the shift in the $\pi-\pi^*$ transition in leucoemeraldine base from 315 nm (3.94 eV) at pH 2 to 298 nm (4.17 eV) in 9 N H_2SO_4 is obviously associated with protonation of the leucoemeraldine base as given by the equation above. Although the extent of protonation is not known, the electrochemistry seems to suggest that at least half of the protonation has been achieved when the acidity is greater than 1 N HCl. This correlates well to the equal amount of electron transfer and proton transfer during the oxidation of leucoemeraldine to emeraldine (half oxidation of the polymer). On the other hand, no absorption peak at 260 nm, which is the absorption of benzene or the anilinium ion, indicates that full protonation of the polymer may not have been achieved even in 9 N H_2SO_4.

Leucoemeraldine is not stable in air. After 1 day in 10^{-2} N H_2SO_4, the colour changed from transparent yellow to light green-yellow. The spectrum in *Figure 5* shows that the leucoemeraldine base form is oxidized. Thus the peak in non-protonated leucoemeraldine base at 315 nm (3.94 eV) (*Figure 4*) has shifted to 327 nm (3.79 eV). At the same time a new peak at 425 nm (2.92 eV), characteristic of polyaniline oxidized to an oxidation state slightly lower than emeraldine (*Figure 5*), has appeared.

Change in spectrum of leucoemeraldine during electrochemical oxidation

The step-wise electrochemical oxidation of leucoemeraldine was carried out at a constant pH of 0.3, i.e. 0.5 N H^+. As shown in the above discussion, leucoemeraldine base is only slightly protonated at this pH value, whereas emeraldine base is about completely protonated[1,4] at pH 0.3.

The study of electrochemical potential (V) *versus* electric charge (Q) was performed in order to determine the potential range for which the polyaniline could be oxidized for the following spectral studies. A plot of the electric charge released by leucoemeraldine as a function of increasing applied potential is given in *Figure 1*. This $Q-V$ curve shows the potentials with an inflection point at ~0.7 V *versus* Pb. At a potential greater than ~1.0 V a constant potential was obtained which continued indefinitely. This may be caused by the polyaniline being chemically reduced by some species in the electrolyte as rapidly as it was oxidized electrochemically. By plotting the data in *Figure 1* as V *versus* dQ/dV, the curve in *Figure 6* is obtained. A maximum at ~0.5 V *versus* Pb/Pb^{2+} and a minimum at ~0.70 V *versus* Pb/Pb^{2+} are clearly observed. This plot is equivalent to a cyclic voltammogram.

As the polyaniline was oxidized electrochemically from 0.20 to 0.93 V in an electrolyte consisting of 0.1 M $Pb(BF_4)_2$ + 0.5 M HBF_4, several changes in the spectrum were observed (see *Figure 3*). These were as follows.

1. The maximum at 1.45 eV in curve A increased in intensity and shifted to 1.78 eV (curve H).
2. Two peaks were observed on this absorption at low oxidation potential (curve B) and high oxidation potential (curve H).
3. The minimum at 1.7 eV (curve B) changed to 2.6 eV in curve H.
4. A shoulder at ~2.70 eV (curve B) developed rapidly into a well defined peak at 2.75 eV in curve C. On further oxidation this grew and shifted to a maximum at 2.90 eV (curve E). On further oxidation it decreased slightly in intensity and shifted to 3.1 eV (curve G).
5. As oxidation proceeded the intensity of curve A at 3.54 eV (the end of the spectrum) decreased, as can be seen by the values of curves B, C, D, E, F, G and H at 3.54 eV. The maximum was not obtained due to the high absorption of conducting glass at the deep u.v. range.

The spectrum of completely reduced polyaniline has been discussed in the previous section. The two new major absorption peaks (at 1.5 eV and 2.7 eV) appearing between the $\pi-\pi^*$ transition seems to suggest the creation of common polaronic and bipolaronic band structures during the p-doping process, similar to that of polythiophenes and polypyrroles. In these polymers, two new within-gap defect bands are created during the oxidation process. However, the band structure calculation by Stafstrom *et al.* using VEH gives a totally different conclusion[6], and predicts that only one defect band exists within the gap states during the oxidation of polyaniline. A polaronic band structure was proposed for the half-oxidized polyaniline (emeraldine salt) in this calculation, which is consistent with magnetic studies[3]. A schematic band structure based on theoretical calculations[6,27,34] is summarized in *Figure 7*. The reduced state of polyaniline (leucoemeraldine) has a $\pi-\pi^*$ transition between the highest occupied band (band a) and lowest unoccupied band (band x) at 3.9 eV as described in the previous section. When the polymer is oxidized to form emeraldine salt, half of the electrons in the valence band (band a) are removed. Due to the destabilization of this highest occupied band, the band moves up slightly to form the within-gap defect band (polaron band). The lowest unoccupied band (band x) is so flat that the stabilization of the upper polaron defect band (band x′) does not shift the band down too much. Therefore, the bands x and x′ are nearly degenerate. The

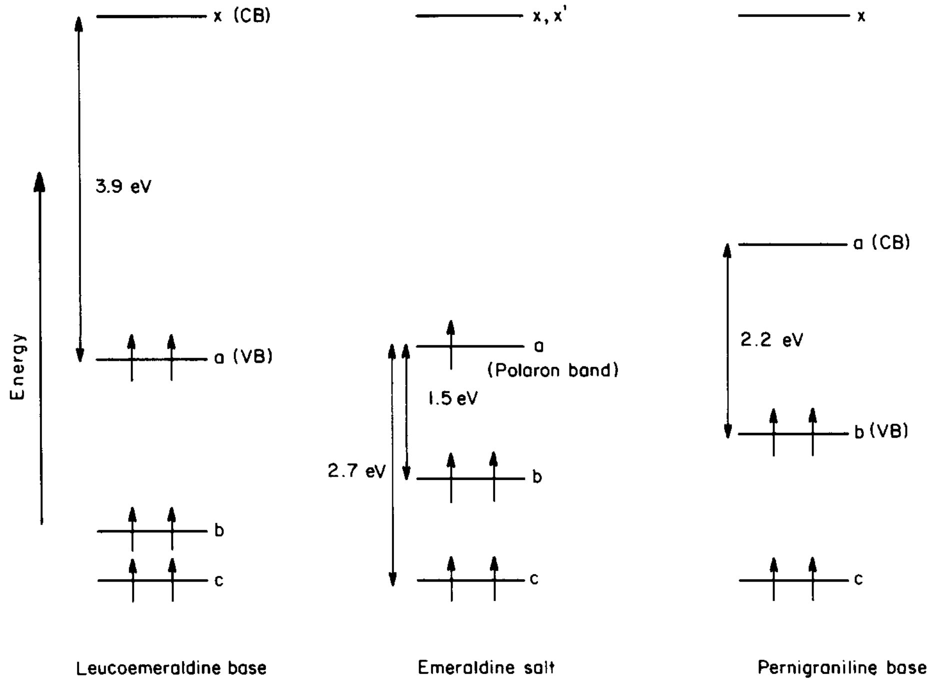


Figure 7 Schematic energy level diagrams of leucoemeraldine base, emeraldine salt and pernigraniline (CB, conduction band; VB, valence band)

observed absorption at 1.5 eV is due to the transition from band b to band a (polaron band), and the absorption at 2.7 eV is the transition from band c to band a. When the polymer is further oxidized to pernigraniline (fully oxidized polyaniline), band a is completely empty, forming the lowest unoccupied band. The absorption at 2.2 eV corresponds to the transition from band b to band a. The value of 2.2 eV is based on the recent calculation by Santos and Bredas[34]. Based on their choice of parameters, the calculation shows that the valence band (VB) and the conduction band (CB) globally extend over 2.9 eV and are separated by a gap of 1.4 eV. With this data, it is expected that the absorption maximum of the spectrum is around 2.2 eV. The experimental result is around 2.35 eV[35]. For simplicity, only the absorption maximum is illustrated in *Figure 7*, not the band gap transition (band edge). Also, the levels used do not represent the real energy bands.

Spectrum A in *Figure 3* represents a fully reduced polyaniline (leucoemeraldine) at an applied potential of 0.2 V *versus* Pb/Pb^{2+}. No absorption within the band gap is found. Spectrum E corresponds approximately to the emeraldine salt oxidation state which is half oxidized as indicated at the minimum of the $Q-V$ curve ($V = 0.7$ V) in *Figure 6*. The growth of the peaks at 1.5 eV and 2.7 eV with blue shift during oxidation from 0.2 V (spectrum A) to 0.7 V (spectrum E) is consistent with the shift of energy band as illustrated in *Figure 7*. The depletion of electrons in band a (polaron band) to form empty energy states results in an increase of probability of electron transitions from bands b and c to band a, hence the absorption peaks grow with the increase of applied potential. In this case, the higher the potential applied to the polymer, the greater the number of electrons that will be removed from band a. The shift of the polaron band to higher energy due to the destabilization of this defect band accounts for the blue shift of the absorption maxima in these spectra. When the polymer is oxidized further to nigraniline from spectrum E (at 0.7 V) to spectrum H (at 0.93 V), there is a significant deprotonation of the polymer as described in a previous paper[2]. The continued growth of the adsorption maximum at 1.5 eV with blue shift to 1.78 eV (from spectrum E to spectrum H) means that the non-protonated quinone–imine segments formed during the partial deprotonation of polyaniline still contribute to the overall absorption in this range. However, these quinone–imine segments do not contribute any absorption to the range near the absorption maximum at 2.7–3.0 eV, and hence cause the decrease of intensity at this absorption peak. This can be easily understood by looking at the emeraldine base and pernigraniline base. Both of them contain non-protonated quinone–imine segments. Emeraldine base has an absorption maximum at 2.1 eV and pernigraniline base has an absorption maximum at 2.3 eV. The absorption in this range will contribute to the higher energy part of the absorption maximum at 1.5–1.78 eV, as shown in spectra E to H. On the other hand, neither emeraldine base nor pernigraniline base has an absorption maximum near 2.7–3.0 eV. If there is no separated domain of dimerized quinoid segments in the lattice structure, a single peak at around 1.5–1.78 eV is expected. Therefore, the double peak at 1.78 eV on spectrum H may be due to the existence of an inhomogeneous distribution of deprotonated segments in the polymer chain.

Change in spectrum during protonic acid doping of emeraldine base

In the late 1960s and early 1970s, Jozefowicz and co-workers[36,37] published a series of papers on polyaniline. One of their major areas of study was the conductivity and pH relationship; at that time, they did not know that polyaniline undergoes insulator to metal transition during acid treatment. Recent literature clearly shows that this acid treatment is true protonic acid doping on a conducting polymer. In this section, the change of band structure during the acid and base treatment using u.v.-visible-near i.r. spectra will be discussed.

As can be seen from *Figure 8*, the spectra at pH 6.0

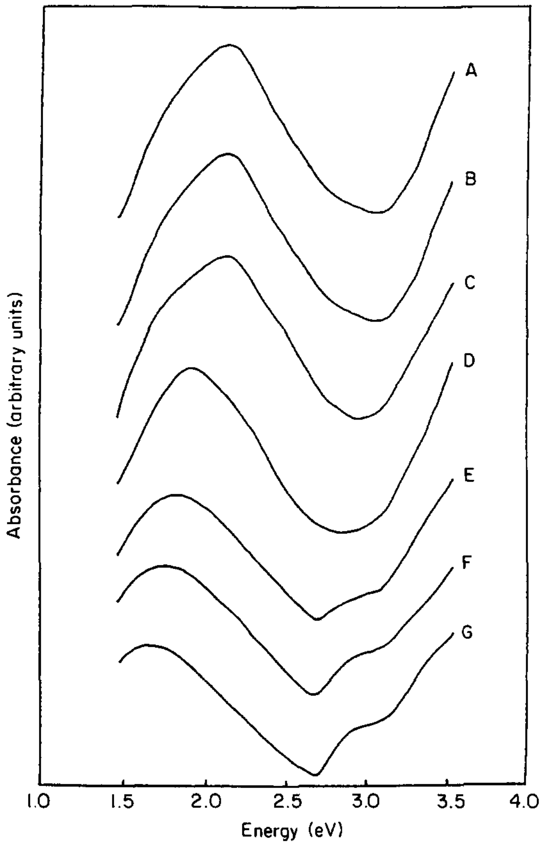


Figure 8 The change in the absorption spectrum of emeraldine base during its protonation: A, pH 6, 16 h; B, 10^{-4} M HCl, 24 h; C, 2 × 10^{-4} M HCl, 3 h; D, 4 × 10^{-4} M HCl, 4.5 h; E, 6 × 10^{-4} M HCl, 2 h; F, 8 × 10^{-4} M HCl, 16 h; G, 10^{-3} M HCl, 2 h

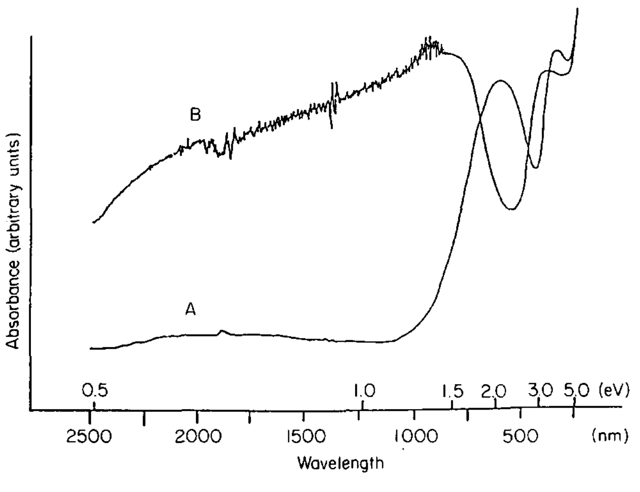


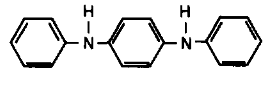
Figure 9 Absorption spectra of A, emeraldine base and B, emeraldine hydrochloride

(A) and pH 4.0 (1.0 × 10^{-4} N HCl) (B) are essentially identical. As the acidity was increased from pH 3.7 (2.0 × 10^{-4} N HCl) to pH 3.0 (1.0 × 10^{-3} N HCl), i.e. spectra B to G inclusive, the maximum at ~2.1 eV in B decreased monotonically to ~1.6 eV in G. At the same time the minimum in B decreased from ~3.1 to ~2.8 eV in D. In E a new absorption appeared at ~3.0 eV which became progressively more well defined in spectra F and G.

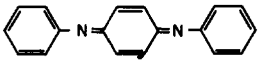
As shown in *Figure 9*, the emeraldine base in 0.1 M aqueous KOH exhibits an absorption maximum at 2.1 eV and another absorption maximum at ~3.9 eV. The absorption peak at ~2.1 eV tails down to ~1.2 eV. Extrapolation of the slope down to the baseline gives a value of ~1.4 eV. Between the two absorption maxima, there is a minimum at ~2.7 eV; there is also a second minimum at ~4.8 eV. On the other hand, the emeraldine hydrochloride in 1 N HCl solution shows one absorption maximum at ~1.4 eV and another maximum at ~3.0 eV. The absorption peak at ~1.4 eV tails down to the i.r. regime of the spectrum reaching a value of 0.5 eV at the cut-off of the spectrum. Between these two absorption maxima there is a minimum at ~2.3 eV. A second small minimum appears at ~4.8 eV.

Protonic acid doping of polyaniline has been extensively investigated. The polymer goes through an insulator ($\sigma < 10^{-10}$ S cm^{-1}) to conductor (~10 S cm^{-1}) transition during protonation of the emeraldine base form. It has been proved that the conducting state (emeraldine salt) is metallic with a significant amount of Pauli magnetic susceptibility[3]. The doping process involves the conversion of alternating benzenoid amine nitrogen units (reduced unit) and quinoid imine nitrogen units (oxidized unit) to a semiquinone nitrogen cation type polaronic lattice as shown in *Figure 10*. The metallic emeraldine salt form shows a finite density of states at the Fermi energy level[6].

Studies have recently been carried out[38–40] on oligomers of polyaniline in order to understand the structure of the emeraldine oxidation state of polyaniline. For example, diphenyl-*p*-phenylenediamine



is a dimer of aniline with a phenyl ring as a cap on the end, with an absorption peak[38,41,42] around 4.1 eV. This compound is completely oxidized to diphenyl-*p*-phenylenediimine



which has an absorption peak around 2.8 eV in EPA solvent (a mixture of ether, isopentane and ethanol, in 8:3:5 ratio). A simple correlation between emeraldine base and this compound can be achieved by assuming that the benzenoid amine units cause the 3.9 eV

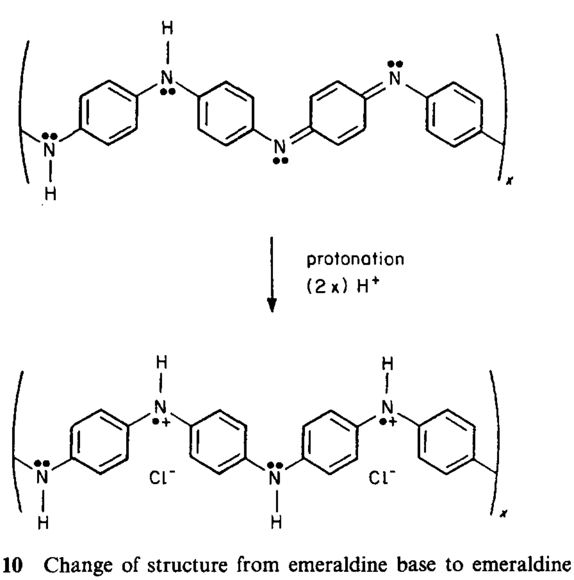


Figure 10 Change of structure from emeraldine base to emeraldine salt during protonation

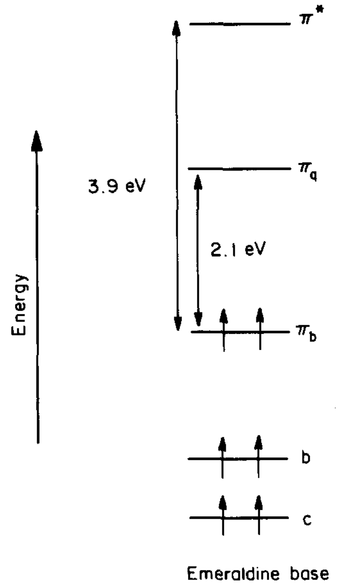


Figure 11 Energy level diagram of emeraldine base

absorption similar to that (4.1 eV) of the diamine (described above) and the quinoid imine units cause the 2.1 eV absorption similar to that (2.8 eV) of the diimine. This simplified correlation is not far from the theoretical calculation. The absorption at 2.1 eV for the emeraldine base has been attributed by Stafstrom *et al.*[43] to the excitation from HOMO (highest occupied molecular orbital, π_b) of the three-ring benzenoid part of the system to LUMO (lowest unoccupied molecular orbital, π_q) of the localized quinoid ring and the two surrounding imine nitrogens (see *Figure 11*). The excitation of the 3.9 eV peak was attributed to two different transitions. One is the π–π^* transition, similar to that of leucoemeraldine, and the other one is a transition from low-lying orbitals to the π_q orbital.

All the theoretical calculations on the emeraldine base form of polyaniline were based on our proposed structure, which contains alternating benzenoid amine nitrogen units and quinoid imine nitrogen units. This has been indirectly proved by electrochemistry[2,4], chemical analysis[44] and e.s.r. studies[45,46]. Recently, n.m.r. studies[47,48] have provided the strongest evidence for this proposed structure.

In order to understand the change of band structure during protonation of the imine nitrogens of emeraldine base, protonation experiments were carried out at different pH values. It was found that the band structure underwent a great change between pH 4 and 3. Therefore, one experiment was performed under conditions very close to equilibrium at six different pH values between 4 and 3. The emeraldine salt film was then deprotonated in distilled water for more than 16 h and was equilibrated at pH 4 overnight.

The curves in *Figure 8* clearly show the tendency of the peak to shift from ~2.1 to ~1.5 eV when the HCl concentration increases from 10^{-4} to 10^{-3} M HCl. At the same time, the peak at ~3.0 eV starts to grow during this change. The observation of this peak is consistent with the deprotonation of the polymer when the potential of polyaniline *versus* Pb/Pb^{2+} is above 0.7 V as discussed in the previous section. This indicates that deprotonation can be achieved either by decreasing the proton concentration in the solution or by increasing the applied oxidizing potential. If we increase or decrease the proton concentration, the reaction is only an acid/base reaction and the polymer retains the same oxidation state.

The shift of the peak at 2.1 to 1.5 eV during protonation means that the peaks at 1.5 and 2.1 eV have the same origin. In the theoretical calculation for polyaniline by Sjogren and Stafstrom[49], the 2.1 eV peak in the spectrum of emeraldine base is shown to have the same origin as the 2.3 eV peak in the spectrum of pernigraniline. As shown in *Figure 7*, band a is the half-filled polaronic band in emeraldine salt. At the same time, band a is the empty conduction band of pernigraniline. The shift of peak position (from 2.1 to 1.5 eV) starts at pH 4, which is consistent with the onset of conductivity during protonic acid doping of polyaniline as reported before. The sharp change in spectrum between pH 4 and 3 was also observed recently by Wan[50]. However, in this study the peak at 2.1 eV does not shift slowly to 1.5 eV; instead the peak at 2.1 eV decreases while the peak at 1.5 eV increases simultaneously. Similar results to that of Wan have been reported by other authors[14]. However, Weiss *et al.*[51] showed that the peak at 1.5 eV shifted systematically about 260 nm (approximately 70 nm per pH unit) over the pH range 3–7 on the spectra of their polyaniline/dinitrocellulose composite film. We believe that the formation of two peaks is simply an indication of the formation of protonated and non-protonated domains in the polymer at such a low protonation level. If the polymer chain is not in a confined condition and is allowed to equilibrate with the surroundings, a single peak in the spectrum is expected.

Protonation of polyaniline results in an increase in the amount of charge on the polymer backbone, thus increasing the conductivity. However, it is clear that the dramatic 10-fold increase in conductivity from insulator to conductor is due to lattice distortion of the polymer chain, which then increases the mobility of the charges in the polymer, and not simply due to the increase in the amount of charge on the chain. The half-filled polaronic band model explains the observation of metallic behaviour in the emeraldine salt form of polyaniline. Emeraldine salt will not be completely protonated until the pH of the solution reaches 0. When the pH of the solution is 3, it is expected that the polymer will be protonated to only a very small extent. The shift of the peak at 2.1 eV to 1.5 eV between pH 3 and 4 indicates that the lattice distortion of the polymer backbone occurs even with a small amount of protonation.

Emeraldine salt

As shown in *Figure 12*, the spectrum of a solution of chemically made emeraldine base in 80% acetic acid is almost identical to that of the free-standing electrochemically made emeraldine·$2HClO_4$ film. Hence the spectra are not affected by the nature of perchlorate or acetate anion.

Figure 13 gives a series of spectra at different concentrations of emeraldine base in 80% acetic acid. The intensity of each peak decreases when the concentration decreases. The intensity of each peak is roughly proportional to the concentration. In general, peaks A, B and C more or less obey Beer's Law, i.e. $A = abc$, where A is absorbance, a is molar absorptivity, b is sample cell length and c is concentration.

Mohilner *et al.*[52] suggested in 1962 that anodically formed polyaniline is principally emeraldine. They

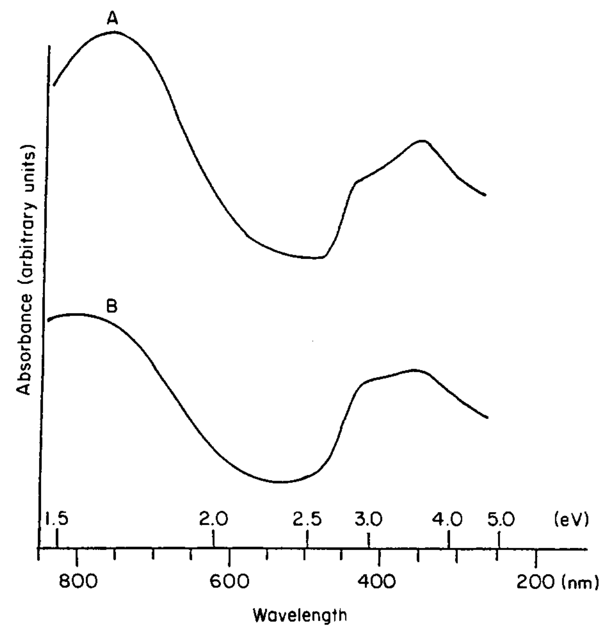


Figure 12 Absorption spectra of A, emeraldine base in 80% acetic acid and B, electrochemically grown emeraldine hydroperchlorate film

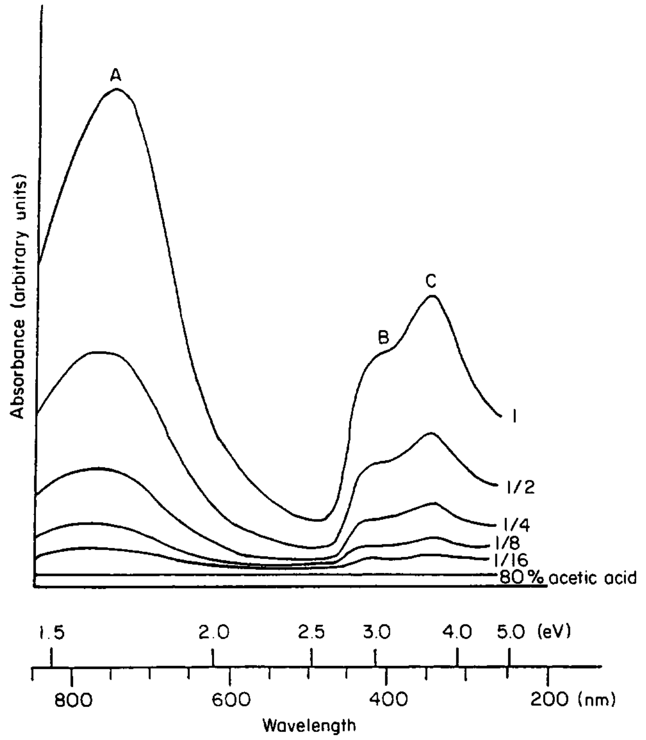


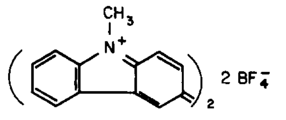
Figure 13 Absorption spectra of emeraldine base in 80% acetic acid at relative concentrations of 1, 1/2, 1/4, 1/8 and 1/16. Peaks A, B and C are discussed in the text

reported examples of similar behaviour between electrochemically synthesized and chemically made material. Both materials were reported to be amorphous and neither melted up to 300°C. In addition, it was found that the electrochemically made emeraldine base dissolved in cold 80% acetic acid to give the same green colour as chemically made emeraldine base dissolved in cold 80% acetic acid. Both were reported to have similar i.r. spectra. No visible spectra were reported.

We obtained the solution spectrum of emeraldine base dissolved in 80% acetic acid and compared it to that of electrochemically grown film. Identical spectra were obtained as shown in *Figure 12*. Since the chemically made powder shows the same optical properties as electrochemically grown film, all discussions based on electrochemically grown film are also valid for chemically made powder. Furthermore, these solutions should exhibit significant electronic conductivity as well as ionic conductivity. The identical electrochemical behaviour of chemically made and electrochemically made polymer has been demonstrated previously[2]. Both materials exhibit reversibility in both oxidation/reduction and acid/base reactions.

In the previous section we pointed out that the high conductivity of emeraldine salt was attributed to the low absorption edge extended through the i.r. regime of the band at ~1.5 eV, which is consistent with metallic behaviour. This raises the question of whether any absorption band is attributed to the interchain interaction. To answer this we can either apply high pressure to a piece of film or dilute the polymer solution to see the change in the spectrum.

Yakushi *et al.*[29] could not obtain direct experimental evidence for an interchain transition, because high pressure did not significantly affect the transmittance data of polypyrrole. On the other hand, Wellinghoff *et al.*[53], studying polycarbazole, found in their model compound 9,9-dimethyl-3,3′-dicarbazolyl tetrafluoroborate



that there is an intermolecular charge transfer band at 1900 nm, because the intensity of the 1900 nm transition increased continuously relative to the other band absorbance at 8500 nm with increasing solution concentration.

The observed absorption spectra of the emeraldine salt (*Figure 13*) do not show any interchain effects. This is proved by diluting the solution of polyaniline in 80% acetic acid. If there is any absorption peak due to interchain interaction, when the polyaniline concentration decreases the peak will disappear or decrease dramatically. The experimental results demonstrate that the absorption bands do not deviate significantly from Beer's law. Although no significant interchain interaction was found in the emeraldine salt, the experimental results of Wan[50] on emeraldine base in *N*-methylpyrrolidone (NMP) solution show a red shift of the peak at 630 nm when the concentration of the polymer solution is high. This suggests that there is some interchain interaction which decreases the excitation energy needed to transfer the electrons from the benzenoid rings to the quinoid rings in the polymer chain. Wan thinks this shift may be due to an unpaired electron on the quinoid segment of the polyemeraldine chain. Stafstrom *et al.*[43] have shown that any charge removed from the benzenoid amine segments to form positive polarons or any charge added to the quinoid imine segments to form negative polarons will cause a transition lower than the 2.0 eV absorption. Therefore, any charge separation in the same chain or charge transition from one chain to the other will cause a red shift of this 2.0 eV absorption peak.

As shown in *Figure 14*, the spectrum of emeraldine hydrochloride in 70% H_2SO_4 ($H_0 = -5.65$) is identical

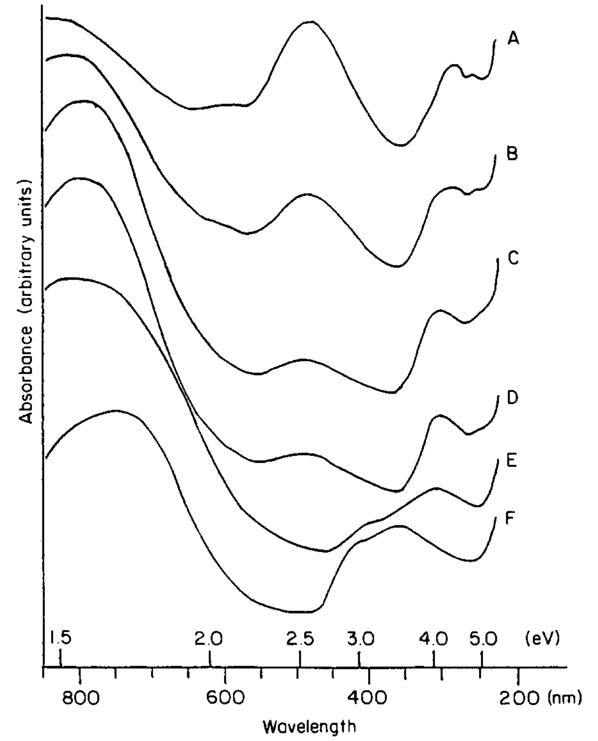
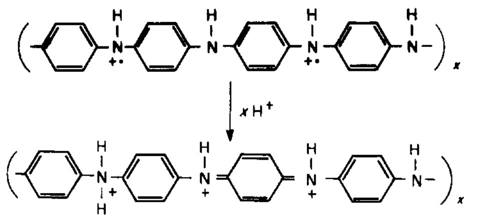


Figure 14 Absorption spectra of emeraldine hydrochloride in H_2SO_4 solutions of various acid strengths (H_0 refers to the Hammett acidity function): A, 96% H_2SO_4 ($H_0 = -8.98$); B, 90% H_2SO_4 ($H_0 = -8.27$); C, 85% H_2SO_4 ($H_0 = -7.66$); D, 80% H_2SO_4 ($H_0 = -6.97$); E, 75% H_2SO_4 ($H_0 = -6.30$); F, 70% H_2SO_4 ($H_0 = -5.65$)

to that of emeraldine base in 80% aqueous acetic acid as observed in *Figure 13*. When the acidity is increased, the peak at ~3.0 eV decreases in intensity. This peak disappears between the concentration of 75% and 80% H_2SO_4. Above 80% H_2SO_4, a new peak at ~2.5 eV starts to grow and becomes very intense. On the other hand, the peak at ~1.6 eV decreases in intensity. The colour of the solution changes from green to blue to violet to brown when the concentration increases from 70% to 96%. When concentrated H_2SO_4 was added to the more dilute solutions, spectra characteristic of the more concentrated solutions were obtained. Hence the effects are reversible.

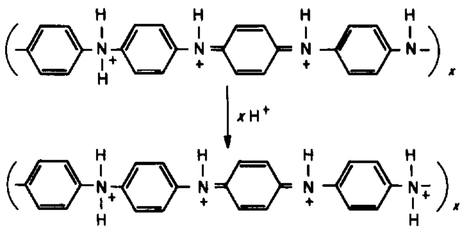
Since 12 M HCl has an acidity function of only $H_0 = -4.41$ compared to $H_0 = -5.65$ for 70% H_2SO_4, the acidic strength is still not high enough to cause significant protonation on the polyaniline in 12 M HCl. We would not expect any change of spectra in 12 M HCl.

The spectra shown in *Figure 14* have a transition between 75% and 80%, where the peak at ~3.0 eV disappears. We believe this could be related to the transition from polarons to bipolarons due to significant protonation.



It has been found both experimentally[39] and theoretically[49] that the bipolaron lattice is preferred in the tetramers at their half oxidation state. Therefore, we believe that this transition is due to significant protonation which breaks the conjugation into small segments, thus the lattice structure changes from polaronic to bipolaronic.

When further protons are added to the amine nitrogen, a peak at ~2.5 eV starts to grow and the peak at 1.5 eV starts to decrease. This could indicate that the quinoid segment now has localized positive charges, when all the amine nitrogens are protonated.



The peak at ~2.5 eV may be due to the electron transition from the benzenoid rings to the quinoid rings, similar to the case of emeraldine base or pernigraniline. The fine structure at ~4.8 eV is an indication of the existence of isolated benzene rings due to the extensive protonation of amine nitrogens.

Figure 15 is a qualitative study of the slow oxidation of emeraldine salt to pernigraniline. The peak at ~1.6 eV shifts to higher energy during the treatment with ammonium persulfate. Two peaks at ~3.0 and ~3.6 eV decrease in intensity. Another small peak appears at

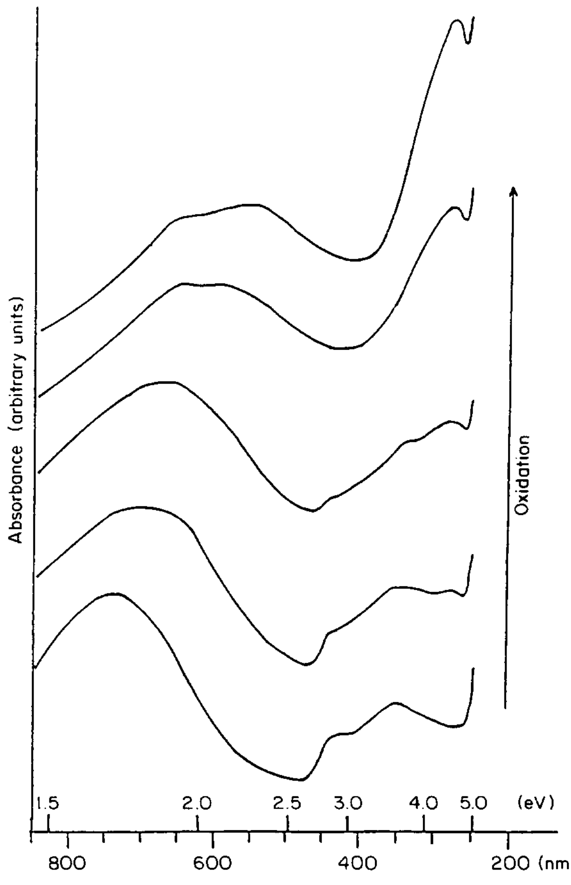


Figure 15 Absorption spectra of emeraldine base in 80% acetic acid during treatment with ammonium persulfate

~4.5 eV (278 nm) and becomes more intense during treatment with $(NH_4)_2S_2O_8$.

Recently Sun *et al.*[35] synthesized a pernigraniline form of polyaniline that has two absorption maxima, at 528 nm (~2.35 eV) and 320 nm (~3.88 eV). The absorption at 528 nm is the transition through the Peierls gap of the dimerized pernigraniline structure. The absorption at 320 nm is probably the transition from the low-lying orbitals to the conduction band. Due to the big absorption peak at 278 nm, the peak at 320 nm is not clearly shown in *Figure 15*.

CONCLUSION

Our experimental findings have provided detailed information on the electronic structures of polyaniline at various oxidation and protonation stages. We have investigated the interconversion of band structures using optical-absorption data in two ways: (1) changing the degree of protonation by changing the acid strength of the polymer surroundings; and (2) changing the degree of oxidation by changing an applied electrochemical potential or treating the polymer with different amounts of oxidizer.

When the pH is above 2, very little protonation occurs on leucoemeraldine base. It has a π–π^* absorption peak at 3.94 eV. When pH < 2, the polymer is protonated. In 9 N H_2SO_4 solution, the absorption peak shifts to 4.17 eV. This is an indication of reduced conjugation length due to the protonation on the amine nitrogens, which then divides the polymer chain into small conjugated segments.

The oxidation of leucoemeraldine in 0.1 M $Pb(BF_4)_2$ + 0.5 M HBF_4 solution causes two absorption bands to rise within the π–π^* absorption band. It is believed that a polaronic lattice structure has been formed in this oxidation process. The 1.5 eV absorption peak is due to the transition from the valence band to the polaronic defect band. The 2.7 eV absorption peak is due to the transition from the lower-lying band to the polaron band. Both peaks show blue shift during the oxidation of the polymer from 0.2 to 0.7 V *versus* Pb. Above 0.7 V, the oxidation state exceeds the level of emeraldine and a significant deprotonation causes the peak near 2.9 eV to decrease in intensity. When the polymer is oxidized to pernigraniline, the dimerized structure contains a Peierls gap of 2.35 eV.

Emeraldine base has an absorption at 2.1 eV which is due to the electronic excitation from benzenoid rings (π_b) to quinoid rings (π_q). The peak at 3.9 eV was attributed to two different transitions: one is the π–π^* transition similar to that of leucoemeraldine; the other is a transition from low-lying orbitals to the π_q orbital. When the pH changes from 4 to 3, the absorption at 2.1 eV shifts to 1.5 eV, due to lattice distortion of polyaniline to a polaronic structure by protonation of the imine nitrogens. When the acid strength increases to above $H_0 = -5.65$ (70% H_2SO_4), significant protonation seems to break down the polaronic structure to a confined bipolaronic structure. In highly acidic solution ($H_0 = -8.98$), the existence of isolated quinoid imine nitrogen units (~2.5 eV) and benzene units (~4.8 eV) seems to be obvious.

The optical-absorption study of different concentrations of emeraldine salt in 80% acetic acid does not show any interchain interaction. However, the study of emeraldine base in NMP by Wan seems to indicate some interchain interaction in the high concentration range of polymer solution.

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