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Electrical properties of thin films of polyphenylacetylene doped with iodine or arsenic pentafluoride

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ELECTRICAL PROPERTIES OF THIN FILMS OF
POLYPHENYLACETYLENE DOPED WITH IODINE OR
ARSENIC PENTAFLUORIDE

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Polyphenylacetylene¹(PPA) is a soluble polymer with a bandgap of 2.3 eV. The doping reaction can be carried out in solution, and this allows the formation of uniformly-doped, chemically stable semiconductors in fast doping reactions.

The resistivity-composition relations were determined for $[(C\phi = CH)(AsF_5)_y]_x$ and for $[(C\phi = CH)(I_2)_y]_x$ formed from cis-rich PPA² and doped in chloroform. Both materials show dramatic increases in conductivity upon doping at small y, like p-doped polyacetylene and polyphenylene. The conductivity (σ) of PPA-AsF₅ pellets tends toward a plateau of 10^{-4} (ohm-cm)⁻¹ at y = 0.1 to 0.7 ($\sigma > 10^{-2}$ could be obtained in films doped in vacuo in gas-solid reactions). Some iodination of skeletal double bonds takes place in PPA-I₂, and σ is about 10^{-6} (ohm-cm)⁻¹ in films at y = 0.8, in agreement with the results of Cukor et al.³ For undoped PPA,⁴ $\sigma \leq 10^{-14}$ (ohm-cm)⁻¹.

Schottky barriers were formed with PPA-I₂ and PPA-AsF₅, and p-type conductivity was established in both of these materials at moderate to heavy doping by experimenting with metals having different work functions. Analysis of the capacitance-voltage relation yields 2.6 eV for the electron affinity of PPA and 4.9 eV for its work function. Photoconductivity measurements in 1-5 μ m films, using an AM-1 source and peripheral illumination, yielded ratios of photocurrent to dark current as high as 5. The photocurrent spectrum of PPA-AsF₅ parallels the absorption spectrum.

The unpaired spins responsible for the esr signal in undoped PPA are attributable to structural (or "conformational") defects created irreversibly upon thermal and photoisomerization.⁵ Their concentration increases moderately in heavily doped PPA-AsF₅ and PPA-I₂, but remains several orders of magnitude below the concentration of dopant molecules.⁶ One can conclude that the large increase in conductivity upon doping is associated with the creation of spinless PPA cations. This seems to be similar to what occurs in doped polyphenylene.⁷

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