

'Organic Metals'. New Classes of *p*-Type Dopants for Converting Polyacetylene, (CH)_x into the 'Metallic' State

By SHEK-CHUNG GAU, JOANN MILLIKEN, ADAM PRON, ALAN G. MACDIARMID,* and ALAN J. HEEGER†
(Department of Chemistry and †Department of Physics, Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19104)

Summary When *ca.* 85% *cis* films of the semiconducting polymer, 'polyacetylene,' (CH)_x, are treated with H₂SO₄, HClO₄, (NO₂)(SbF₆), (NO)(SbCl₆), and (NO₂)(BF₄) two new classes of dopants are introduced to give golden, flexible films exhibiting high conductivities characteristic of the metallic state.

It has been shown that the semiconducting polymer, 'polyacetylene,' (CH)_x, can be doped, either chemically or electrochemically with halogens, AsF₆, *etc.* to yield at first either *p*- or *n*-type semiconductors and ultimately, silvery or golden flexible films exhibiting the electronic properties of metals.^{1,2} We report two new classes of *p*-type dopants, one of which gives films having a conductivity as large as any so far observed for non-oriented (CH)_x.

When the vapour from H₂SO₄ (98%) or HClO₄ (71%) is pumped over *ca.* 85% *cis*-(CH)_x for 1—2 days at room temperature, flexible golden silvery films are obtained which undergo almost no change in appearance or conductivity after two days' exposure to air (Table). The conductivity is electronic, not ionic, and is not caused by the presence of free acid since passage of *ca.* 20 times the number of coulombs needed to completely polarize free acid, if it were present, caused almost no change in the resistance of the samples. It is surprising that protonic acids act as such excellent and stable dopants. It is not yet clear whether the (H₃O)⁺ group causes conduction by partly withdrawing electrons from the (CH)_x π-system or whether actual addition of a proton to a (CH) carbon atom occurs. In either case, the positively charged carbon atom could be stabilized, at least in part, by co-ordination of free water molecules when these are available.

TABLE. Selected *p*-type dopants for converting (CH)_x into the metallic state^a.

	Conductivity ^b Ω ⁻¹ cm ⁻¹
<i>cis</i> -(CH) _x	1.7 × 10 ⁻⁹
<i>trans</i> -(CH) _x	4.4 × 10 ⁻⁵
[CHI _{0.30}] _x	5.5 × 10 ²
[CH(AsF ₆) _{0.1}] _x ^c	1.1 × 10 ³
[CH(H ₂ SO ₄) _{0.106} (H ₂ O) _{0.070}] _x ^d	1.2 × 10 ³
[CH(HClO ₄) _{0.127} (H ₂ O) _{0.297}] _x ^e	1.2 × 10 ³
[CH(SbF ₆) _{0.05}] _x ^f	4.0 × 10 ²
[CH(SbCl ₆) _{0.0095}] _x ^g	1.0 × 10 ⁻¹
[CH(SbCl ₆) _{0.009}] _x ^h	2
[CH(BF ₄) _{0.09}] _x ⁱ	1.0 × 10 ²

^a All analyses were carried out at Galbraith Laboratories, Inc., Knoxville, Tennessee. ^b Conductivity was measured at 25 °C by d.c. four-probe technique. ^c σ_{RT} = 1096 Ω⁻¹ cm⁻¹, increasing to a maximum at -43 °C of 1129 Ω⁻¹ cm⁻¹, giving a σ_{max}:σ_{RT} = 1.03:1. ^d Composition determined by C, H, and S analyses. ^e Composition determined by C, H, and Cl analyses. ^f Composition determined by C, H, F, N (found: 0.37%), and Sb analyses. ^g Composition determined by C, H, Cl, N (found: <0.05%), and Sb analyses. ^h Composition determined by C, H, Cl, and Sb analyses. ⁱ Composition determined by C, H, B, F, and N (found: 0.73%) analyses.

We find that anions such as (SbF₆)⁻ can be readily introduced into (CH)_x simply by treating a (CH)_x film (*ca.* 85% *cis* isomer) with a MeNO₂-CH₂Cl₂ solution of appropriate (NO)⁺ or (NO₂)⁺ salts. Thus (NO₂)⁺(SbF₆)⁻ yields golden, flexible highly conducting films (Table) of [CH(SbF₆)_{0.05}]_x, with liberation of NO₂. The final product contains a negligible amount of N by elemental analysis. Since the SbF₆ group must exist essentially as an ion of -1 charge, it would appear that the (CH)_x must be in the form of a poly-

carbonium ion chain and that the interaction between the CH and the SbF_5 must be largely ionic, e.g. $[(\text{CH})^{+0.05}(\text{SbF}_6)^{-0.05}]_x$.

In the case of $(\text{NO})^+(\text{SbCl}_6)^-$ the reaction is somewhat complex; in solution, highly conducting (Table) films of $[\text{CH}(\text{SbCl}_6)_{0.0095}]_x$ or $[\text{CH}(\text{SbCl}_6)_{0.009}]_x$ are obtained depending on slight variations in experimental procedure. The SbCl_6 species is formulated as consisting of a Cl_3^- ion coordinated to SbCl_5 . In the vapour phase at room temperature, predissociation of $(\text{NO})^+(\text{SbCl}_6)^-$ to NOCl and SbCl_5 apparently occurs since the product then consists of conducting films of $[\text{CH}(\text{SbCl}_6)_{0.022}]_x$ (Table). These are at least formally analogous to the highly conducting $[\text{CH}$ -

$(\text{AsF}_6)_{0.1}]_x$ films we have reported earlier.¹ A complex reaction occurs with solutions of $(\text{NO}_2)^+(\text{BF}_4)^-$ in neat MeNO_2 to yield highly conducting films of $[\text{CH}(\text{BF}_2)_{0.09}]_x$, and, possibly, MeF , NO_2F , and NO_2 (Table). It is possible that the material contains the $(\text{BF}_2)^-$ ion.

The $(\text{NO})^+$ and $(\text{NO}_2)^+$ ions are apparently excellent species for oxidizing the π -system of $(\text{CH})_x$ and are capable of concomitantly introducing anions which stabilize the polycarbonium ion chains.

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