

Poly(sulfur nitride), $(\text{SN})_x$,
Synthesis, Structure, and Conductivity

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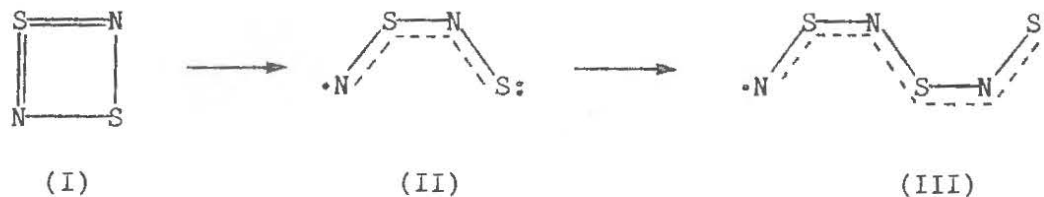
Literature Seminar

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Poly(sulfur nitride), $(\text{SN})_x$, is a compound that has attracted great attention in the scientific community in the last 15 years. Studies have concentrated on a wide variety of areas: synthesis; physical and electronic structure, formation, and electrical properties [1]. Perhaps the most striking aspect of $(\text{SN})_x$ is its metal-like properties of high conductivity (on the order of mercury), metallic reflectivity, and the superconductive transition at 3K. Despite the large number of publications on $(\text{SN})_x$, only recently has a consistent picture of the properties begun to emerge.

Poly(sulfur nitride) was first synthesized by F. P. Burt in 1910 [2]. His method consisted of passing hot S_4N_4 vapor through silver or glass wool and collecting the resulting S_2N_2 on a cold finger and allowing it to polymerize to $(\text{SN})_x$. In many respects, this mode of synthesis has not undergone drastic revision [3]. In addition to the above method, there have been some more recent synthetic routes which include the low temperature polymerization of S_4N_2 in THF [4], the high temperature reaction of $\text{S}_4\text{N}_3\text{Cl}$ and silver wool [5], the decomposition of $\text{Ph}_3\text{P}=\text{NSN}=\text{S}=\text{S}$ [6], and others [7]. There have also been some chemical (soln) reactions [8] and electrochemical synthesis [9].

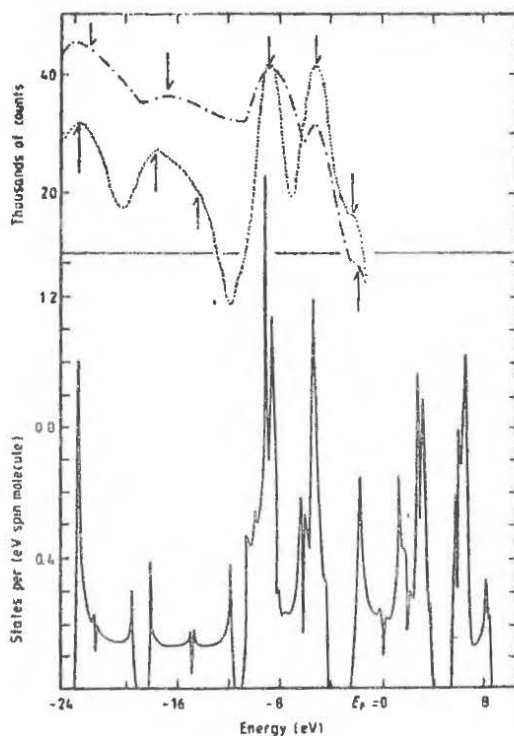
To gain an understanding of the electrical properties of $(\text{SN})_x$ several studies of the solid-state polymerization of S_2N_2 have been carried out. Early theories [2] involved a simple ring cleavage of the S_2N_2 unit and the subsequent "chain reaction" formation of the polymer.



Molecular orbital studies predict that the driving force for the reaction might involve the "development" of a new sigma orbital in the open form (II) that was formerly an antibonding pi orbital in (I) [10]. An alternate theory postulates that the d orbital functions are involved in electron delocalization which leads to an extravalent N---S d function interaction driving the dimerization at 4 Kcal/mole [11]. Structural studies have revealed that during the polymerization process there is substantial crystal imperfection due to crystal twinning, an event which ultimately is responsible for the compound's electronic properties [12].

In addition to electronic formation studies, there have been many views of the electronic structure of the polymer. One study predicts that in the idealized single chain linear structure there is a metal-insulator Peierls distortion manifested in a charge density wave (CDW) [13]. Interchain interaction and defect sites are responsible for suppressing the metal to insulator 1-D transition. Band structure calculations have ranged from the early 1-D structure postulate, to two recent structures that predict that the conductivity is due to

degenerate pi orbitals at the Fermi level rendering the Pierls distortion ineffective at suppressing the metallic conductivity [14]. X-ray photoelectron spectrum (XPS) has shown that the density of states at the Fermi level to be 0.14 states per (eV spin molecule) as predicted in above model (Fig. IV) [14].



Comparison of the density of states obtained by the present calculation (full curve) with the XPS results reported by two different experimental groups, the chain curve obtained by Ley and the dotted curve obtained by Mengel *et al.*

(IV)

Polarized reflectivity spectra in the VUV region found that the tight binding band model is successful in describing the electronic structure [15]. It also postulates that the conduction takes place in a 1-D manner in the conduction band involving electron and hole gaps above the Fermi surface.

One of the properties still undergoing debate is how conductivity varies with temperature. Early measurements of conductivity record an increase of conductivity to approximately 30 K at which point, the conductivity decreases. Recently, it has been shown that the conductivity increases down to the superconducting transition [16]. This new data supports current thinking that $(\text{SN})_x$ should be considered a 3-D semi-metal.

The future of $(\text{SN})_x$ and related chemistry promises to be fruitful. There are already several patents of applications in diodes and batteries. The intercalate with bromine, $(\text{SNBr}_y)_x$, has shown to have conductivities on the order of 10^3 times greater than undoped $(\text{SN})_x$. Future studies of related compounds - $(\text{SeN})_x$ - for example, might prove to have electrical properties that surpass $(\text{SN})_x$ in metallic behavior. $(\text{SN})_x$ promises to be the first in a class of metallic main group compounds with a host of unique properties.

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