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

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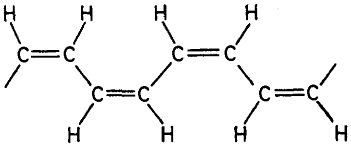
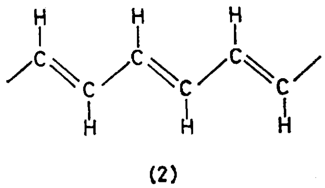
Summary When silvery films of the semiconducting polymer, *trans* 'polyacetylene', $(CH)_x$, are exposed to chlorine, bromine, or iodine vapour, uptake of halogen occurs, and the conductivity increases markedly (over seven orders of magnitude in the case of iodine) to give, depending on the extent of 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-coloured films of the *cis*-isomer (**1**) and silvery films of the *trans*-isomer (**2**) of this conjugated polyene from acetylene in the presence of a Ziegler catalyst, and have developed techniques for controlling the ratio of *cis* and *trans*-isomers in the product.[5,6] *X*-Ray diffraction and scanning electron micrograph studies show that films of *cis* and *trans*-isomers of all compositions 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 [$\sigma(273\ \text{K}) = 4{\cdot}4 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$] than the *cis*-isomer [$\sigma(273\ \text{K}) = 1{\cdot}7 \times 10^{-9}\ \Omega^{-1}\ \text{cm}^{-1}$].[7]



(1)



(2)

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

The conductivity of the $(\text{CH})_x$ films were measured by four-probe d.c. techniques at room temperature in a glass vessel to which a bulb containing the halogen was attached. This bulb was held at various temperatures to produce known halogen vapour pressures. When $(\text{CH})_x$ is exposed to 1 Torr of bromine vapour at room temperature for 10 min the conductivity rapidly increased by approximately four orders of magnitude to give silvery films of $(\text{CHBr}_{0.05})_x$ having a conductivity of $0{\cdot}5\ \Omega^{-1}\ \text{cm}^{-1}$ at room temperature. Bromination for longer periods gives silvery-black films having the composition $(\text{CHBr}_{0.23})_x$ and a slightly lower conductivity [$\sigma(298\ \text{K}) = 0{\cdot}4\ \Omega^{-1}\ \text{cm}^{-1}$]. 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 vapour reacts with *trans*-$(\text{CH})_x$ at room temperature, the i.r. 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 the Figure. The maximum conductivity [$\sigma(298\ \text{K}) = 38\ \Omega^{-1}\ \text{cm}^{-1}$] was observed for a silvery-black film of composition $(\text{CHI}_{0.22})_x$.‡ The appearance of the $(\text{CH})_x$ film remained essentially unchanged until the approximate composition $(\text{CHI}_{0.05})_x$ 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 $(\text{CHI}_{0.22})_x$ gave an average conductivity of $30\ \Omega^{-1}\ \text{cm}^{-1}$. This material has the largest room temperature conductivity observed for any covalent organic polymer. Moreover, preliminary studies with iodinated *cis*-$(\text{CH})_x$ indicate that it has an even greater maximum conductivity, approximately one order of magnitude greater than that found for iodinated *trans*-$(\text{CH})_x$.

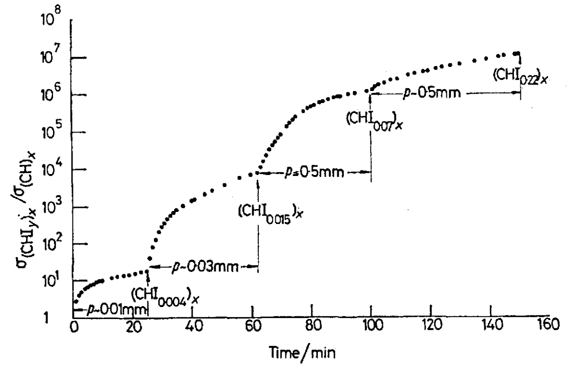


FIGURE. Increase in the room temperature conductivity of *trans*-polyacetylene, $(\text{CH})_x$ as a function of time at fixed iodine vapour pressures. The initial room temperature conductivity is $3{\cdot}2 \times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$. (In the last experiment some iodine was sublimed onto the glass walls of the conductivity apparatus in order to promote attainment of the equilibrium vapour pressure of the iodine at room temperature in the vicinity of the film).

We believe that charge-transfer complexes are formed between $(\text{CH})_x$ and halogens when they are permitted to react under certain conditions, as has been observed previously with iodine and polycyclic hydrocarbons.[9] However, in the case of $(\text{CH})_x$ the absolute conductivities obtained are considerably greater.

The highly conducting polyacetylene bromides and iodides may be charge-transfer π complexes of the type believed to be formed during the halogenation of olefins. Stable coloured 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]

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.* $10\ \Omega^{-1}\ \text{cm}^{-1}$,[11] while that of a compressed pellet of polycrystalline $(\text{SN})_x$ at room temperature is *ca.* $20\ \Omega^{-1}\ \text{cm}^{-1}$.[12] The conductivity of the latter material decreases on lowering the temperature and exhibits an activation energy, E_a, of *ca.* 0·02 eV. Later experimental results on single crystals of $(\text{SN})_x$ have shown that the conductivity increases with decrease in temperature, ($E_\text{a} = 0$), in a manner characteristic of a metal.[1] In the polycrystalline $(\text{SN})_x$ sample, the increase in conductivity on lowering the temperature which occurs within a small, metallic crystal of $(\text{SN})_x$ is apparently more than off-set by the decrease in conductivity involved in the passage of electrons from one crystal to another. Like polycrystalline $(\text{SN})_x$, the conductivity of the most highly conducting composition, $(\text{CHI}_{0.22})_x$, decreases slowly on decreasing the temperature ($300\ \text{K} > T > 4{\cdot}2\ \text{K}$) with an activation energy, E_a, of *ca.* 0·016 eV [for comparison the

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‡ Satisfactory microanalytical data were obtained for this compound.

activation energy, E_a, for *trans*-(CH)$_x$ is *ca.* 0·3 eV[7]]. These results suggest metallic behaviour; experiments are underway to clarify the origin of the very small activation energy.

Although the randomness of the halogenated polyacetylene may be playing an important role, the overall behaviour 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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