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SYNTHESIS OF ELECTRICALLY-CONDUCTING ORGANIC POLYMERS: HALOGEN --ETC(U)
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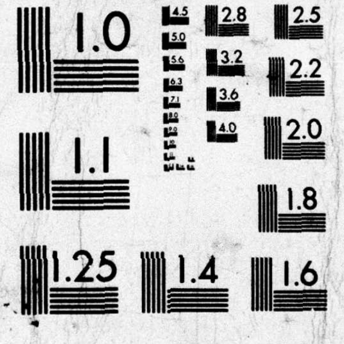
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

When silvery films of the semiconducting polymer, trans "polyacetylene," $(CH)_x$, are exposed to chlorine, bromine or iodine vapor, uptake of halogen occurs, and the electrical conductivity increases markedly (over seven orders of magnitude in the case of iodine) to give, depending on the extent of halogenation, silvery or silvery-black films, some of which have a remarkably high conductivity at room temperature.

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by

Hideki Shirakawa, Edwin J. Louis, Alan G. MacDiarmid,
Chwan K. Chiang[†] and Alan J. Heeger[†]

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Synthesis of Electrically-Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, $(CH)_x$

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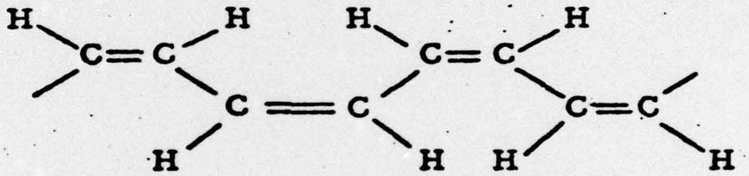
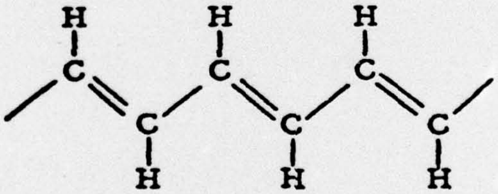
Summary - When silvery films of the semiconducting polymer, trans "polyacetylene", $(CH)_x$, are exposed to chlorine, bromine or iodine vapor, uptake of halogen occurs, and the conductivity increases markedly (over seven orders of magnitude in the case of iodine) to give, depending on the extent of halogenation, silvery or silvery-black films, some of which have a remarkably high conductivity at room temperature.

Considerable interest has recently been shown in the synthesis and study of metallic covalent polymers such as $(SN)_x$[1] and $(SNBr_y)_x$[2]. In attempting to find a covalent organic polymer which would be a metal or at least have a high conductivity, we have focused our attention on the simplest organic polymer, "polyacetylene", $(CH)_x$. In a series of studies, Shirakawa *et al.*[3-7] have succeeded in synthesizing high quality flexible copper-colored films of the *cis* isomer



and silvery films of the *trans* isomer



of this conjugated polyene from acetylene in the presence of a Zeigler catalyst, and they have developed techniques for controlling the *cis* and *trans* content.[5,6] X-ray diffraction and scanning electron micrograph studies show that films of any *cis* and *trans* composition are crystalline and consist of matted fibrils.[5] These materials are semiconductors;[7] the *trans* isomer, which is the thermodynamically stable form at room temperature, has a higher conductivity ($\sigma_{273\ K} = 4.4 \times 10^{-5}$ ohm^{-1} cm^{-1}) than the *cis* isomer ($\sigma_{273\ K} = 1.7 \times 10^{-9}$ ohm^{-1} cm^{-1})[7].

Shirakawa and Ikeda[8] have noted that when $(CH)_x$ films are exposed to bromine or chlorine vapor at room temperature for a few minutes, a dramatic decrease in infrared transmission (4,000 $cm.^{-1}$ to 400 $cm.^{-1}$) occurs without any visible change in appearance of the films. Complete halogenation to yield, e.g. $(CHBr)_x$, results again in high infrared transmission with concomitant production of a white film. The initial reduction in infrared transmission suggests that the halogen-doped material might have unusual electronic properties. The results of studies involving the halogenation of films of trans-$(CH)_x$ are summarized below.

The conductivity of the $(CH)_x$ films were measured by four probe dc techniques at room temperature in a glass vessel to which was attached a bulb containing the halogen. This bulb was held at various temperatures to produce known halogen vapor pressures. When $(CH)_x$ is exposed to 1 Torr of bromine vapor at room temperature for 10 min. the conductivity rapidly increases by approximately four orders of magnitude to give silvery films of $(CHBr_{0.05})_x$ having a conductivity of 0.5 ohm^{-1} $cm.^{-1}$ at room temperature. Longer bromination gives silvery-black films having the composition $(CHBr_{0.23})_x$ and a slightly smaller conductivity ($\sigma_{298\,K}$ = 0.4 ohm^{-1} $cm.^{-1}$). The films are stable both in vacuum and when exposed to air for at least several hours at room temperature. Qualitatively similar results are obtained with chlorine, but the increase in conductivity is smaller (about three orders of magnitude).

When iodine vapor reacts with $(CH)_x$ at room temperature, the infrared transmission decreases in a manner similar to that described above for bromine. However, the increase in conductivity is even more remarkable, over seven orders of magnitude, as shown in Figure 1. The maximum conductivity ($\sigma_{298\,K}$ = 38 ohm^{-1} cm.$^{-1}$) was observed on a silvery-black film of composition $(CHI_{0.22})_x$*. The appearance of the $(CH)_x$ film remained essentially unchanged until the approximate composition $(CHI_{0.05})_x$ was reached, after which it began to darken. The stability of the iodinated films is similar to that of the brominated material. Separate measurements of three samples of $(CHI_{0.22})_x$ gave an average conductivity of 30 ohm^{-1} cm.$^{-1}$. This material has the largest room temperature conductivity observed for any covalent organic polymer.

We believe that charge-transfer complexes are formed between $(CH)_x$ and halogens when they are permitted to react under certain conditions, as has been observed previously with iodine and polyphenylene.[9] However, in the case of $(CH)_x$ the absolute conductivities obtained are four to five orders of magnitude greater.

The highly conducting polyacetylene bromides and iodides may be charge-transfer pi complexes of the type believed to be formed during the halogenation of olefins. Stable colored compounds which may be charge-transfer and/or carbonium ion complexes of this type have been obtained by the action of bromine on certain substituted ethylenes.[10]

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*Analytical data (Galbraith Laboratories, Inc. Knoxville, Tenn. 37921): Calcd. for $(CHI_{0.22})_x$, C, 29.34; H, 2.46; I, 68.20. Found: C, 29.14; H, 2.62; I, 68.26%. (Total = 100.02%).

We note for comparison that the room temperature conductivity of a compacted, polycrystalline pellet of the organic charge transfer metallic salt, (TTF)(TCNQ) is ca. 10 ohm^{-1} $cm.^{-1}$,[11] while that of a compressed pellet of polycrystalline $(SN)_x$ at room temperature is ca. 20 ohm^{-1} $cm.^{-1}$.[12] The conductivity of the latter material decreases on lowering the temperature and exhibits an activation energy, E_a, of about 0.02 eV. Later experimental results on single crystals of $(SN)_x$ have shown that the conductivity increases with decrease in temperature, ($E_a = 0$), in a manner characteristic of a metal.[1] In the polycrystalline $(SN)_x$ sample, the increase in conductivity on lowering the temperature which occurs within a small, metallic crystal of $(SN)_x$ is apparently more than off-set by the decrease in conductivity involved in the passage of electrons from one crystal to another. Like polycrystalline $(SN)_x$, the conductivity of the most highly conducting composition, $(CHI_{0.22})_x$, decreases slowly on decreasing the temperature (300 K > T > 4.2 K) with an activation energy, $E_a \simeq 0.016$ eV (for comparison the activation energy for trans-$(CH)_x$ is $E_a \simeq 0.3$ eV [7]). These results are suggestive of metallic behavior; experiments are underway directed toward clarification of the origin of the very small activation energy.

Although the randomness of the halogenated polyacetylene may be playing an important role, the overall behavior is like that of a series of semiconductors with activation energies which vary with halogen content. However, a detailed study of the temperature dependence of the conductivity indicates that a simple semiconductor model involving a single activation energy is inadequate to describe the conductivity of the material. We believe the polyacetylene halides may be the forerunners of a new class of organic polymers with electrical properties which may be systematically and controllably varied over a wide range by chemical doping.

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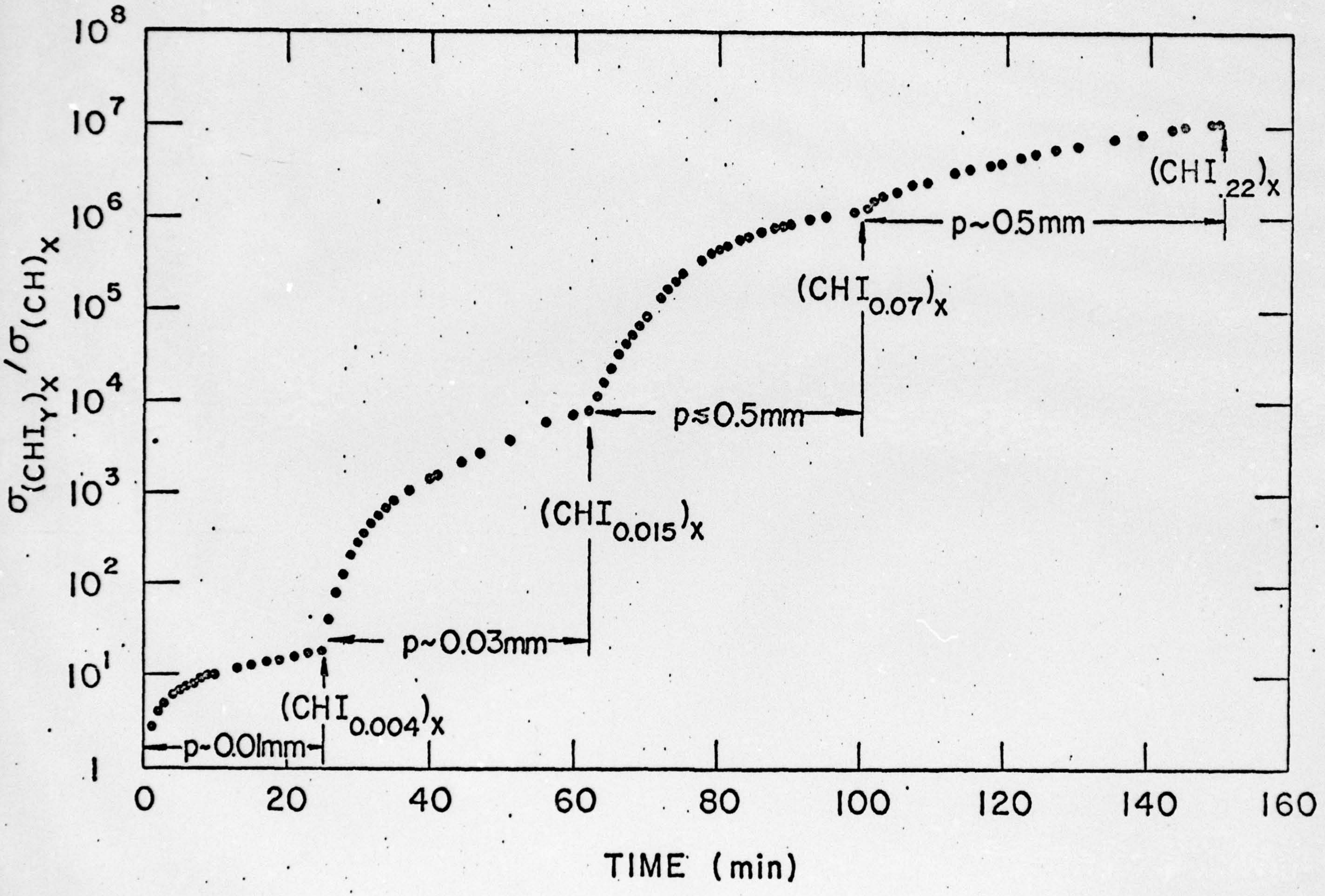
Figure Caption:

Figure 1: Increase in the room temperature conductivity of trans-polyacetylene, $(CH)_x$, as a function of time at fixed iodine vapor pressures. The initial room temperature conductivity is 3.2×10^{-5} $(\text{ohm-cm})^{-1}$. [In the last experiment some iodine was sublimed onto the glass walls of the conductivity apparatus in order to promote attainment of the equilibrium vapor pressure of the iodine at room temperature in the vicinity of the film.]


$\sigma_{(CHI_y)_x}/\sigma_{(CH)_x}$
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
1
0
20
40
60
80
100
120
140
160
TIME (min)
p~0.01mm
$(CHI_{0.004})_x$
p~0.03mm
$(CHI_{0.015})_x$
p≲0.5mm
$(CHI_{0.07})_x$
p~0.5mm
$(CHI_{.22})_x$

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