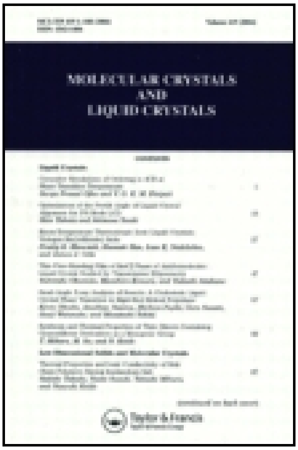

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One Dimensional Conducting Polymers

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One Dimensional Conducting Polymers

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Simultaneously with a study of the properties of the one dimensional polymeric metal poly(sulfur nitride),[1,2] we have attempted to incorporate one dimensional strands of poly(iodine) atoms and poly(sulfur nitride) into the canals of clathrating hosts. If such structures could be prepared, modification of the clathrating structure and its polarizability might result in another approach to the Little model[3] of conjugated "spines" surrounded by polarizable "side groups" leading to an excitonic mechanism of superconductivity.

POLY(SULFUR NITRIDE)

It has now been clearly established that the electrical conductivity of single crystals (really highly oriented fiber bundles) of $(SN)_x$ is highly anisotropic with a metal-like temperature dependence,[1,2] and that the polymer becomes superconducting at ~0.26°K.[4a] Conductivity maxima are observed at temperatures between 20 and 34°K depending on the quality of crystals,[2] but all crystals studied show the superconducting transition between 0.22 and 0.26°K irrespective of the occurrence of this conductivity maximum.[4b]

POLY(IODINE) CHAINS[5]

A variety of canal type complexes of iodine has been prepared in single crystal form—analogs of the familiar polyiodine chain formed in the starch helix. In all of the complexes studied, channels of iodine form in the host matrix; typically the iodine atoms are equi-distant with a spacing of ~3.1 Å.[6,7] The limitation in these systems is that the average length of the poly(iodine) chains is probably <30 atoms.[7c,8,9] Herbstein [10] has recently questioned the exact equivalence of iodine atoms in these structures.

TABLE I

D.C. Conductivity of iodine chain complexes at room temperature

Compound	$\sigma, \Omega^{-1}cm^{-1}$ Along iodine chain	$\sigma, \Omega^{-1}cm^{-1}$ $\perp$ Iodine chain	Ea eV
(2,6-diphenyl-γ-pyrone)$_2$·HI$_5$	10^{-5}	10^{-8}	0.78
Coumarin·KI·I$_2$	10^{-5}	—	0.90
(Trimesic acid · H$_2$O)$_{10}$ · HI$_5$	10^{-8}	10^{-10}	—
α-cyclodextrin·polyiodide	10^{-7}	10^{-8}	0.61
Benzamide·HI$_3$[a]	10^{-5}	—	—
Benzamide·KI$_3$[a]	10^{-4}	—	—

[a] Very unstable crystals.

Table I presents data on a variety of such canal complexes. As can be seen, these materials do not exhibit metallic conductivity. Bersohn and Isenberg[11] have presented a band model for such a complex indicating its metallic nature assuming equivalent bond lengths. If the interatomic distances of the iodines alternate, as proposed by Stein and Rundle,[12] then the band model proposed could easily be modified to imply an activated temperature dependent conductivity. An interrupted strand model may also be considered, i.e. carrier migration from strand to strand has an activation energy.

POLY(SULFUR NITRIDE) CANAL COMPLEXES[13]

The aim of this work was to prepare metallic $(SN)_x$ chains constrained in dielectric matrices. It has been shown that both urea and thiourea are capable of occluding several small organic molecules within channels which run throughout the crystal lattice,[14] and that the guest molecules can then be polymerized to form stereospecific long chain polymers. It was hoped therefore to introduce molecules of S_2N_2 into such channels and polymerize these in situ to form highly conducting $(SN)_x$ chains within a host matrix. In this manner the effect of the matrix on the conductivity could be studied.

Several preparations were tried but in all but one case the unstable nature of the S_2N_2 prevented the formation of the inclusion complex before polymerization occurred. On one occasion however, the thiourea/S_2N_2 inclusion complex was thought to have been obtained, characterized by the formation of long needle shaped crystals which remained after standing for several days.[15] Subsequent attempts to polymerize the S_2N_2 by heat led to the loss of the guest molecules from the channels, and formation of polymer outside the crystal lattice. S_2N_2 was polymerized in the channels of thiourea by cobalt-60 radiation, however, resulting in a dark, amorphous thiourea-$(SN)_x$ complex. Experiments were also performed with benzophenone as the matrix.

Shiny, bronze-colored crystals of polysulfur nitride were formed by allowing a solution of S_2N_2 and benzophenone in tetrahydrofuran to evaporate slowly in a nitrogen atmosphere. Experiments are continuing to determine if a benzophenone-polysulfur nitride channel complex had been formed and decomposed. Evaporation of a solution of S_2N_2 in tetrahydrofuran did not result in the formation of shiny $(SN)_x$ crystals. Further work on this approach to achieving $(SN)_x$ in dielectric matrices is now underway.

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