# A 'Metallic' Derivative of Polymeric Sulphur Nitride: Poly(thiazyl bromide), $(SNBr_{0\cdot4})_x$

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*Summary* Crystals and films of $(SNBr_{0\cdot4})_x$, a derivative of polymeric sulphur nitride, $(SN)_x$, have been characterized; visible and i.r. reflectance and room-temperature conductivity are consistent with metallic behaviour.

POLYMERIC sulphur nitride (polythiazyl), $(SN)_x$, is the first example of a covalent polymer which is metal-like even though it contains no metal atoms.[1] It exists as golden crystals and has attracted considerable attention during the past 4 years because of its remarkable electronic properties which include superconductivity below 0·3 K.[2] As part of a continuing study of the properties of $(SN)_x$ we have been investigating its reactions with halogens. In 1969 Patton[3] reported briefly that $(SN)_x$ reacts with chlorine to give NSCl. Bernard *et al.*[4] reported recently that $(SN)_x$ reacts with bromine vapour at room temperature to give a grey-blue solid of unknown composition.

We find that crystals of $(SN)_x$ (*ca.* 1—10 mm$^3$) react during *ca.* 1 h at room temperature with bromine vapour (60 Torr) to give shiny, black crystals of $(SNBr_{0\cdot4})_x$ having a blue-purple tinge. The density of the new compound (2·67 g cm$^{-3}$) is significantly greater than that of $(SN)_x$ (2·30 g cm$^{-3}$). The volume increase calculated from the formula and density data is 46%, in reasonable agreement with the observed changes in crystal dimensions upon bromination. There is no significant change in the length of the crystal in the *b* crystallographic direction [the direction parallel to the $(SN)_x$ polymer chains]. Although the crystals appear well formed, *X*-ray studies show they have very considerable defect structure. The fibrous nature characteristic of $(SN)_x$ crystals when mechanically pulled apart is preserved in $(SNBr_{0\cdot4})_x$.

Crystals of $(SNBr_{0\cdot4})_x$ appear to react with air to a negligible extent during 1 h at room temperature. After 2 days the crystals have undergone no detectable change in weight but they are visibly tarnished. When crystals of $(SNBr_{0\cdot4})_x$ were heated *in vacuo* at 86 °C for *ca.* 30 h they were converted into copper-coloured crystals of $(SNBr_{0.25})_x$ which have conductivities comparable to $(SNBr_{0\cdot4})_x$.

The reflectance of polarized light from a crystal face of $(SNBr_{0\cdot4})_x$ is dependent on the relative orientations of the crystal and the plane of polarization of the incident light. Films of $(SN)_x$ on glass or aligned epitaxial films of $(SN)_x$ on Mylar[5] may be brominated in a similar manner to $(SN)_x$ crystals to give high quality films. The brominated epitaxial films show reflectance anisotropy in the visible region. Reflectance measurements from a brominated $(SN)_x$ film on glass show a broad minimum in the visible region

increasing to metallic reflection in the i.r. region. The plasma edge is shifted from 2·55 eV in $(SN)_x$ into the i.r. region near 1·6 eV for $(SNBr_{0\cdot4})_x$. Four-probe d.c. measurements of the electrical conductivity indicate values an order of magnitude greater than those of the $(SN)_x$ crystals from which the $(SNBr_{0\cdot4})_x$ was synthesized. These initial studies suggest metallic behaviour. The synthesis of $(SNBr_{0\cdot4})_x$ implies that a whole class of metallic derivatives of $(SN)_x$ may possibly exist.

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