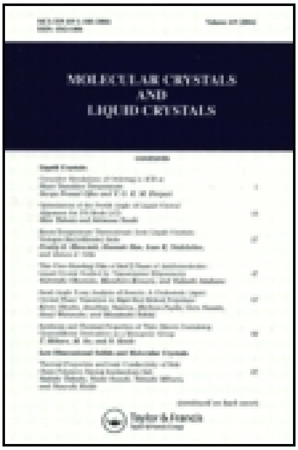

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# “Polyaniline”: Interconversion of Metallic and Insulating Forms

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# "POLYANILINE": INTERCONVERSION OF METALLIC AND INSULATING FORMS

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Abstract "Polyaniline" has been synthesized in various forms both chemically and electrochemically in aqueous media. The quinoid-benzenoid-diimine form, an insulator, is doped by dilute aqueous protonic acids to the metallic regime ($\sigma = 5$ ohm$^{-1}$cm$^{-1}$; compressed pellet) to give the corresponding iminium salt. This represents a new type of p-doping phenomenon in a conducting polymer. Both these forms are stable in the presence of air and/or water. The doping process is reversed by treatment with aqueous alkali. Cyclic voltammetry studies in an aqueous electrolyte show excellent reversibility between selected reduced and oxidized forms of polyaniline.

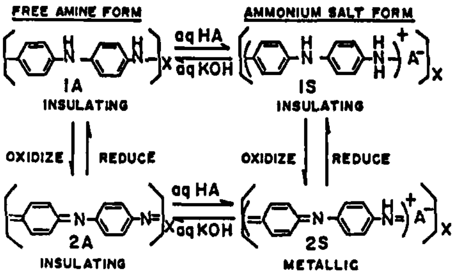
## INTRODUCTION

"Polyaniline" has been described in many papers[1] during the past approximately 100 years in various, usually ill-defined forms such as "aniline black", "emeraldine", "nigraniline", etc., synthesized by the chemical or electrochemical oxidation of aniline, $(C_6H_5)NH_2$. The present study involves an investigation of some of the different forms in which polyaniline may exist and also its novel p-doping to the metallic regime by a simple acid/base reaction involving no formal oxidation of the polymer.

## CONSTITUTION OF POLYANILINE

We believe polyaniline can be prepared in the four idealized forms given below, at least when its synthesis and any subsequent treatment are carried out in aqueous media. The polymers in the left-hand column are considered as being derived from the amine, 1A

(A = amine), and are hence designated (in increasing degree of oxidation) as 1A and 2A.



These forms may be interconverted at will by chemical and/or electrochemical oxidation or reduction. The chemical or electrochemical oxidation of 1A to 2A involves the reaction:

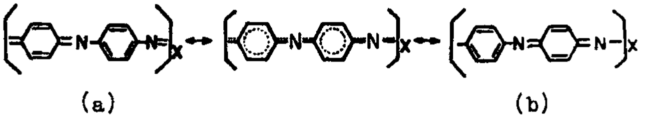
$$1A \rightarrow 2A + 2H^{+} + 2e^{-} \qquad (1)$$

The materials in the right-hand column are regarded as being derived from the ammonium salt, 1S (S = salt), and are hence designated (in increasing degree of oxidation) as 1S and 2S. These forms may also be interconverted at will by chemical and/or electrochemical oxidation or reduction.

Preliminary electrochemical studies suggest that it may be possible to oxidize both the 2A and 2S forms further to forms 3A and 3S i.e, to $[(=(C_6H_4)=N-(C_6H_4)-N=)^{+y}A^{-}_{y}]_x$ and $[(=(C_6H_4)=N-(C_6H_4)-N(H)=)^{(y+1)+}A^{-}_{(y+1)}]_x$ respectively. These 3A and 3S forms must remain as speculative only, until they have been characterized.

A given "A" form, e.g. 1A, may be converted to a given "S" form, e.g. 1S, by treatment with an aqueous protonic acid, such as HCl. The acid may be removed to regenerate the "A" form by treating the "S" form with an aqueous solution of a base such as KOH. Elemental analysis of form 2S shows that even when form 2A is treated with concentrated (10 molar) aqueous HCl that only one of the two N atoms in the monomer unit is protonated. This is not surprising since in a weak base containing two N atoms, protonation of the first N atom is expected to be easier than protonation of the second.

Form 2A is of particular interest since, like $(CH)_x$, it appears to have a degenerate ground state, (a) and (b), viz.,



and hence it might exhibit defect states in the form of solitons.

## SYNTHESIS OF POLYANILINE

In the present investigation polyaniline was synthesized chemically as a dark blue/black powder, $[(=(C_6H_4)=N-(C_6H_4)-N(H)=)^+Cl^-]_x$, (form 2S) by treating a 1 molar solution of aqueous HCl containing dissolved aniline, with the oxidizing agent ammonium peroxydisulfate, $(NH_4)_2S_2O_8$. Protonation was completed by washing the powder with 1 molar aqueous HCl followed by drying under a dynamic vacuum ( ~ 10 microns) at room temperature for several days to remove water and HCl. After this time the conductivity (compressed pellet; four probe) had decreased to a constant value of ~ 5 $ohm^{-1}$ $cm^{-1}$. Elemental analysis of several samples (e.g., %C + %H + %N + %Cl = 97.5%; 0%S) showed that a maximum of one HCl combined with each monomer repeat unit (containing two N atoms). Nonvolatile acids such as $H_2SO_4$ should not be used in any stage in the synthesis as a substitute for HCl since upon removal of the water under vacuum a thin film of concentrated $H_2SO_4$ will remain on the particles of the powder.

The 2S form can be converted to the 2A form, a dark purple/black powder exhibiting a copper glint ( $\sigma$ , 2 probe of compressed copper-colored pellet, ~ $10^{-11}$ $ohm^{-1}cm^{-1}$) by stirring with a 0.5 molar solution of KOH in a water/methanol mixture followed by washing with a water/methanol mixture and drying under a dynamic vacuum. Elemental analysis shows that essentially all the HCl is removed by this procedure. For example, in one preparation only 0.04 mole of HCl remained for every mole of monomer repeat unit (%C + %H + %N + %Cl = 97.37%; S, "trace").

Excellent cohesive dark green films of form 2S (containing fluoroborate anion) were synthesized electrochemically on Pt foil in 5 ml of 48% aqueous $HBF_4$ containing 1 ml of aniline and 10ml of distilled water. Successive increments of 0.05V were applied between two Pt electrodes (each 1 $cm^2$; 1 cm apart) until a potential of 0.75V was reached. The current was not permitted to rise above 1 mA. The potential was then held at this value (anode potential 0.72V vs. SCE, NaCl salt bridge) for 20 hours and the anode on which the film (ca. 3 mg.) had been deposited was washed with 16% aqueous $HBF_4$ and dried under dynamic vacuum. Free standing films can be prepared using a conducting glass anode. The I/R spectra of the chemically and electrochemically synthesized forms of 2S were identical except for differences attributed to the different anions.

Form 2A may be reduced to form 1A chemically by a reducing agent such as hydrazine, $N_2H_4$, or electrochemically at a potential of ~ 0.8V (vs. $Zn^{+2}/Zn$). The electrochemically prepared 1A exists as a very pale yellow, semitransparent thin film.

## PROTONIC ACID DOPING

The conventional method of p-doping (oxidizing) an organic polymer involves removal of electrons from the pi system of the polymer by chemical or electrochemical oxidation:

$$\text{(polymer)} \rightarrow \text{(polymer)}^{+y} + ye^- \qquad (2)$$

$$\text{e.g. } (CH)_x + (1.5xy)I_2 \rightarrow [(CH)^{+y}(I_3^-)_y]_x \qquad (3)$$

In principle it should be possible to p-dope a conducting polymer by adding a proton, which may interact with and hence partly depopulate the pi system with concommitant increase in conductivity of the polymer:

$$\underset{\text{(base)}}{\text{(polymer)}} + \underset{\text{(acid)}}{yH^+} \rightarrow \underset{\text{(salt)}}{(\text{polymer}H_y)^{+y}} \qquad (4)$$

This is a simple acid/base interaction, in which no formal oxidation or reduction occurs.

We have found that when form 2A is washed with an aqueous protonic acid such as HCl or $HBF_4$ it undergoes an insulator-metal transition involving an increase in conductivity of ~ $10^{11}$:

$$\underset{\text{(form 2A)}}{[=(C_6H_4)=N-(C_6H_4)-N=)} + xHCl \rightarrow \underset{\text{(form 2S)}}{[(=(C_6H_4)=N-(C_6H_4)-N(H)=)^+Cl^-]_x} \qquad (5)$$

This transition is readily reversed by treatment with aqueous base.

The extreme sensitivity of the conductivity of form 2A to the pH of the aqueous HCl solution with which it is equilibrated is illustrated in Figure 1.

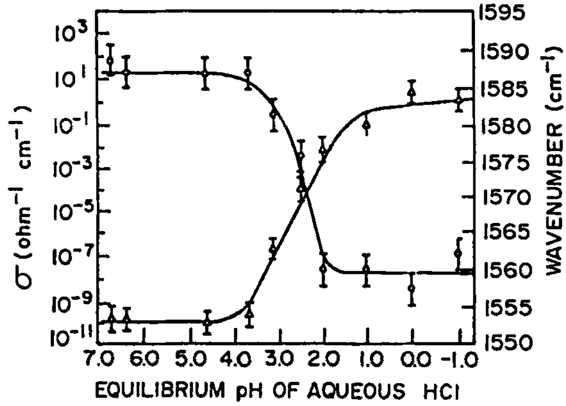


FIGURE 1 Relationship between the final (equilibrium) pH of the aqueous HCl with which polyaniline (form 2A) is washed and (1) the conductivity of the resulting dried powder, (Δ); (2) the frequency of the ring breathing absorbance, (O), of the dried powder.

Each data point gives the conductivity of a ~ 250 mg sample of form 2A after it had been stirred with 500 ml of aqueous HCl of various selected concentrations. After 55 hours the pH of the solution was measured, the resulting polyaniline powder was dried under dynamic vacuum for 24-72 hours and its conductivity, I/R spectra and elemental composition were determined.

The relationship between the conductivity of selected samples and the percent doping is given in Figure 2. Since each HCl molecule which reacts with form 2A is associated with a $Cl^-$ ion, the (Cl:N ratio)•100 will represent the percent of the N atoms which are protonated, i.e. will represent the percent doping. The curve given in Figure 2 is characteristic of conventional doping of a conducting polymer, i.e., the conductivity rises rapidly at the beginning of the doping process and then shows little change even though the polymer becomes more highly doped.

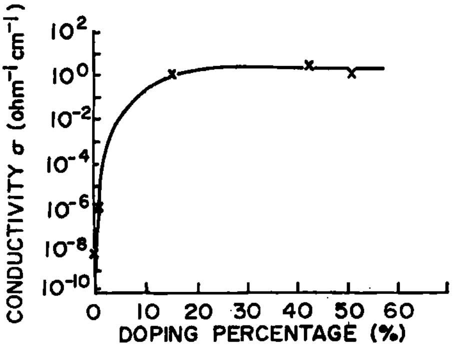
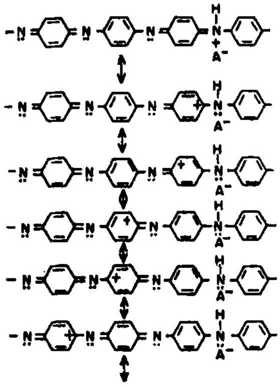


FIGURE 2 Relationship between the conductivity of polyaniline (form 2A) and percentage of protonation, i.e. percentage doping.

Also shown in Figure 1 is the change in the frequency of the I/R ($C_6H_4$) ring breathing absorbance. As can be seen, the frequency of this absorbance decreases as the conductivity increases. If the proton should interact and partly depopulate the pi system of the polymer the frequency of this mode may decrease with increasing protonation since the C-C bond order (and hence, force constant) in the ($C_6H_4$) ring decreases with decreasing population of the bonding pi orbitals. As can be seen from the classical resonance forms of form 2S given below, it is to be expected that positive charge will be transferred in part from the N to the pi system of the ($C_6H_4$) rings. This will result in a partial delocalization of positive charge along the polymer chain. The charge will naturally be pinned close to the anion, $A^-$ and delocalization will become less extensive as the distance from the $N^+$ atom increases.



## ELECTROCHEMISTRY

In order to obtain a more complete understanding of the oxidation/reduction relationship between the 1A and 2A forms of polyaniline, cyclic voltametry studies (Zn reference electrode) were performed using polyaniline electrochemically deposited as a thin film on a Pt electrode as described above (see Figure 3). The electrolyte, (1.0M $ZnCl_2$ + 0.5M $NH_4Cl$) has a pH ~ 4. At this pH, as can be seen from Figure 1, the polyaniline will exist predominantly in the "A" form. Potentials vs. the normal hydrogen electrode, NHE, may be obtained by subtracting 0.76V from the experimental values observed vs. the Zn reference electrode.

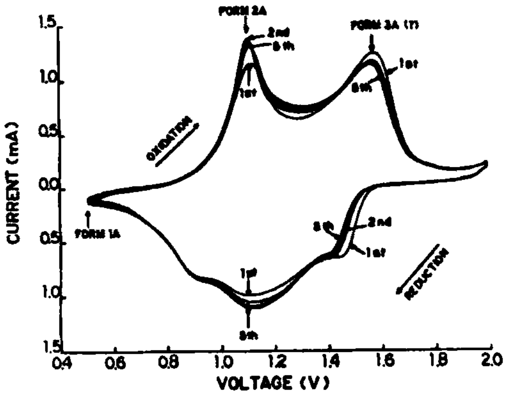


FIGURE 3 Five cyclic voltammograms between 0.50V and 2.0V (5mV/sec) of polyaniline in (1.0M $ZnCl_2$ + 0.5M $NH_4Cl$; pH ~ 4) vs. $Zn^{+2}/Zn$ reference electrode.

It should be noted that good cyclic voltammograms are usually obtained more readily with thin films than with powders. The cyclic voltammograms described here cannot, therefore, be correlated exactly with a given form of the chemically synthesized polyaniline described above.

In the oxidation cycle the pale yellow form 1A is characterized by a potential of ~ 0.50V; a dark green form, possibly form 2A, by a peak potential at 1.10V and a dark blue form, possibly form 3A, by the potential at 1.58V. It is possible that the dark blue material characterized by the peak at 1.58V might actually be form 2A and the dark green material characterized by the peak at 1.10V might merely be partly oxidized form 1A. However, until the nature of the peak at 1.58V is clarified, the peak at 1.10V will be assumed to be characteristic of form 2A. It should be stressed that the cyclic voltammograms are very sensitive to changes in the pH of the electrolyte. The cyclic voltammograms discussed here are not necessarily characteristic of polyaniline in electrolytes other than that used in these studies.

In view of the less than ideal reversibility of the above redox processes a second set of cyclic voltammograms were obtained under identical experimental conditions using an identical film of polyaniline except that the oxidation step was arbitrarily terminated at 1.40V. These are shown in Figure 4.

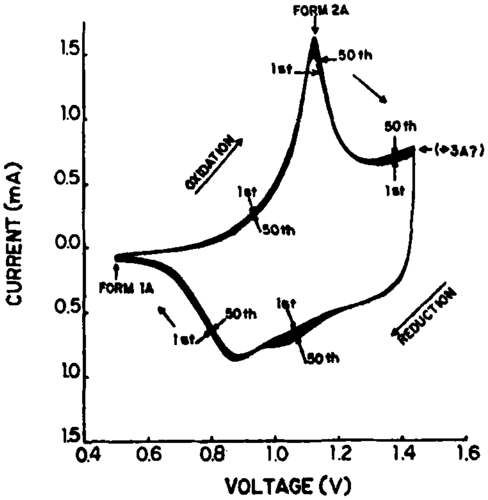


FIGURE 4 Fifty cyclic voltammograms between 0.50V and 1.40V, (5mV/sec) of polyaniline in (1.0M $ZnCl_2$ + 0.5M $NH_4Cl$; pH ~ 4) vs. $Zn^{+2}/Zn$ reference electrode.

It can be seen that excellent reversibility is obtained under these conditions, the coulombic capacity decreasing to only 99.1% after the 50th cycle. These observations are of importance in our battery studies described elsewhere.[2]

## CONCLUSIONS

It is apparent that the diverse forms in which polyaniline may be synthesized and interconverted results in this material having a potentially large and rich chemistry, electrochemistry and physics. The novel protonic acid doping of the quinoid benzenoid diimine form of polyaniline to the metallic regime is of particular experimental and theoretical interest.

## ACKNOWLEDGEMENTS

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2. A. G. MacDiarmid, S. L. Mu, N. L. D. Somasiri and W. Wu, reported elsewhere in these proceedings.