Electrochemistry of Polyacetylene, $(CH)_x$: Electrochemical Doping of $(CH)_x$ Films to the Metallic State

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Summary When silvery films of the semiconducting polymer, *cis*-'polyacetylene,' $(CH)_x$, are used as the anode in the electrolysis of aqueous KI solutions or methylene chloride solutions of $[Bu^n_4N]^+[ClO_4]^-$, films of $(CHI_y)_x$ and $[CH(ClO_4)_y]_x$, respectively, are obtained which, for the compositions $[CHI_{0\cdot07}]_x$ and $[CH(ClO_4)_{0\cdot0645}]_x$ have high conductivities characteristic of the metallic state.

The semiconducting polymer 'polyacetylene,' $(CH)_x$, can be doped by various vapours or solutions to yield at first either *p*- or *n*-type semiconductors and ultimately films exhibiting the electronic properties of metals.[1–3] We report here the first electrochemical studies of $(CH)_x$ films. The results indicate a new, simple, general method for doping $(CH)_x$ with a wide range of chemical species.

It was found that when a 1 cm × 3 cm × 0·01 cm strip of $(CH)_x$ film (*ca.* 82% *cis*-isomer) was used as the anode in the electrolysis of aqueous 0·5 M KI solution with a potential of 9 V it was doped during *ca.* 0·5 h to the metallic state, to give, by elemental analysis, $(CHI_{0\cdot07})_x$. The current increased from 1 to 43 mA during this time. It is important to note that the flexible, golden-silvery films contained no oxygen (total C, H, and I content 99·8%) and hence had undergone no hydrolysis and/or oxidation during the electrolytic doping process. The room temperature conductivity of the initial film was *ca.* $1 \times 10^{-8}\ \Omega^{-1}\ \text{cm}^{-1}$ and that of the doped film was $9{\cdot}7\ \Omega^{-1}\ \text{cm}^{-1}$. This value is consistent with that previously observed for $(\text{CH})_x$ films doped with iodine to the same extent[3] by exposure of the $(\text{CH})_x$ films to iodine vapour. Under the conditions employed, the film was not doped to as high levels, *ca.* $[\text{CHI}_{0\cdot 2}]_x$, as attained through vapour phase doping. It was shown in a separate experiment, using appropriate amounts of $[\text{CHI}_{0\cdot 19}]_x$ and 0·5 M KI solutions, that part of the iodine was removed from the film to give material of composition $[\text{CHI}_{0\cdot 11}]_x$. The doped film apparently enters into equilibrium with the KI solution according to equation (1).

$$[\text{CHI}_{0\cdot 19}]_x + 0{\cdot}04\text{KI} \rightleftharpoons [\text{CHI}_{0\cdot 11}]_x + 0{\cdot}04\text{KI}_3 \qquad (1)$$

When the $(\text{CH})_x$ was used as the anode in the electrolysis of 0·5 M $[\text{Bu}^n{}_4\text{N}]^+[\text{ClO}_4]^-$ in CH_2Cl_2 at 9 V, doping occurred during *ca.* 1 h to give flexible films which, by elemental analysis, had the composition $[\text{CH}(\text{ClO}_4)_{0.0645}]_x$. The current increased from 0·95 to 3·4 mA during this time. The resulting room temperature conductivity (four-probe technique) was $970\ \Omega^{-1}\ \text{cm}^{-1}$. Lower doping levels obtained during shorter electrolysis times gave material having conductivities in the semiconductor region. Raman studies show that the iodinated[4] and brominated[2] films should be formulated as $[(\text{CH})^{+y}(\text{X}_3)_y{}^-]_x$ where X = Br or I. By analogy, we believe that $[\text{CH}(\text{ClO}_4)_{0\cdot 0645}]_x$ is probably the ionic polycarbonium perchlorate, $[(\text{CH})^{+0.0645}(\text{ClO}_4)^-{}_{0\cdot 0645}]_x$. Similar results were obtained by the electrolysis of methylene chloride solutions of $[\text{Bu}^n{}_4\text{N}]^+[\text{SO}_3\text{CF}_3]^-$ and $[\text{Pr}^n{}_3\text{NH}]^+[\text{AsF}_6]^-$, both of which gave highly conducting golden-silvery flexible films. The former is assumed to contain the $\text{SO}_3\text{CF}_3{}^-$ ion and the latter the $\text{AsF}_4{}^-$ ion, since elemental analysis of the film gave a composition corresponding to $[\text{CH}(\text{AsF}_4)_{0.077}]_x$. We believe the $\text{AsF}_4{}^-$ ion is formed by a reaction sequence involving proton abstraction from $[\text{Pr}^n{}_3\text{NH}]^+$ by fluorine atoms from $\text{AsF}_6{}^-$ during the electrolysis process.

Preliminary experiments indicate that when the $(\text{CH})_x$ films are used as the cathode in the electrolysis of appropriate alkali metal salts in organic solvents *n*-type doping results. Electrochemical oxidation or reduction of the delocalized $(\text{CH})_x$ π-system offers a simple general method for the electrochemical doping of $(\text{CH})_x$ films to *p*- or *n*-type semiconductors or metals with the concomitant introduction of a large variety of stabilizing counter anions or cations. It would appear that many of these materials, *e.g.* $[\text{CH}(\text{ClO}_4)_{0\cdot 0645}]_x$, could not be synthesized by any obvious conventional chemical means. The composition of $(\text{CH})_x$, $(\text{CHI}_{0\cdot 07})_x$, $[\text{CH}(\text{ClO}_4)_{0\cdot 0645}]_x$, and $[\text{CH}(\text{AsF}_4)_{0.077}]_x$ was confirmed by (C and H), (C, H, and I), (C, H, and Cl), and (C, H, As, and F) analyses, respectively.

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