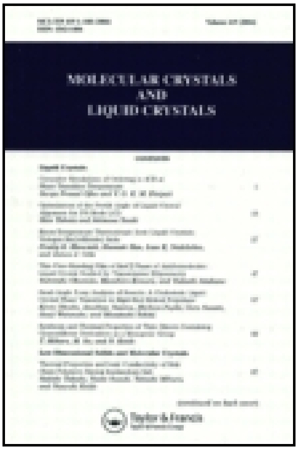

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Polyaniline: Protonic Acid Doping to the Metallic Regime

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POLYANILINE: PROTONIC ACID DOPING TO THE METALLIC REGIME

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Abstract

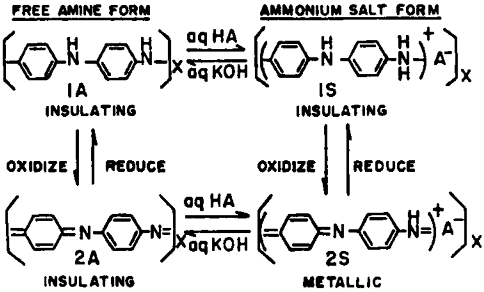
"Polyaniline" has been synthesized in various forms both chemically and electrochemically in aqueous media. The quinoid-benzenoid-diimine form, an insulator, is doped by dilute aqueous protonic acids to the metallic regime ($\sigma \sim 5$ ohm^{-1}cm^{-1}; compressed pellet) to give the corresponding iminium salt. The polymer is not oxidized during the doping process. This represents a new type of p-doping phenomenon in a conducting polymer. Both these forms of polyaniline are stable in the presence of air and/ or water. The doping process is reversed by treatment with aqueous alkali. The mechanism by which doping occurs is discussed.

INTRODUCTION

"Polyaniline" has been described in many papers[1-9] during the past approximately 100 years. It has been reported as existing in various, usually ill-defined forms such as "aniline black", "emeraldine", "nigraniline", etc. synthesized by the oxidative chemical or electrochemical polymerization of aniline. Extensive chemical and electrochemical studies by Jozefowicz et al.[2,3] have demonstrated the high conductivity of certain of the oxidized forms and the dependence of the conductivity on the pH of the solutions with which the polyaniline is treated and the sensitivity of the conductivity to the humidity of the environment to which the material is exposed. Very recent chemical and electrochemical studies by several groups have confirmed certain of these observations and have reported new properties of the materials[4-9]. A better understanding of the chemical composition of the various forms of polyaniline and the processes involved in their chemical and electrochemical interconversion has, however, only very recently started to unfold.

CONSTITUTION OF POLYANILINE

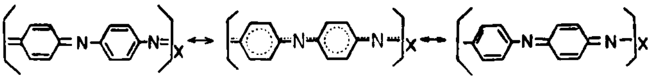
We believe polyaniline can be prepared in the four idealized forms given below, at least when its synthesis and any subsequent treatment are carried out in aqueous media. All forms are insoluble in water. The polymers in the left-hand column are considered as being derived from the amine, 1A (A = Amine),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

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 base such as KOH or NH_4OH. 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.,



(a) (b)

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

PROTONIC ACID DOPING

The oxidized forms of polyaniline, 2A and 2S, may be equilibrated with aqueous acid solution. This will result in partial protonation of the nitrogen atoms, the extent of protonation at equilibrium being a function of the pH of the solution. At a given pH the same degree of protonation is obtained regardless of whether one starts with the 2A or 2S form. At pH values $> \sim 4$ the material exists in essentially the non-protonated 2A form. At pH values $< \sim 0$, e.g. 1M acid or stronger, it exists primarily in the 2S form. This corresponds to ~ 50% protonation i.e. to ~ 50% doping.

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[4] .

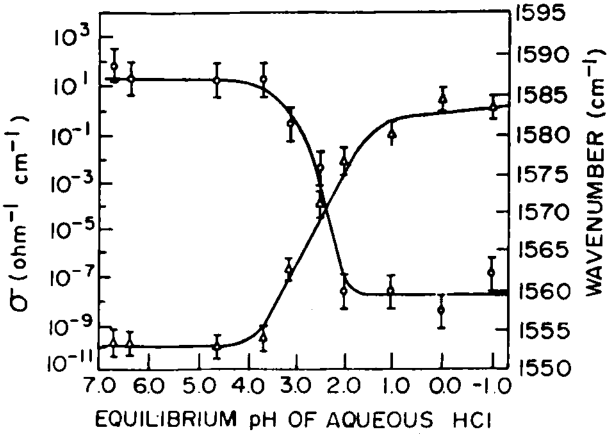


FIGURE 1 Relationship between the final (equilibrium) pH of the aqueous HCl with which polyaniline (form 2A) is washed and (1) the conductivity of the resulting dried powder, (Δ); (2) the frequency of the ring breathing absorbance, (O), of the dried powder.

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, which had attained a constant value, was measured, the resulting polyaniline powder was dried under dynamic vacuum for 24-72 hours and its conductivity, infrared spectra and elemental composition were determined.

The relationship between the conductivity of selected samples and the percent doping is given in Figure 2[4]. 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.

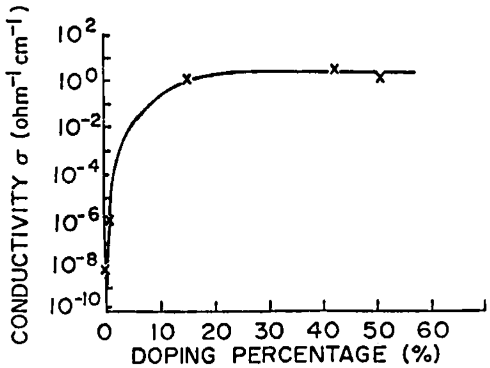


FIGURE 2 Relationship between the conductivity of polyaniline (initially form 2A) and percentage protonation, i.e., percentage doping.

The above results show that when form 2A is washed with an aqueous protonic acid such as HCl it undergoes an insulator-metal transition involving an increase in conductivity of $\sim 10^{10}$:

$$[=(C_6H_4)=N-(C_6H_4)-N=]_x + xHCl \rightarrow \quad [(=(C_6H_4)=N-(C_6H_4)-N(H)=)^+Cl^-]_x \qquad (1)$$

(form 2A) (form 2S)

This transition is readily reversed by treatment with aqueous base. The conductivity of a compressed pellet ($\sigma \sim 5$S/cm) remains constant indefinitely when exposed to laboratory air.

It should be noted that the use of non-volatile acids such as H_2SO_4, either in the synthesis of polyaniline or in its equilibration with acid solutions may lead to problems since when polyaniline wetted with dilute H_2SO_4 is placed in vacuum for drying purposes, the water will evaporate leaving behind a film of concentrated H_2SO_4 on the surface of the polyaniline. The strong H_2SO_4 residue may react at least in part with the polyaniline but at the present time it is not clear how it affects the properties of the material.

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:

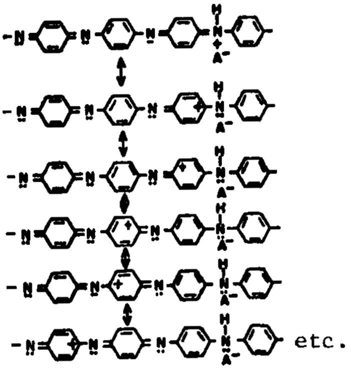
$$(\text{polymer}) \rightarrow (\text{polymer})^{+y} + ye^- \qquad (2)$$

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

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

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

This is a simple acid/base interaction, in which no formal oxidation or reduction occurs. This hypothesis is qualitatively consistent with the change in frequency of the infrared (C_6H_4) ring breathing absorbance shown in Figure 1. 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 should 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.

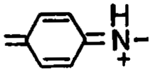
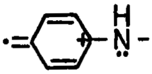


In valence bond terminology the placement of a positive charge on an N atom of a repeat unit of form 2A (to convert it to form 2S) by its reaction with e.g. HCl may be regarded as proceeding via the following hypothetical steps:

$$1)\quad H{-}Cl \rightarrow H\cdot + Cl\cdot \qquad (5)$$

$$2)\quad \underset{SP^2}{=\ddot{N}-} + Cl\cdot \rightarrow \underset{SP^2}{\underset{+}{=\dot{N}-}} + Cl^- \qquad (6)$$

$$3)\quad \underset{SP^2}{\underset{+}{=\dot{N}-}} + H\cdot \rightarrow \underset{SP^2}{\underset{+}{\overset{H}{=\ddot{N}-}}} \qquad (7)$$

The non-bonding electron(s) on the N occupy one of three SP^2 hybrid orbitals. The p_z orbital of the N, which may be regarded as perpendicular to the plane of the paper, containing one N electron, overlaps sideways with the p_z orbital of the adjacent carbon atom on the C_6H_4 ring, which also contains one C electron, to form the pi bond between the C_6H_4 ring and the $\underset{+}{=N(H)-}$, viz.,  . If, due to the positive charge on the N, the electron in the C $2p_z$ orbital were completely transferred to the N p_z orbital, the pi system of the C_6H_4 ring would be depopulated and would assume a positive charge, i.e.  In such a situation the p_z orbital of the N, containing two electrons, would hybridize to form an SP^3 hybrid, one lobe of which would contain a lone pair of electrons. Classical organic chemistry does not, however, predict a complete transfer. A partial transfer of charge only from the C to the N is expected. Resonance forms such as those depicted above are therefore expected, the contribution of forms involving a positive charge on the carbon decreasing with increasing distance from the N, close to which the dopant anion, e.g. Cl^- will reside. From simple electrostatic concepts it is to be expected that positive charge will be more easily delocalized away from the N on to more distant C atoms if the dopant anion is large or if it is solvated. Both these effects will decrease the electrostatic interaction between the positive charge and the anion. Greater delocalization of charge should promote an increase in conductivity of form 2S for a given level of protonation (doping) and decrease the epr line width due to greater electron mobility of any free electrons which may be associated with pi system defects. Preliminary studies suggest that these effects are observed with form 2S[11]. Similar effects have been reported by André, et al.[10] in the n-doping of $(CH)_x$.

The doping of form 2A to the metallic regime (to form 2S) by treatment with aqueous HCl involves a completely new type of p-doping; it does not involve formal oxidation, i.e. loss of electrons from the polymer as is the case in the p-doping of all other conducting polymers. The observation that the reduction potential increases slightly during this conversion does not imply that form 2A has been oxidized. When the potential of form 2A (or form 2S) is measured versus a standard reference electrode such as the standard calomel electrode a very small current flows through the (high impedence) voltmeter. The electrons which pass in this manner reduce a minute amount of form 2A to 1A (or form 2S to 1S). The observed potential is a measure of the ease at which this reduction occurs. However, the actual chemical species involved in the actual reduction is a trace of the protonated species which is always present even at relatively high pH values as shown by equations 8 and 9 below:

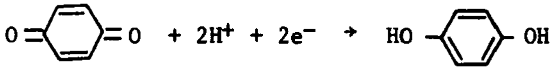
$$\underset{\text{(form 2A)}}{[=(C_6H_4)=N-(C_6H_4)-N=]_x} + (2x)H^+ \rightleftarrows \underset{\text{(completely protonated 2S)}}{[=(C_6H_4)=N(H)-(C_6H_4)-N(H)=]_x^{+2x}} \qquad (8)$$

$$[=(C_6H_4)=N(H)-(C_6H_4)-N(H)=]_x^{+2x} + (2x)e^- \rightleftarrows$$
(completely protonated 2S)

$$[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-]_x \qquad (9)$$
(form 1A)

(The reduction may alternatively be regarded as occuring in consecutive steps involving monoprotonated species.) Hence, the more acidic the solution, the greater will be the amount of protonated species present and the easier it will be to reduce the oxidized form of the polymer. This conclusion is supported by the observation that on decreasing the pH from 5 to 2 the reduction potential increases by 0.053V/pH unit. On decreasing the pH from 2 to 1, the potential increases by an additional 0.023V. In the more acidic solutions the final product is form 1S, the protonated form of 1A.

The processes occuring can be readily understood by examining the analogous more simple, quinone/hydroquinone system which has been extensively studied. The overall reduction reaction ($E^{\circ}_{Red.}$ = 0.70V vs. N.H.E.)



(10)

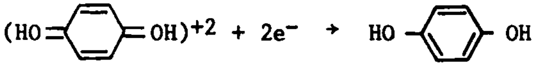
is known to occur in the following steps:

1) Acid/Base Reaction:

(11)

This corresponds to protonic acid doping of 2A (eqs. 1, 8).

2) Reduction Reaction:



(12)

The reduction potential for the overall reduction reaction given by equation 10 is expressed by the relationship:

$$E'_{Red.} = E^{\circ\prime}_{Red.} - \frac{0.059}{n} \log \frac{[HO(C_6H_4)OH]}{[O=(C_6H_4)=O][H^+]^2} \qquad (13)$$

where n is the number of electrons (n = 2) transferred. Step 1 involves no electron transfer and hence is not a redox reaction. The species which is actually reduced in the reduction reaction is not $O=(C_6H_4)=O$ but rather $[HO=(C_6H_4)=OH]^{+2}$. The reduction potential is therefore controlled by the concentration of the $[HO{=}(C_6H_4){=}OH]^{+2}$ and may be expressed by the relationship (derived from equation 12):

$$E''_{Red.} = E^{\circ\,''}_{Red.} - \frac{0.059}{n} \log \frac{[HO-(C_6H_4)-OH]}{[(HO{=}(C_6H_4){=}OH)^{+2}]} \qquad (14)$$

the relative concentrations of the species in the numerator and denominator being a function of the pH as given by equation 11. The analogous relationship in the case of polyaniline (derived from equation 9) is:

$$E''_{Red.} = E^{\circ\,''}_{Red.} - \frac{0.059}{n} \log \frac{[-(C_6H_4)-N(H)-(C_6H_4)-N(H)]_x}{[(=(C_6H_4){=}N(H)-(C_6H_4)-N(H)=)]_x^{+2x}} \qquad (15)$$

where the partly reduced polymer may be considered as a "solid solution" of composition: $[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-]_a[(-N(H){=}(C_6H_4){=}N(H)-(C_6H_4)-)^{+2}]_b$. It is therefore clear that no oxidation occurs during the protonic acid doping of form 2A to form 2S.

CONCLUSIONS

The conventional (oxidative) p-doping of a conducting polymer results in the removal of some of the pi electrons from the polymer with the formation of a polycarbonium ion. Unless there is extensive charge delocalization carbonium ions are known to be very reactive chemically. The smaller the positive charge on a given C atom the more stable will the carbonium ion be. In the highly conducting form 2S of polyaniline most of the positive charge resides on the N atoms. This favors chemical stability since ammonium-type compounds are known to be generally stable to oxygen and water. As is well known, only a relatively small number of electrons need be removed from the pi system of a polymer in order to increase its conductivity by many orders of magnitude. Further removal of electrons results in only a relatively small additional increase in conductivity at the expense of a large increase in chemical reactivity. What should be sought in a conducting polymer, therefore, is the minimum delocalization of positive charge on to the pi system necessary for the desired degree of conductivity. It appears that polyaniline and related compounds represent an ideal class of polymer which permits such chemical fine-tuning of conductivity and chemical stability.

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REFERENCES

1. A. G. Green and A. E. Woodhead, J. Chem. Soc., 2388 (1910).
2. R. de Surville, M. Jozefowicz, L. T. Yu, J. Perichon and R. Buvet, Electrochimica Acta, 13, 1451 (1968).
3. M. Doriomedoff, F. Hautiere-Cristofini, R. deSurville, M. Jozefowicz, L. T. Yu and R. Buvet, J. Chim. Phys., 68, 1055 (1971).
4. A. G. MacDiarmid, J. C. Chiang, M. Halpern, W. S. Huang, S. L. Mu, N. L. D. Somasiri, W. Wu and S. I. Yaniger, Mol. Cryst. Liq. Cryst., in press (1985).
5. A. G. MacDiarmid, S. L. Mu, N. L. D. Somasiri and W. Wu, Mol. Cryst. Liq. Cryst., in press (1985).
6. R. Liedberg, O. Inganas, R. Erlandsson, I. Lundstrom, A. G. MacDiarmid, M. Halpern and N. L. D. Somasiri, Mol. Cryst. Liq. Cryst., in press (1985).
7. E. M. Genies, A. A. Syed and C. Tsintavis, Mol. Cryst. Liq. Cryst., in press (1985).
8. J. P. Travers, J. Chroboczek, F. Devreaux, F. Genoud, M. Nechstein, A. Syed, E. M. Genies and C. Tsintavis, Mol. Cryst. Liq. Cryst., in press (1985).
9. A. Kitani, J. Izumi, J. Yano, Y. Hiromoto and K. Sasaki, Bull. Chem. Soc., Japan, 57, 2254 (1984); T. Kobayashi, H. Yoneyama and H. Tamura, J. Electroanal. Chem., 177, 281 (1984); 177, 293 (1984).
10. J. J. Andre, M. Bernard, B. Francois and C. Mathis, J. de Physique, 44, C3 (1983).
11. A. E. Richter, J. C. Chiang and A. G. MacDiarmid, unpublished observations (1984).