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Highly Conducting Transition Metal Derivatives of Polyacetylene

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Summary Polyacetylene films have been oxidized with transition metal ions to give highly conducting polyolefinic cations; their conductivity can be modified by subsequent treatment with Lewis bases.

Films of polyacetylene [$(CH)_x$] exhibit very high electrical conductivities when treated with acceptors such as bromine, iodine, and AsF_5,[1] or with donors such as sodium naphthalide.[2] We have observed that other metals can be introduced into the fibrous $(CH)_x$ material. When polyacetylene films prepared according to Ito *et al.*[3] are dipped into solutions of silver perchlorate or silver tetrafluoroborate in toluene, incorporation of silver salt takes place to an extent which varies with both the concentration of the toluene solution and the exposure time. Complexes of stoicheiometry $[(CH)Ag_{0\cdot006}]_x$ to $[(CH)Ag_{0\cdot018}]_x$ have been investigated thus far.

Incorporation of the silver salt produces very striking changes in the film conductivity; $[(CH)Ag_{0\cdot018}]_x$, for example, shows a conductivity of 3·0 Ω^{-1} cm^{-1} compared with *ca.* 10^{-5} Ω^{-1} cm^{-1} for the original film. This value is very close to that observed in AsF_5 treated films at the same doping level. Although silver salts are known to display ionic conductivity in other systems, the observed thermopower of 20 μV deg^{-1} is incompatible with ionic conductivity in this case.[4] *X*-Ray diffraction data show that although the peaks corresponding to $(CH)_x$ itself remain unchanged and no silver perchlorate is observed, new peaks appear which can be attributed to free silver. The observed thermopower is too high to be attributable to free silver (1·5 μV deg^{-1} at 25 °C).[5] Moreover, when the silver perchlorate treated films are exposed to ammonia vapour the *X*-ray peaks corresponding to free silver remain unchanged, but the film conductivity decreases rapidly and permanently to levels comparable to those in untreated $(CH)_x$. Thus the enhanced conductivity in the doped films cannot be due to silver metal. The absence of conductivity associated with the free silver, both before and after exposure to ammonia, is explained by electron micrographs which clearly show that the silver exists in discrete islands. The strong wavelength-independent absorption seen in the i.r. region after silver salt treatment, and attributed to metallic behaviour, also disappears on ammonia exposure, allowing the observation of bands attributable to the perchlorate anion. These data suggest that the silver ions are acting as oxidants to give free silver and conducting polyolefinic cations with immobile perchlorate counterions [equation (1)].

$$(CH)_x + yAgClO_4 \rightarrow [(CH)_x^{y+}\ (ClO_4^-)_y] + yAg^0 \qquad (1)$$

The conductivity of the ammonia treated films can be restored by retreatment with $AgClO_4$ or $AgBF_4$ in toluene. In this and in the original doping, solvents other than toluene may be used, but basic solvents such as pyridine must be avoided as these solvents behave like ammonia in rapidly reducing the conductivity of all acceptor doped $(CH)_x$ films. Effects similar to those described for silver salts can also be achieved using the salts of other metals, for example iron and copper.

Although qualitatively similar results are obtained using $(CH)_x$ of either all *trans* or mixed *cis–trans* geometry, Raman spectroscopy shows that exposure to silver perchlorate reduces the intensity of the *trans* bands relative to the *cis* bands. Careful examination of the Raman spectrum of all *trans* $(CH)_x$ shows that the 1080 cm^{-1} band, reported to be the C–C stretch,[6] contains a second peak at 1120 cm^{-1}. Exposure of the all *trans* material to silver perchlorate also causes a reduction of the 1120 cm^{-1} band relative to the 1080 cm^{-1} band. Subsequent treatment with ammonia restores the 1120 cm^{-1} band to its original intensity.

The reaction of bromine with $(CH)_x$ appears analogous to that observed with the silver salts. Oxidation of the $(CH)_x$ chain is in this case accompanied by the formation of linear tribromide anions [equation (2)], as evidenced by the strong Raman fundamental at 160 cm^{-1} (and several overtones). Thus, the oxidation of $(CH)_x$ by bromine also appears to parallel the modification of $(SN)_x$ with bromine.[7] *X*-Ray examination of the brominated $(CH)_x$ shows a new broad peak at 7·31 Å which is 3·56 Å greater than the 3·75 Å main spacing in pristine $(CH)_x$. This suggests the insertion of bromine between the polyacetylene chains in agreement with the previous results on iodinated $(CH)_x$.[8] In contrast to the results observed with silver perchlorate, bromine seems preferentially to decrease the *cis* Raman bands relative to *trans*, and selectively to reduce the 1080 cm^{-1} *trans* band relative to the band at 1120 cm^{-1}.

$$(CH)_x + \tfrac{3}{2}yBr_2 \rightarrow [(CH)_x^{y+}\,(Br_3^-)_y] \qquad (2)$$

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