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Electrical Conductivity in Doped Polyacetylene

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Doped polyacetylene forms a new class of conducting polymers in which the electrical conductivity can be systematically and continuously varied over a range of eleven orders of magnitude. Transport studies and far-infrared transmission measurements imply a metal-to-insulator transition at dopant concentrations near 1%.

We find that films of the semiconducting polymer, polyacetylene, show a dramatic increase in electrical conductivity when doped with controlled amounts of the halogens chlorine, bomine, or iodine, and with arsenic pentafluoride (AsF_5). The concentration dependence in combination with far-infrared transmission data suggests the occurrence of a metal-insulator transition as a function of dopant concentration.

Polyacetylene is one of the simplest linear conjugated polymers with a single-chain structure as shown in Fig. 1. Each carbon is σ bonded to one hydrogen and two neighboring carbon atoms consistent with sp^2 hybridization. The π electrons are therefore available to delocalize into a band. In the idealized situation of a uniform chain, the resulting conduction band would give rise to metallic behavior. However, such a system is unstable with respect to bond alternation, which causes the formation of an energy gap in the electronic spectrum. Studies of π-π^* transitions in short-chain polyenes show that the frequencies do not fall as n^{-2} as expected for a free-electron picture, but appear to saturate at $\Delta E_{(n\ \mathrm{large})}{}^{\pi-\pi^*} \simeq 2.4$ eV.[1] Bond alternation is present in the polymer and would be expected to lead to semiconducting behavior. However, Ovchinnikov[1] has stimmated the bond-alternation energy gap to be too small and attributed the observed value to Coulomb correlation effects, i.e., a Hubbard gap.

In a series of studies Shirakawa and co-workers[2-6] succeeded in synthesizing high-quality polycrystalline films of $(CH)_x$, and developed techniques for controlling the *cis/trans* content.[4,5] These materials are semiconductors[6]; the *trans* isomer is the thermodynamically stable form at room temperature.

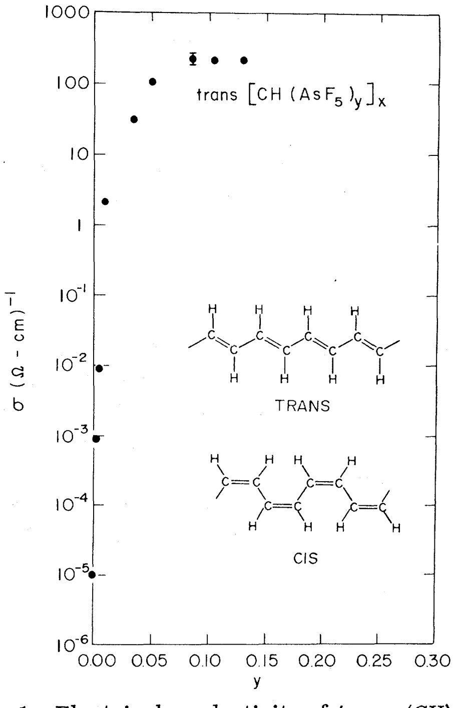

FIG. 1. Electrical conductivity of *trans*-$(CH)_x$ as a function of (AsF_5) dopant concentration. The *trans* and *cis* polymer structures are shown in the inset.

Polyacetylene crystalline films were prepared with the techniques developed by Shirakawa and co-workers[2-6] in the presence of a Zeigler catalyst. X-ray diffraction and scanning-electron micrograph studies show that films of any *cis* and *trans* composition are crystalline and consist of matted fibrils. The *cis*/*trans* content was controlled by thermal isomerization.[4,5] Details of preparation and characterization are published elsewhere.[7,8]

Samples used in the electrical conductivity study were cut from polymer films approximately 0.1–0.5 mm in thickness. Platinum wires and Electroday were used to make electrical contacts to the films which were treated with the vapor of the dopant at room temperature, *in vacuo*, for 3–4 hours. Their resistance was monitored at at intervals. Final compositions of the doped $(CH)_x$ were determined either by the elemental analysis (Galbraith Laboratories, Inc.) of a piece of reference film placed just below the film whose conductivity was being measured and/or by the increase in weight of the reference film during doping. All conductivity measurements used four-probe dc techniques. Far-ir (400–20 cm^{-1}) transmission measurements were made on films of both pure and doped polyacetylene with use of Grubb-Parsons Michelson interferometer with a helium-cooled gallium-doped germanium bolometer detector. Measurements in the middle ir utilized a Perkin-Elmer 225.

Figure 1 shows the room-temperature electrical conductivity of polyacetylene as a function of AsF_5 concentration; the initial sample was *trans*-rich [*trans* content (95–97)%]. After an initial steep rise over about seven orders of magnitude, the values appear to saturate at 220 Ω^{-1} cm^{-1}. Similar results have been obtained for halogen dopants; e.g., *trans*-$(CHI_{0.20})_x$ yields $\sigma(300\ K) \simeq 160\ \Omega^{-1}\ cm^{-1}$.[7-9] The highest-room-temperature results to date have been obtained by doping *cis*-$(CH)_x$ with AsF_5 to yield *cis*-$[CH(AsF_5)_{0.14}]_x$ with $\sigma(300\ K) = 560\ \Omega^{-1}\ cm^{-1}$[8]—a value comparable to that obtained with *single crystals* of the organic metal tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ). The concentration dependences observed in all cases studied thus far are similar to Fig. 1; an initial steep rise over many orders of magnitude followed by a leveling off at concentrations above a few percent.

These results suggest that the residual conductivity in "pure" $(CH)_x$ is probably due to residual impurities or defects at very low levels. The extreme sensitivity to impurities is demonstrated in Fig. 1. Moreover, the residual conductivity can be compensated by trace amounts of donor doping. Exposure of "pure" $(CH)_x$ to vapor of the donor, NH_3, causes the conductivity of *trans*-$(CH)_x$ to fall more than four orders of magnitude ($< 10^{-9}\ \Omega^{-1}\ cm^{-1}$) without detectable weight increase. Subsequent reaction of the compensated film with AsF_5 brings the conductivity back up to metallic levels—an overall change of eleven orders of magnitude.

Far-infrared transmission data were taken on samples of varying concentrations of iodine and AsF_5 with qualitatively similar results. The data for a series of iodinated samples are shown in Fig. 2 for $y = 0.0$, 0.9, 2.0, and 6.0 at.%. In the case of the 6% sample, there is no observable transmission throughout the ir down to 20 cm^{-1}, implying a continuous excitation spectrum; i.e., metallic. For the 2% sample, the transmission was zero at the high end of the spectrum (4000 cm^{-1} to 300 cm^{-1}), but increases below 300 cm^{-1} to about 60% by 40 cm^{-1}, implying an energy gap at low frequencies. The far-ir transmission through the 0.9% sample is near 90% with no significant change from an undoped sample. The inset to Fig. 2 shows the absorption coefficient α (uncorrected for reflection) at 40 cm^{-1} as a function of dopant concentration. The transition is sharp with a critical concentration (n_c) in the range (2–3)%. Similar results have been obtained with AsF_5 although n_c appears to be slightly smaller. The values for n_c as inferred from the ir and dc transport measurements are in agreement.

Although the initial $(CH)_x$ is crystalline, disor-

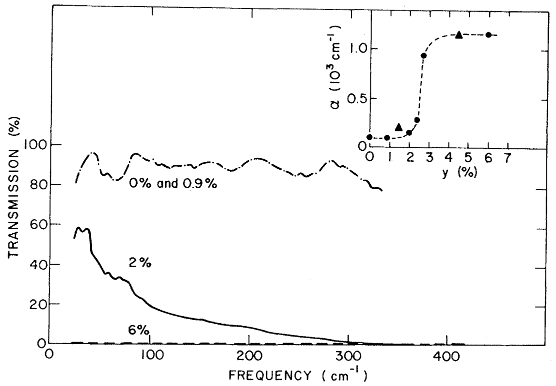

FIG. 2. Far-infrared (20–400 cm^{-1}) transmission of iodine-doped polyacetylene (sample temperature was 77 K). The inset shows the absorption coefficient (uncorrected for reflection) at 40 cm^{-1} vs concentration (solid points, *trans* polymer; triangles, *cis* polymer).

der may play an important role in the doped polymer. In general, we find that plots of $\ln\sigma$ vs $1/T$ do not give straight-line behavior. Plotting the data as $\ln\sigma$ vs $T^{-1/4}$ (or $T^{-1/2}$) tends to give more nearly straight-line behavior at least in the low-concentration range below n_c where the results are typical of transport in disordered and amorphous systems.[10] Variable-range hopping[11] between localized states leads to temperature dependences of the form $\sigma \propto \exp[-(T_0/T)^{1/(d+1)}]$, where d is the dimensionality of the transport (e.g., $d = 3$ for three-dimensional motion, etc.).

A qualitative change in the temperature dependence of the dc conductivity is observed at the critical concentration as shown in Fig. 3, where we plot $\sigma(T)/\sigma(300\text{ K})$ vs T on a linear scale. At low concentrations the curves appear thermally activated with generally upward curvature. Above n_c, the curvature changes and the conductivity decreases slowly with decreasing temperature, heading toward zero approximately linearly in T.

As an initial point of view we treat this transition as similar to that seen in heavily doped semiconductors. If this is the case, one expects the halogen and AsF_5 dopants to act as acceptors with localized hole states in the gap, with the hole bound to the acceptor in a hydrogenlike fashion. For low concentrations, one expects the combination of impurity ionization and variable-range hopping to lead to a combination of activated processes as observed experimentally. However, as extensively discussed by Mott[12] and others,[13] if the concentration is increased to a critical level, then the screening from carriers will destroy the bound states giving an insulator-to-metal transition. This will occur when the screening length becomes less than the radius of the most tightly bound Bohr orbit of the hole and acceptor in the bulk dielectric[12];

$$n_c^{1/3} \simeq (4a_{\text{H}})^{-1}\left(\frac{m^*}{m\epsilon}\right)^2,$$

where a_{H} is the Bohr radius, ϵ is the dielectric constant of the medium, and m^*/m is the ratio of the band mass to the free-electron mass. Assuming $m^*/m \simeq 1$ and using $\epsilon \simeq 3$ from far-ir reflection measurements, we estimate that $n_c \simeq 2 \times 10^{20}\text{ cm}^{-3}$. Since the density of carbon atoms is about $2\times10^{22}\text{ cm}^{-3}$, n_c would be at about 1%, assuming one carrier per dopant. The excellent agreement with our experimental results is fortuitous in view of the much over-simplified model. However, the scale is correct; the transition occurs at about 1% because of the relatively small dielectric constant. Although we have discussed the metal-insulator transition from the point of view of simple semiconductor theory, the relative importance of Coulomb correlation effects must be considered.[2]

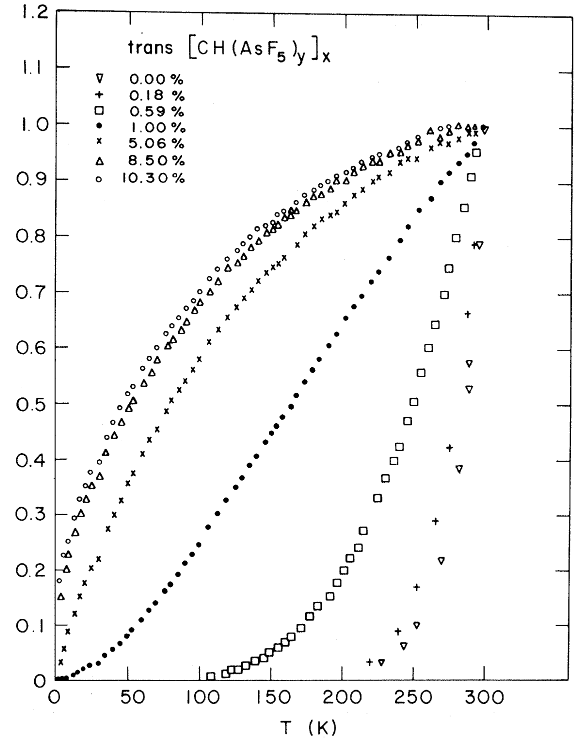

FIG. 3. Temperature dependence of the normalized conductivity at several doping levels (AsF_5).

The polymer structure of polyacetylene implies strong π overlap along the chain with weaker interchain coupling since the intrachain carbon-carbon–bond length is about 1.4 Å whereas the interchain spacing is 3.6 Å.[2-5] Thus we expect the resulting metal to be anisotropic, and possibly quasi-one-dimensional. The temperature dependence of the conductivity above n_c is consistent with that expected for a disordered one-dimensional metal.[14] Since all states are localized in such a system,[15] the static conductivity goes to zero at $T = 0$ K. However, when the electron-phonon interaction is taken into account, phonon-assisted diffusion through the localized states leads to finite conductivity with a temperature dependence determined by the number of thermal phonons in the modes to which the conduction electrons are strongly coupled.[14] In addition interfibril contact may be playing a role. Studies of the temperature dependence of the conductivity of polycrystalline $(\text{SN})_x$[16,17] and organic conductors such as TTF-TCNQ[18] often show monotonically decreasing conductivity even though the single-crystal data indicate metallic behavior.

In the metallic state, the carrier mobility may be estimated from $\sigma = ne\mu$, where n is the carrier density, e is the electronic charge, and μ is the mobility. Using $\sigma = 560\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for *cis*-$[\mathrm{CH(AsF_5)_{0.14}}]_x$ and assuming one carrier per $\mathrm{AsF_5}$, we find $\mu \simeq 1\ \mathrm{cm^2/V\ sec}$—surprisingly high when compared with typical polymer photoconductors[19] ($\mu \sim 10^{-7}\ \mathrm{cm^2/V\ sec}$) or even with copper metal ($\mu \sim 20\ \mathrm{cm^2/V\ sec}$). Given the anisotropic polymer structure and the fibrous nature of the low-density as-grown films,[2-6] higher conductivities may be expected from aligned films of $(\mathrm{CH})_x$ derivatives.

In summary, we have shown that doped polyacetylene forms a new class of conducting polymers in which the electrical conductivity can be systematically and continuously varied over a range of eleven orders of magnitude. Transport studies and far-ir transmission measurements imply a metal-insulator transition at dopant concentrations near 1%. We have obtained room-temperature conductivities for polycrystalline films of the doped polymer comparable to that found on single crystals of the organic metal TTF-TCNQ. Use of different dopants and replacement of the H atoms in $(\mathrm{CH})_x$ with organic or inorganic groups should lead to a large new class of conducting polymers with electrical properties that can be controlled over the full range from insulator to semiconductor to metal.

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[9] The more recent iodination experiments involving *trans*-$(\mathrm{CH})_x$ yield significantly improved electrical properties ($\sigma = 160\ \Omega^{-1}\ \mathrm{cm}^{-1}$) as compared with earlier results (Ref. 7) ($\sigma = 30\ \Omega^{-1}\ \mathrm{cm}^{-1}$). This increase may be related to the rate of iodination leading to more uniform doping through the thickness of the films. Detailed studies of the effects of film thickness, reaction rate, etc., are underway.

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