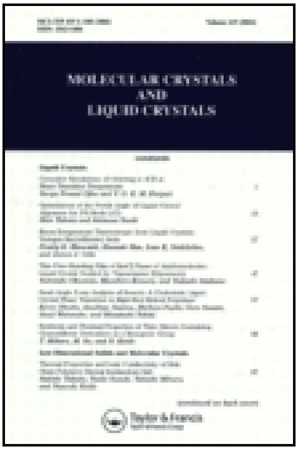

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Physical Characterization of Some Polyaniline, (øN)^{x}

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PHYSICAL CHARACTERIZATION OF SOME POLYANILINE, $(\phi N)_x$

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Abstract Polyaniline, $(\phi N)_x$, is found to exhibit a low energy absorption edge beginning near 1800 cm^{-1} (ca: 0.22 eV), and a strong anion-induced absorption from about 800 to 1200 cm^{-1}. Electrical conductivity has an activation energy of 0.05(±15%) eV consistent with an anion-induced energy gap of about 0.1 eV.

INTRODUCTION

In recent years, a variety of electrically conducting organic polymers have been studied [1]. So far, only polyacetylene, or $(CH)_x$, can exist in two energetically equivalent ground states; which gives rise to a variety of phenomena associated with bond-alternation-defects, or solitons [2,3]. We have begun a series of physical studies of polyaniline, $(\phi N)_x$, Fig. 1. This structure has been proposed for "aniline blacks", which, in impure uncharacterized form, have a long history. The presence of the alternating benzoid-quinoid structure corresponds to bond alternation along the polymer chain. An interchange of the single and double bonds results in an energetically equivalent ground state, which, in principle, should allow a form of bond-alternation-defect. Symmetry indicates that such a defect could be involved in a doping process, as opposed, for example, to bipolarons which are important in polymers without equivalent ground states, e.g. polypyrrole.

EXPERIMENTAL

Powder samples of form 2A (A = amine form) and 2S (S = salt form) were prepared at the University of Pennsylvania, as discussed separately [5]. In Linköping, powders were pressed, under mild vacuum, into pellets (10 tons total pressure over about 1 cm^2, thickness ≃ 0.1 mm). All samples are black powders, which yield pellets with a dark blue cast for S material, and a slight copper cast for A material. Four-point-probe σ (T) and XPS (X-ray Photoelectron Spectroscopy, or ESCA) measurements were carried out in UHV, while FTIR studies of pellets of powders mixed with KBr were done only under mild vacuum. Both FTIR and XPS spectra have been analyzed by comparison with respective spectra of a variety of appropriate model molecules.

RESULTS

The 2A material reported here was not pure form 2A. It contained between 30 and 40% protonated N-atoms (see Fig. 1), according to chemical analysis [5]. At 297 °K, $\sigma \sim 10^{-5}$ $(\Omega\text{-cm})^{-1}$. The $\sigma(T)$ data fit to a straight line on a ln σ versus T^{-1} plot, (not shown) with an activation energy $E_A \approx 0.05(\pm 15\%)$ eV. Due to the high resistivity, only a limited T-range was investigated. For completely deprotonated form A, $\sigma \lesssim 10^{-10}$ $(\text{ohm-cm})^{-1}$ (Ref. 6).

Samples of the salt form (2S), with $A^- = SO_4^{-2}$, or (nominally) BF_4^{-1}, or Cl^- ions, contained approximately two aniline units per A^- unit (some variations were encountered). Conductivities at room temperature varied from 0.3 $(\Omega\text{-cm})^{-1}$ for SO_4^{-2} to over 10 $(\Omega\text{-cm})^{-1}$ for (nominally) BF_4^- anions. The T-dependence of σ for form 2S samples was similar to that of form 2A i.e., $E_A \sim 0.05(\pm 15\%)$ eV, Fig. 1, corresponding to $E_{gap} = 2E_A \approx 0.1$ eV. When plotted as ln $(\sigma \cdot T^{1/2})$ versus $T^{-1/4}$, for a variable range hopping (VRH) model [7], the data is also a straight line, with $T_o = 7(\pm 10\%) \times 10^6$ °K, Fig. 2. The value of T_o for Polypyrrole is 1×10^5 °K [8], and about 2×10^6 °K for $(CH(I_3)_{0.017})_x$ and 4×10^5 °K for $(CH(I_3)_{0.042})_x$. (Ref. 9).

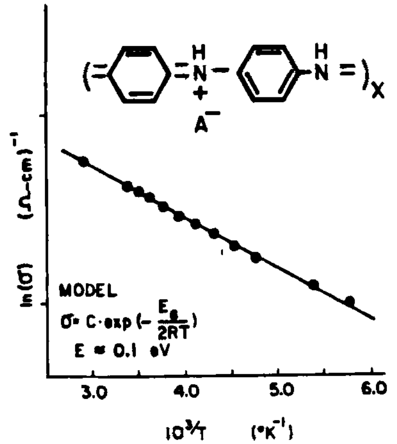

FIGURE 1: Electrical Conductivity

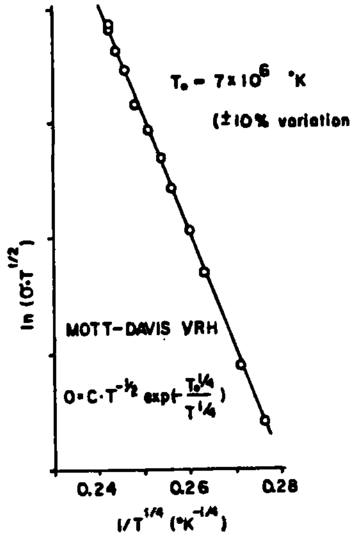

FIGURE 2: VRH Plot

Some FTIR data are shown as absorption spectra in Fig. 3. For form 2A, all seven major absorption peaks can be identified as benzene-derived. The major benzene breathing mode near 1590 cm^{-1} shifts to lower frequency by about 30 cm^{-1} in 2S, material. The absorption which begins near 1800 cm^{-1} continues into the visible, consistent with the "black color" of both 2A and 2S samples. An electronic-like absorption begins near 1800 cm^{-1} (0.22 eV) and is only weakly dependent upon form. There also is a strong absorption from 800 cm^{-1} (0.1 eV) to above 1200 cm^{-1} (0.15 eV), however, that may indeed be at least partially electronic in nature, because (a) it is broad, (b) its strength increases with conductivity, (c) it is independent of the identity of the anion, and (d) the intensity of a portion of it is strongly temperature dependent. The sharp peaks on top of the broad absorption on the middle curve of Fig. 3 are due to BF_4^-, by comparison with standards. SO_4^{-2} also has has two sharp peaks in this region. Cl^{-1} ions, however, have no internal vibrational frequencies, but the broad absorption remains.

Nominally form 2A material ($\sigma \sim 10^{-5} ohm^{-1} cm^{-1}$) has an X-band esr line width of about 12 Gauss, and is assymetric. For form 2S material ($\sigma \sim 10\ ohm^{-1}cm^{-1}$), the esr line width is 2.7 to 3.0 Gauss, almost Lorentzian in shape and increases in intensity relative to form 2A. The signal strength in 2S corresponds to a concentration of nearly 10^{20} spins per gram [10].

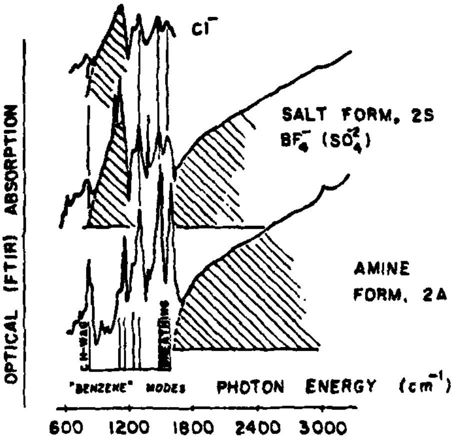

FIGURE 3: FTIR spectra of one 2A and several 2S samples

Preliminary XPS results indicate that $(\phi N)_x$ can be remarkably oxygen free (less than one O-atom per 100 C-atoms), and insensitive to air exposure. The two inequivalent C-atoms and inequivalent *N-atoms (protonated versus deprotonated)* are observed. A strong shake-up satellite structure is observed on the C(1s) spectrum (but not on the N(1s) spectrum), consistent with XPS spectra of gas phase aniline. The satellite intensity is stronger in form 2S material than in 2A material, however. XPS valence band spectra are under investigation in connection with model CNDO/S model calculations[11].

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