Polyaniline: Non-Oxidative Doping of the Emeraldine Base Form to the Metallic Regime

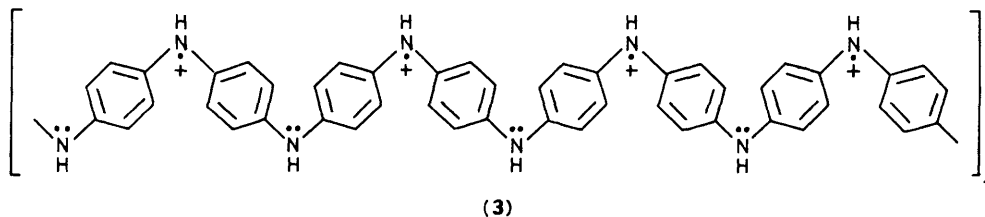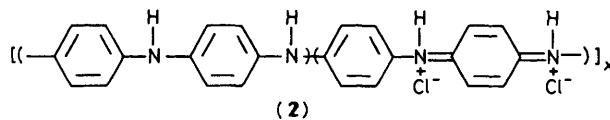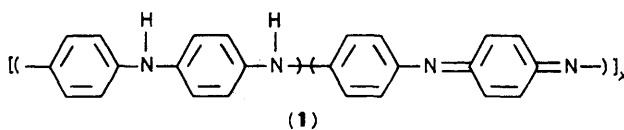Wu-Song Huang,[a] Alan G. MacDiarmid,*[a] and Arthur J. Epstein[b]

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Evidence is provided which proves that the emeraldine base form of polyaniline is 'doped' by protonic acids to the metallic conducting regime by a process involving neither oxidation nor reduction of the polymer, thus introducing a new concept of doping to the conducting polymer field.

A number of recent studies[1,2] have confirmed earlier reports[3] that 'polyaniline' can be doped to the metallic conducting regime by aqueous acids. We have shown, for example, that treatment of the analytically pure emeraldine base form of polyaniline (1) with 1 M aqueous HCl converts it into the corresponding emeraldine hydrochloride salt (2), which we believe[4] is present as a polysemiquinone radical cation (3). This protonation raises the polymer's conductivity by $\sim 10^{10}$ to a final value of ~ 5 S cm^{-1}, consistent with a very large increase in the number and density of charge carriers and/or

(1)

(2)

(3)

1A; reduced repeat unit

2A; non-protonated oxidized repeat unit

2S'; mono-protonated oxidized repeat unit

2S"; diprotonated oxidized repeat unit

Figure 1

Scheme 1

Figure 2. Relationship between the equilibrium potential of poly-aniline film (having an oxidation state approximately that of emeral-dine) and the Hammett acidity function of the solution in which the polymer was equilibrated. Hammett acidity functions[8] reflect the proton donating ability of highly acidic solutions more accurately than pH. In dilute solutions the Hammett function and pH are identical. ○ and ● refer to studies using samples of polyaniline film synthesized in different experiments. □ refers to an identical study performed under argon.[9] The equilibrium potential even in the most acidic medium is, not unexpectedly, smaller than the potential used for the electrochem-ical oxidative polymerization of the monomer (~0.7 V vs. S.C.E.).
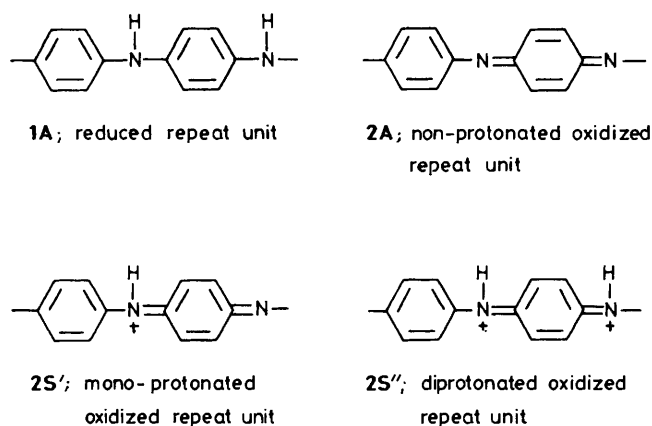
increase in mobility of charge carriers. All previous doping of organic polymers to the metallic regime has been accompli-shed by oxidation or reduction processes.[5] Circumstantial evidence suggests that the doping of polyaniline involves a new concept in conducting polymers in that there is no apparent change in the number of electrons associated with the polymer during the doping process.[6] In this study, we present definitive evidence that this is indeed the case as well as information concerning the doping process.

Thin films of emeraldine fluoroborate were deposited electrochemically[7] on five pieces of platinum foil at ~0.7 V [vs. standard calomel electrode (S.C.E.)] in an aniline–HBF$_4$ electrolyte. These were converted into emeraldine hydro-chloride by treatment with aqueous NH$_4$OH followed by 0.1 M HCl. The equilibrium potential vs. S.C.E. of each of these films was measured at different pH values in aqueous HCl–NaCl solutions of constant ionic strength. Additional measurements on films synthesized in different experiments were also obtained at selected pH values either in the presence or absence of air. The data are shown in Figure 1.

The nomenclature illustrated in Figure 1 will be used in the following discussion.

A relationship between the potential of the polyaniline and the pH of the solution in which it is equilibrated is derived below based on the assumptions that:

(1) the emeraldine base form of polyaniline employed in the study consists of equal numbers of reduced and oxidized repeat units, i.e. $n(1A) = n(2A)$ where n designates the number of a given type of repeat unit in the solid;

(2) only the imine nitrogen atoms are protonated to any significant extent[6] in the pH range studied;

(3) no oxidation or reduction process occurs during proto-nation, i.e. the relative numbers of oxidized and reduced groups remains constant, viz., equation (1), where $n(2)$ refers to the sum of all oxidized species, whether unprotonated, partly protonated, or completely protonated;

$$n(1A) = n(2) = [n(2A) + n(2S') + n(2S'')] \qquad (1)$$

(4) protonation/deprotonation occurs in two steps, (i) $2S'' \rightleftharpoons 2S' + H^+$ and (ii) $2S' \rightleftharpoons 2A + H^+$, giving two equilibrium constants, K_{A1} and K_{A2};

$$K_{A1} = \frac{[2S'][H^+]}{[2S'']} \quad (2) \qquad K_{A2} = \frac{[2A][H^+]}{[2S']} \quad (3)$$

(5) the potential of the polyaniline is dominated by the $n(1A)$: $n(2S'')$ ratio. The redox couple of $2S'$ and its reduced
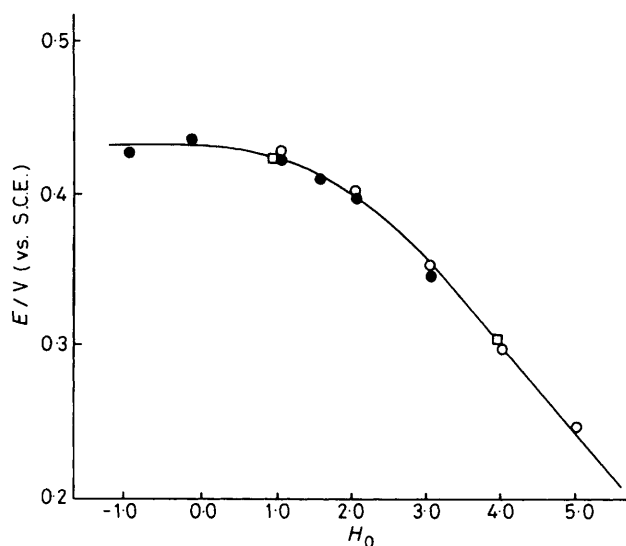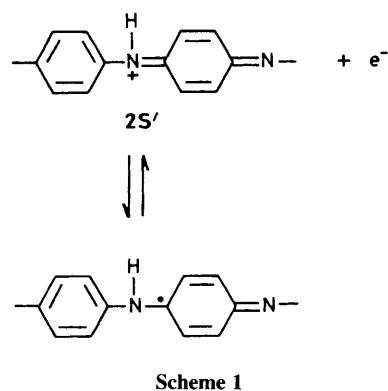
free radical form (Scheme 1) is not expected to affect the potential of the polymer. Monoprotonation of $2A$ to produce $2S'$ might well result in an increase in conductivity; however, the concentration of the corresponding reduced free radical form (which might be expected to disproportionate spon-taneously to equal numbers of $1A$ and $2A$ units), having an oxidation state intermediate between that of the $1A$ and $2A$ forms initially present in the polymer, will be negligible, if, according to assumption (3) above, no oxidation or reduction of the polymer occurs.

The potential of a redox system such as the emeraldine oxidation state of polyaniline containing oxidized and reduced groups which differ by two electrons, $(2S'' + 2e^- \rightleftharpoons 1A)$ is given by the Nernst equation (4). Since, at a Hammett acidity function value, $H_0 = -0.2$ (1 M HCl), we find experimentally that $E = 0.431$ V (vs. S.C.E.) and that, by elemental analysis, emeraldine base is 50% protonated,[1,4] indicating that $n(1A) =$

$n(2S'') = n(2)$. Hence from equation (4), $E = E^\circ = 0.431$ V. This gives rise to the general equation (5). Equations (1)—(5) can be algebraically rearranged and combined to give equation (6). The curve given in Figure 1 is drawn using equation (6) using $K_{A1} = 8.91 \times 10^{-2} (pK_{A1} = 1.05)$, and $K_{A2} = 2.82 \times 10^{-3} (pK_{A2} = 2.55)$.

$$E = E^\circ -0.0296 \log ([1A]/[2S'']) \qquad (4)$$

$$E = 0.431 -0.0296 \log ([1A]/[2S'']) \qquad (5)$$

$$E = 0.431 -0.0296 \log \left\{ \frac{K_{A1} K_{A2} + K_{A1}[H^+] + [H^+]^2}{[H^+]^2} \right\} (6)$$

The excellent agreement between the curve and the experimentally determined data points over a six order of magnitude change in hydrogen ion concentration strongly suggests that the five assumptions on which equation (6) is based are valid and that the protonic acid doping of the emeraldine oxidation state of polyaniline to the metallic regime involves no oxidation or reduction of the polymer. It should be noted that, contrary to expectations from the relative base strengths of amine and imine nitrogen atoms, it is the imine nitrogen atoms which are preferentially protonated, possibly owing to the extensive resonance we have previously postulated[6] in emeraldine salts.

We thank Dr. B. D. Humphrey and Dr. J. C. Chiang for helpful discussions concerning the interpretation of the data obtained in certain of the electrochemical studies. We also thank Mr. J. C. Chiang for carrying out the potential–pH studies in the presence of argon. We gratefully acknowledge financial support of this investigation by the Office of Naval Research.

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