'Organic Metals.' Synthesis of a New Type of Organic Metal derived from Polyacetylene, $(CH)_x$

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Summary When *ca.* 85% *cis* films of the semiconducting polymer, polyacetylene, $(CH)_x$, are doped with bromine to compositions such as $[CHBr_y]_x$ ($y = ca.$ 0·15—0·35) and then partly dehydrobrominated at 150 °C, they yield new semi-conducting polymers such as $[CH_{0\cdot85}Br_{0\cdot11}]_x$ which can then be doped with I_2 or AsF_5 to yield new highly conducting organic metals such as $[CH_{0\cdot89}Br_{0\cdot09}I_{0\cdot12}]_x$ and $[CH_{0\cdot82}Br_{0\cdot13}(AsF_5)_{0\cdot12}]_x$, respectively.

POLYACETYLENE is the simplest organic polymer. We have shown previously that it can be prepared in either the *cis*- or *trans*-forms as silvery, flexible films which can be treated with either n- or p-type dopants to yield a series of semiconductors which at higher dopant levels are converted into organic metals.[1,2] In principle, the hydrogen atoms can be replaced either in whole or in part by organic, inorganic, or organometallic groups to give an almost unlimited number of organic semiconductors and 'metals' having a wide range of chemical and physical properties.

We report that we have been successful in replacing up to *ca.* 20% of the hydrogen atoms in films of *cis*-rich $(CH)_x$ with bromine to give golden, relatively flexible p-type semiconducting films representing a new composition of matter, $[CH_qBr_y]_x$, where $(q+y) =$ *ca.* 0·82—0·98. Films having values of $q =$ *ca.* 0·75—0·90 and $y =$ *ca.* 0·07—0·16 have been studied most extensively. Films having lower values of y can be obtained, but the upper value is not yet well defined. These films can be doped readily with I_2 or AsF_5 vapour to give relatively flexible films conducting in the metallic regime. The former are shiny silvery-black and the latter are shiny golden in appearance.

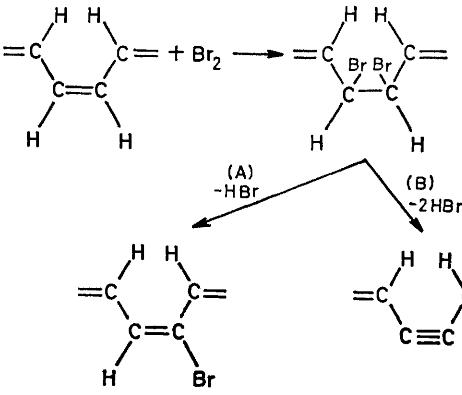
Ca. 85% *cis*-$(CH)_x$ films were treated with Br_2 vapour ($\leqslant$ 10 Torr) at room temperature as we have described previously[3,4] to yield bright lustrous purple to blue-green films of $[CHBr_y]_x$ ($y =$ *ca.* 0·15—0·35). The conductivity and thermoelectric power of a typical film (sample 1) are given in the Table. The values are characteristic of a p-type metal.[5,6] When these films are heated *in vacuo* from 120 to 150 °C in a sealed container, HBr and Br_2 are first evolved. This gaseous mixture is then permitted to react further with the film at room temperature and is then reheated. After this procedure has been repeated several times, all the Br_2 is absorbed and HBr is the only gaseous material formed. The volume of HBr evolved, together with elemental analysis for C, H, and Br, show that compositions such as $[CH_{0\cdot85}Br_{0\cdot11}]_x$ are obtained. The actual composition can be varied by altering the extent of the original doping before thermolysis and the temperature and duration of heating. Typical conductivities of samples of this material from different preparations were in the range (1—5×10^{-6} ohm^{-1} cm^{-1}) at room temperature and showed thermoelectric power values of *ca.* +500—600 μV/K (see Table, sample 2). The activation energy for electrical conduction was *ca.* 0·2 eV. These data are consistent with a p-type semiconductor.[3,5,6]

TABLE. Conductivity and thermoelectric power data for selected $(CH)_x$ derivatives.

Sample	Composition	σ/ohm^{-1} cm^{-1} [a]	S/μV K^{-1}
1	$[CHBr_{0\cdot16}]_x$ [b]	20·8	26·9 ± 0·5
2	$[CH_{0\cdot82}Br_{0\cdot14}]_x$ [c]	$2{\cdot}1 \times 10^{-6}$	650 ± 30
3	$[CH_{0\cdot89}Br_{0\cdot09}I_{0\cdot12}]_x$ [d]	10·0	18·0 ± 0·2
4	$[CH_{0\cdot82}Br_{0\cdot13}(AsF_5)_{0\cdot12}]_x$ [e]	12·0	13·2 ± 0·5

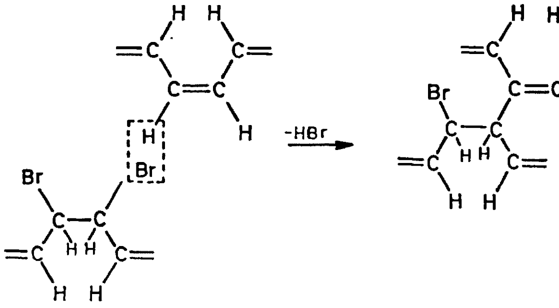
[a] Measured by 4-probe method at 25 °C. [b] Composition by weight uptake. [c] Composition by weight uptake and by volume of HBr evolved. Elemental analysis (sum of C, H, and Br = 98·52%) of another sample the composition $[CH_{0\cdot85}Br_{0\cdot11}]_x$. [d] Composition by weight uptake of Br and I and by volume of HBr evolved. Elemental analysis (sum of C, H, Br, and I = 99·55%) of another sample gave the composition $[CH_{0\cdot78}Br_{0\cdot11}I_{0\cdot07}]_x$. [e] Composition by weight uptake of Br and AsF_5 and by volume of HBr evolved. Elemental analysis (sum of C, H, Br, As, and F = 100·35%) of another sample gave the composition $[CH_{0\cdot76}Br_{0\cdot07}(AsF_6)_{0\cdot09}]_x$.

We have reported previously[1,4] that $(CH)_x$ can be doped easily with I_2 or AsF_5 vapour to give highly conducting metallic films. Analogous results are obtained with $[CH_qBr_y]_x$. For example, we find that on doping $[CH_{0\cdot89}Br_{0\cdot09}]_x$ with I_2 vapour and $[CH_{0\cdot82}Br_{0\cdot13}]_x$ with AsF_5 vapour at room temperature, films of composition $[CH_{0\cdot89}Br_{0\cdot09}I_{0\cdot12}]_x$ and $[CH_{0\cdot82}Br_{0\cdot13}(AsF_5)_{0\cdot12}]_x$, respectively, are obtained. Typical room temperature conductivity and thermoelectric power data for these materials (Table, samples 3 and 4, respectively) are characteristic of p-type metals.[5,6]



SCHEME 1

We believe that on heating the brominated films, addition of bromine to the double bond takes place and that partial dehydrobromination also occurs to liberate HBr. This results in the replacement of some of the hydrogen atoms by bromine [Scheme 1, path (A)]. Since the value of $(q+y)$ in $[CH_qBr_y]_x$ is usually in the range *ca.* 0·82—0·98 some dehydrobromination also apparently occurs to remove both the H and Br substituents from a given C atom as illustrated in Scheme 1, path (B). This could also occur between chains as, for example, shown in Scheme 2. Although the *cis*-isomer is depicted in Scheme 2, it is quite probable that



SCHEME 2

isomerization to the *trans* form may take place during the processes involved Dehydrobromination could, of course, also take place with this isomer

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