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Polysulfur Nitride—A Metallic, Superconducting Polymer

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I. Introduction

A. Historical

Polysulfur nitride (also known as polythiazyl; hereinafter referred to as $(SN)_x$) is the first example of a polymeric metal. It is interesting to note that suggestions of its metallic character have been in the literature since its first crystalline preparation by Burt[1] in 1910. By the method which is still used today (with small, but important modifications), Burt cleaved tetrasulfur tetranitride, S_4N_4, by passing the hot vapor in vacuo through heated silver gauze; he observed a thin blue film and a thicker coating which became opaque and had a metallic, bronze-like luster by reflection. When S_4N_4 was being sublimed at 300 °C in vacuo through quartz wool, Burt also collected some large, bronze-colored crystals (weighing about 4 mg each), and with rather primitive analytical techniques showed that, within 3%, the compound analyzed as $(SN)_x$. Thus, although the metallic luster clearly should have inspired someone to measure its conductivity, and the observation of crystallinity should have inspired someone to study the interesting polymerization leading to such a highly crystalline product, it took about 50 years for interest in this compound to be kindled.

Further early history worthy of mention is the observation by Usher[2] that S_4N_4 cleavage through silver gauze heated at 124–125 °C leads to a ruby-red film, which turns blue slowly at 50 °C, rapidly at 60 °C, and takes between ½ h to 2 days at room temperature to yield a blue film. Usher concluded the material was identical with $(SN)_x$ obtained by Burt.

It was not until Becke-Goehring (her early papers published under the name Goehring) undertook some systematic work in the 1950s that the details of chemistry of $(SN)_x$ formation began to emerge.[3]

Cleavage of S_4N_4 vapor on silver wool is thought to occur in two stages.[4] Firstly, S_4N_4 reacts with Ag in a nearly complete decomposition:

$$S_4N_4 + 8Ag \rightarrow 4Ag_2S + 2N_2$$

Secondly, the Ag_2S catalyzes the thermal splitting:

$$S_4N_4 \xrightarrow{Ag_2S} 2S_2N_2$$

Disulfur dinitride S_2N_2 was recognized by Becke-Goehring as being the important intermediate in the preparation of $(SN)_x$.[5] It is a white volatile crystalline solid, stable only at low temperatures, which polymerizes to $(SN)_x$ in the solid state. Becke-Goehring states "... polysulfur nitride ... is diamagnetic and forms fibre-like crystals with a metallic sheen, and shows the remarkable property that it is a semiconductor. At 25° the specific resistance of the pressed powder, extrapolated to infinite pressure, is 0.01_3 ohm cm. The resistance of the powder decreases with rising temperature ...".[3a]

No further study of the properties of $(SN)_x$ occurred until Labes et al.[6] studied the electrical conductivity, thermal conductivity, and thermoelectric effect in $(SN)_x$. The conductivity showed a very small activation energy of less than 0.02 eV, and it was speculated that conductivity might be metallic superimposed on which is a temperature-dependent mobility. Yoffe et al.[7] obtained similar results on the conductivity of $(SN)_x$, reported electronic and vibrational spectra, and presented a band model to explain the semiconductivity of $(SN)_x$.

Several workers had noted explosive hazards associated with the intermediate dimer, S_2N_2.[3,6] It was this fact which prevented a detailed exploration of the properties of $(SN)_x$. However, a French group[8] presented information which indicated that the danger of explosion could be minimized, and they presented crystal structure information and conditions under which crystal growth of $(SN)_x$ could be achieved. This led Labes et al.[9] to

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TABLE I. Conditions for the Ag Wool Pyrolysis of S_4N_4 to S_2N_2

Investigator	ref	pressure, μ	S_4N_4 temp, °C	Ag wool temp, °C	cold finger temp, °C
Becke-Goehring	15	?	80	300	−80
Patton	4	15	80–95[a]	290–305[a]	−196
Douillard	26	<1	88–92	140–160	−196
WLP	9	<1	80	200	−80[b]
Hsu and Labes	10	<1	140	200	−80[c]
SAGGG	37	<0.1	80	325	−196
MRSMGH	35a	<0.01	85	220	−196

[a] Patton[4] claims that below 280 °C, unreacted S_4N_4 passes through the Ag zone, and above 305 °C, the product is contaminated with a product having a red-orange tint. [b] $(SN)_x$ crystals were also formed *directly* by polymerization of S_2N_2 on a 0 °C cold finger. [c] $(SN)_x$ crystals were also formed *directly* by polymerization of S_2N_2 on a 8 °C cold finger.

reinvestigate the properties of $(SN)_x$ in the form of ''crystals,'' really oriented fiber bundles. The surprising and exciting result that $(SN)_x$ is a metal down to liquid helium temperature was published at the end of 1973[9] and led to considerable activity. Details of the measurements of the metallic properties of $(SN)_x$ crystals and films were published in 1974;[10] measurements of specific heat,[11] optical reflectivity,[12] and magnetic susceptibility[13] confirmed the essentially metallic nature of the polymer down to 1.2 K. The activity on $(SN)_x$ was then further stimulated by the exciting observation of superconductivity in $(SN)_x$ at 0.26 K.[14]

This historical perspective on $(SN)_x$ has been presented to set the stage for a summary of our current understanding of the electronic and optical properties of the material.

B. Previous Reviews

Several reviews on the preparation and properties of $(SN)_x$ have been written. Among the most recent are two by Street and Greene.[15] Other reviews are those by Geserich and Pintschovius,[16] and by MacDiarmid et al.[17] A brief review has been written by Baughman.[18] A description of the chemical properties of $(SN)_x$ and related materials is given in ''Gmelins Handbuch der anorganischen Chemie'',[19] by Heal,[20] and by Goehring.[3]

General reviews of low-dimensional systems are given in two volumes edited by Keller,[21] and one edited by Schuster.[22] The most recent survey of low-dimensional systems is in the volume edited by Miller and Epstein.[23]

The chemistry and physics of $(SN)_x$ is developing very rapidly. It is the purpose of this review to describe the more important developments in this field in a systematic way into the first quarter of 1978. The papers included are intended to by typical of those on a given subject, rather than to be all inclusive.

II. Preparation of Polysulfur Nitride

A. Tetrasulfur Tetranitride

The starting material for the synthesis of $(SN)_x$ in all current work is tetrasulfur tetranitride, S_4N_4, which is prepared by the reaction between ammonia and disulfur dichloride.[24,25] The preparation usually yields a material with a melting point of 178 °C; sublimation (preferably gradient sublimation) yields a material with a melting point ~10 °C higher. Douillard[26] uses the old technique of Burt and Usher[27] of subliming S_4N_4 through silver wool at 100 °C to remove traces of sulfur (the silver wool being at too low a temperature to catalyze the cleavage of S_4N_4 to S_2N_2). Note that the sensitivity of S_4N_4 toward both shock and temperature increases with purity. It is *not* advisable to take a melting point in a conventional glass melting point apparatus; even a melting point capillary of S_4N_4 can explode violently. Perhaps a better way of assessing the purity and melting point is by differential scanning calorimetry (DSC), where explosions of the heated sample present no danger to the operator or apparatus. In the authors' laboratory, the melting of S_4N_4 determined by DSC is typically sharp, between 185 and 189 °C, and *almost always accompanied by an audible explosion slightly above the melting point.*[28]

Tetrasulfur tetranitride is a thermochromic orange crystalline solid at room temperature. At ca. 100 °C it is a deep red in color. At ca. −30 °C and lower temperatures, it is light yellow. The molecular structure is an eight-membered cradle shaped ring of D_{2h} symmetry which has coplanar nitrogen atoms. The vibrational spectra[29] of S_4N_4 and S_2N_2 have been studied by Bragin and Evans. The electronic structure of S_4N_4 has been studied by a number of authors.[30] The sublimation pressure of S_4N_4 has been measured between 70 and 90 °C.[31] It was found to be 3.51×10^{-2} Torr at 90 °C. Crystalline solid S_4N_4 is an insulator which has a conductivity, $\sigma = 10^{-14}\ \Omega^{-1}\ \text{cm}^{-1}$ at 25 °C.[32]

B. Disulfur Dinitride

Disulfur dinitride, S_2N_2, is a clear colorless crystalline solid at room temperature with a saturation pressure of ca. 0.021 Torr at 0 °C.[33] The Raman spectra of S_2N_2 and partially polymerized S_2N_2 films have been reported by Iqbal and Downs.[34] The electronic structure of S_2N_2 must be written as a resonance hybrid.[35] A CNDO/2 localized molecular orbital study of S_2N_2 leads to the conclusion that the molecule is formed from six π electrons in three-center bonds and four unshared electron pairs superimposed on a square-planar (D_{2h} symmetry) σ-bond structure.[36]

Various conditions have been used for the cleavage of S_4N_4 to S_2N_2. In general S_4N_4 is heated to a temperature of 80 °C or greater at a pressure of $<1\ \mu$ and passed through a catalytic zone. The best catalyst found so far is silver wool. Copper wool, quartz wool, and coatings of silver or copper on quartz wool have all been utilized with less success.

A summary of conditions utilized by various investigators is given in Table I. At first glance there are a large number of discrepancies in this table. Patton[4] varied conditions rather widely and found that below 280 °C considerable S_4N_4 passes through the silver zone, and above 305 °C, the product is contaminated with a product having a red-orange tint, presumably S_4N_2. Douillard's work[26] was an attempt to minimize explosive hazards by lowering the temperature of the catalytic zone. He reports the best yield of S_2N_2 at temperatures between 140 and 160 °C, albeit some S_4N_4 passes through the heated zone. S_4N_4 is easy to isolate, however, from S_2N_2 because of a large difference in volatility. Also S_4N_2 is less volatile than S_2N_2. Thus, a vacuum fractionation train (Figure 1) allows collection of S_2N_2, S_4N_4, and other contaminants. However, S_2N_2 can be separated cleanly from these contaminants by using various low-temperature baths on the fractionation train. The final transport of S_2N_2 from one trap to another is important to the size and perfection of S_2N_2 crystals, and therefore to the ultimate formation of $(SN)_x$.

The discrepancies in synthetic conditions probably arise from variations in pressure in the system. Since volatile products are being formed, the local pressure controlling the transport rate of S_4N_4 through the catalytic zone will depend on pumping speeds, constrictions in the line, etc. In the authors' laboratory,[9,10] we prefer a catalytic zone at 200 °C and do not obtain good yields of S_2N_2 at 140–160 °C as Douillard[26] did. The IBM group[37] prefers the higher temperature of 325 °C, where Patton[4] claims contamination with S_4N_2, but use a lower pressure than other groups report. The Penn group[35a] use conditions intermediate between these conditions. Obviously the local pressure in the catalytic zone as well as the temperature are needed to specify the concentration–reaction rate profile, and this has not been measured.

C. Polysulfur Nitride

1. Synthesis

Prior to the work of Douillard et al.[8e,26] $(SN)_x$ had only been prepared in polycrystalline form, with the important exception of Burt's[1] accidental observation of crystal formation. Douillard's thesis[26] describes the solid-state polymerization of S_2N_2 crystals to $(SN)_x$. Although it had been realized that the polymerization seemed to be a case of topochemical polymerization, Douillard's observation that S_2N_2 crystals yield $(SN)_x$ crystals triggered the recent wave of studies of the electronic and optical properties. *In the authors' laboratory,*[9,10] *crystals of* $(SN)_x$ *were grown by* impinging S_2N_2 vapor on cold fingers at 0 to 8 °C with polymerization taking between 4 and 48 h. S_2N_2 was also collected at −80 °C and allowed to polymerize by slow programmed warming up to room temperature over a 2-week period. In these growth processes, a liquid nitrogen trap on the sublimation train always trapped additional S_2N_2, as well as traces of a red contaminant. In more recent work in the authors' laboratory, S_2N_2 was purified in a manner similar to Douillard's procedure and crystal growth of S_2N_2 was conducted at 0 °C followed by attempts at polymerization at temperatures varying from −196 to 30 °C.

The IBM group[37] isolated S_2N_2 in a liquid nitrogen trap, warmed it to 0 °C, and allowed polymerization to occur for 5 days; the crystals were then pumped on for 24 h to remove unpolymerized S_2N_2. The Penn group[35] allowed the polymerization of S_2N_2, isolated in a rectangular trap at liquid nitrogen temperatures, to occur at 0 °C for 48 h, followed by warming to room temperature for 60 h, followed by heating at 75 °C for 2 h. The Penn group[35] has stated that fewer distortions are introduced in the S_2N_2 crystals if their flat faces grow on flat rather than rounded glass surfaces. On a scale of molecular dimensions, all such glass surfaces are obviously not flat and there appears little need for using this specific design of the apparatus.

All groups seem in their most recent work to agree that formation of S_2N_2 crystals of good quality is the key to success, and that crystal growth of S_2N_2 at 0 °C is most desirable. Often it is desirable to transport S_2N_2 to a 0 °C trap and allow crystal growth in this trap. After good colorless transparent crystals are formed, polymerization can be conducted at room temperature. Whether an anneal at 75 °C is desirable or not is the subject of debate. It may be preferable to allow the polymerization to be completed by several weeks storage at room temperature rather than run the risk of creating voids in the crystal by heating to 75 °C and removing unpolymerized S_2N_2. The Penn group[38] claims that annealing at 75 °C produces improved crystals presumably by allowing grain growth to achieve a more largely monocrystalline $(SN)_x$. Annealing at 75 °C with N_2 pressurization of 70 atm yields good quality crystals.[15a]

It can be seen that there have been no real innovations in the preparation of $(SN)_x$ since 1910; simply the realization that solid-state polymerizations, if truly topochemical, should depend on crystal perfection. Thus, various groups have attempted to find conditions to grow S_2N_2 and allow it to convert to $(SN)_x$ at various rates. All groups, in fact, find variations in crystal quality and crystal properties, and the criteria of most importance is the relationship of crystal quality to the property being measured. This relationship will be discussed in detail below with regards to the electrical properties.

In the preparation of colorless S_2N_2 *from* S_4N_4 *several authors* have noted the presence of various colored species described at times as pink, red, orange, and/or tan as side products in the reaction.[4,35] Several of these products have been isolated and found to polymerize to form golden lustrous crystals of $(SN)_x$.[33] Among these are a paramagnetic species which is a dark red crystalline solid at room temperature and appears to be the SN· radical, and a dark brown crystalline monomer with a molecular weight of 92. This is discussed in more detail in section II.C.7.

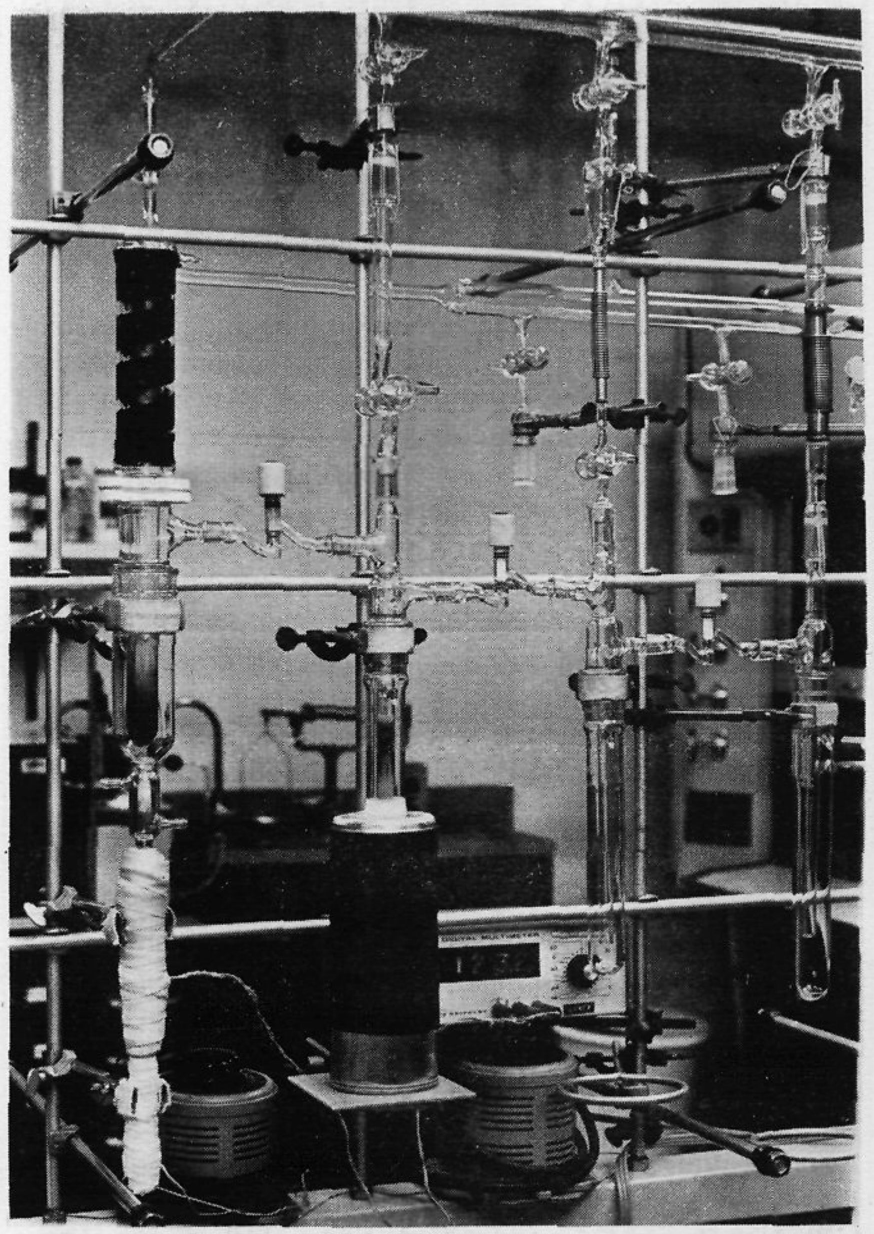


Figure 1. One version of S_4N_4 pyrolysis unit and high-vacuum fractionation train used by Temple group for preparation and isolation of S_2N_2. A comparable "U" trap system is also used.

A mass spectrometric study of the pyrolysis of S_4N_4 over quartz wool at temperatures ca. 250 °C has shown the formation of SN, S_2N_2, S_3N_3, and S_4N_2.[39] *Patton had indicated that* S_4N_4 is stable in the presence of Pyrex wool at this temperature.[4] However, he reported formation of some S_4N_4 pyrolysis products formed over Pyrex wool heated at 300 °C. Recently Louis et al. have reported the formation of epitaxial crystalline $(SN)_x$ by the pyrolysis of S_4N_4 heated to ca. 275 °C over Pyrex or quartz wool.[35b]

2. Topochemical Polymerization

Polymerization in the solid state occurs in cases where there is considerable similarity in crystal structure between the lattices of monomer precursor and polymer; notable examples are the polymerization of trioxane[40] and the more recent work on preparation of polydiacetylenes.[41,42] $(SN)_x$ is, clearly, an example of this type of polymerization. According to Douillard,[26] the polymerization of S_2N_2 monocrystals to $(SN)_x$ occurs even at liquid nitrogen temperature (in about 8 or 9 weeks). This observation may be associated with impurity or photoinduced polymerization, since other workers have stored S_2N_2 for long periods of time at liquid nitrogen temperature. Cohen et al.[43] and Baughman, Chance, and Cohen[44] have attempted to analyze the solid-state reaction by comparing crystal structure data on S_2N_2, partially polymerized S_2N_2, and $(SN)_x$. Douillard[26] had already suggested that the reaction proceeded by the formation of SN radicals by simultaneous two-bond cleavage of planar S_2N_2 and the polymer chain perpetuated normal to the plane of S_2N_2 molecules. However, this is unlikely in view of the more rapid rate of polymerization of the red SN· species as compared to the rate of polymerization of S_2N_2 as followed by electron paramagnetic resonance spectroscopy.[28]

Baughman, Chance, and Cohen[44] predict the reaction mode

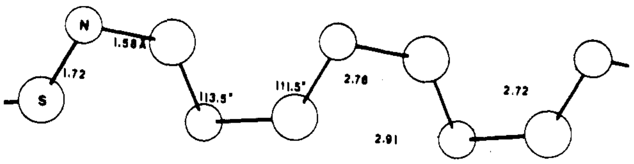


Figure 2. Intramolecular bond distances and angles of $(SN)_x$ (from ref 49).

by estimating that mode which requires least motion, i.e., minimize the root-mean-square displacements required for reaction, using the Penn group crystal structure data.[38] They conclude that an SN radical mechanism is unlikely; it is more likely that a one-point ring cleavage occurs to form the (cis-trans) polymer. The *b* axis of $(SN)_x$ develops along the a axis direction of S_2N_2, i.e., normal to the S_2N_2 plane. Their analysis leads to the conclusion that characteristic defect structures are difficult to avoid in this solid-state polymerization. Twinning, molecular scale disorder, and differing crystallite orientations are all to be expected. Boudeulle[45] observed by electron microscopy that the crystallite size normal to the chain direction is 100–150 Å, and that twinning occurs on this scale (and perhaps even smaller).

3. Physical Properties

The polymer $(SN)_x$ is a shiny metallic solid which in single crystal form consists of highly oriented parallel fiber bundles. The fibers which consist of parallel $(SN)_x$ chains are on the order of several hundred angstroms in diameter as shown by scanning electron microscopy.[15a] Single crystals of $(SN)_x$ are typically on the order of several millimeters in length and are often twinned. Well-formed crystals of $(SN)_x$ are bright golden and lustrous in appearance. The reflectivity from crystal facets is highly anisotropic. The ends of the crystals, which consist of fiber bundle tips, are notable in that they are blue-black in appearance.

Heating $(SN)_x$ in air leads to explosive decomposition at ca. 240 °C.[15a] When heated in an inert gas atmosphere, e.g., He, $(SN)_x$ decomposes by sublimation starting slowly ca. 140 °C with a major differential scanning calorimetry endotherm at 248 °C.[33] This is followed immediately by a strong and often explosive exothermic reaction.[15a,33] When heated in vacuo $(SN)_x$ crystals readily sublime at ca. 135 °C.[46]

The vapor pressure, *P*, of $(SN)_x$ as a function of temperature has been measured by Weber and Ewing.[47] It is described by the equation, $\ln P = 37.64 - 16351/T$. From this one calculates a value of 0.0037 torr at 135 °C. The enthalpy and entropy of vaporization reported by Weber and Ewing are 32.49 ± 0.99 kcal/mol and 80.98 ± 2.48 cal/(mol K), respectively. The enthalpy value compares favorably with the heat of sublimation of 29.0 ± 0.5 kcal/mol determined in mass spectrometric studies,[48] and a value of 29 ± 3 kcal/mol determined by thermogravimetric analysis.[33]

4. Crystal Structure

Early crystallographic investigations were performed by Goehring and Voigt,[5b] who performed X-ray powder diffraction studies. Douillard[8b,26] repeated these studies on both $(SN)_x$ powders and films; he noted that the films showed a marked tendency to preferential orientation of the crystallites, and that the powder patterns underwent a gradual change indicative of two forms of $(SN)_x$ during irradiation in the X-ray beam. Boudeulle[45] began a study of "crystallites of monocrystalline appearance", the fibrous bundles of $(SN)_x$ which we have continuously been referring to in this review as $(SN)_x$ crystals. The periodicity along the fiber is 4.43 Å (in accord with Goehring and Voigt's[5b] observation); normal to the fibers the repeat distance is 7.50 Å. The patterns indicated the presence of considerable twinning; very many reflections were split. Boudeulle concluded that Douillard's two forms are *not* the results of decomposition in an X-ray beam, but that there are two polymorphs of $(SN)_x$, an α and β form, which are very similar to one another, the α being metastable. The α form is often found in thin films of $(SN)_x$ which appear amorphous, but really consist of small dimension crystallites. Sometimes the polymer grows as aggregates of very short fibers which also seem to be the α form of $(SN)_x$. The very long fibers generally observed in $(SN)_x$ are the so-called β-$(SN)_x$. We will concentrate in this review on its properties. Furthermore, no satisfactory results have been obtained on the crystal structure of α-$(SN)_x$, and most authors deal with only one form (β) of $(SN)_x$.

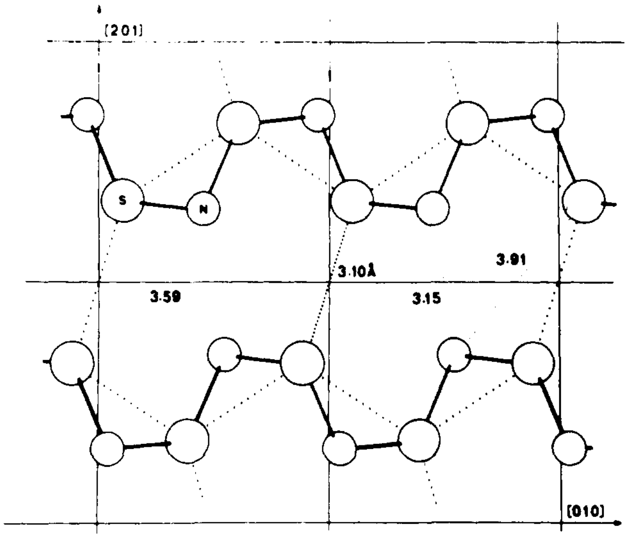


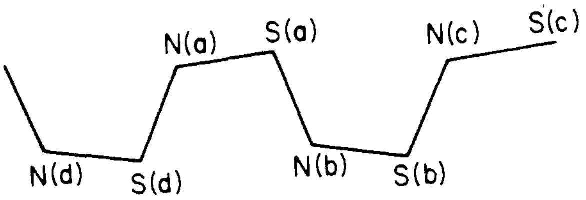
Figure 3. Projection of $(SN)_x$ structure on $(10\bar{2})$ which shows layer-like packing of chains (from ref 49).

The results of the Boudeulle thesis[45] have recently been summarized in a communication.[49] From Weissenberg photographs and "single" crystal diffractometry (Cu Kα), the following results were obtained: β-$(SN)_x$ has a monoclinic unit cell, space group $P2_1/c$ with the cell parameters a = 4.12 (5), *b* = 4.43 (3), *c* = 7.64 (5) Å; β = 109.5 (5)°. There are four (SN) units per unit cell.

The detailed structure was determined using electron diffraction, since severe twinning interfered with the X-ray method. Intramolecular bond distances and angles, with deviations of 0.08 Å and 5°, respectively, are given in Figure 2.

The sulfur and nitrogen atoms form infinite molecular chains which deviate from planarity by about 0.17 Å for both S and N. Note the distances between nondirectly bonded atoms are shorter than normal van der Waals distances. Two polymeric chains run parallel to each other through the unit cell with their mean plane close to $(10\bar{2})$. All the contacts between chains *except* that between sulfur atoms related by an inversion center are at normal van der Waals distances; the close S–S distance is 3.10 Å, indicative of a layer-like packing of chains (but not a true layer compound) (Figure 3). Thus the strong bonding is restricted to the chain direction and probably explains the fibrous character of the crystals.

Another attempt at crystal structure determination has been made by the Molecular Structure Corporation on crystals furnished by the Penn group,[38,43] by X-ray technique. The unit cell parameters are essentially the same as the Boudeulle structure: *a* = 4.153 (6), *b* = 4.439 (5), *c* = 7.637 (12) Å, with β = 109.7 (1)°, but the bond lengths are nearly equal, e.g., 1.593 (5) and 1.628 (7) Å, and the bond angles are somewhat different than the Boudeulle structure, e.g., NSN = 106.2 (2)° and SNS = 119.9 (4)°, respectively. The closest intermolecular distance in the Penn structure is 3.48 Å between sulfur atoms on adjacent chains in the $(\bar{1}02)$ plane. As will be seen below, these two estimates of the extent of interchain coupling affect the calculation of the band structure of the polymer. A view of the structure by the Penn group is given in Figure 4.



Atoms	Distance (Å)
S(a)-N(a)	1.593 (5)
S(a)-N(b)	1.628 (7)
S(a)-N(c)	2.864 (5)
S(a)-S(b)	2.789 (2)
N(a)-N(b)	2.576 (7)
	Angle (°)
S(a)-N(b)-S(b)	119.9 (4)
S(b)-S(a)-S(d)	105.5 (1)
N(b)-N(a)-N(d)	119.0 (5)
N(a)-S(a)-N(b)	106.2 (2)

Figure 4. Structure and details of $(SN)_x$ obtained from Penn group crystals (from ref 35a).

5. *Band Structure*

The high conductivity, the possible one-dimensionality implied by the conductivity anisotropy, the absence of a Peierls distortion, and the observation of superconductivity in $(SN)_x$ all generated considerable activity in calculating its band structure.

Chapman et al.[7] had put forth a simple band model to explain the small energy gap observed in the conductivity of $(SN)_x$ as measured in the early 60s.[6] Modifying these arguments, Walatka, Labes, and Perlstein[9] presented a simple molecular orbital model of the one-electron band structure predicting the metallic behavior of $(SN)_x$. Parry and Thomas[50] undertook the first calculation of the valence electron band structure and density of states of $(SN)_x$ in a one-dimensional tight-binding computation using empirical extended Hückel methods; a planar chain structure, differing from the Boudeulle structure,[26,27] was used. Kamimura et al.[51] also derived the band structure for a single $(SN)_x$ chain in a semiempirical calculation using the Boudeulle crystal structure, in which the nonplanarity of S and N was included. In contrast to the Parry and Thomas model, where the Fermi level is located exactly at the zone edge, this calculation indicated that the Fermi level crosses two overlapping energy bands.

A number of additional calculations then followed. Rajan and Falicov[52] performed a LCAO calculation on three different planar structures with conclusions similar to Kamimura et al.[51] Friesen et al.[53] used the extended Hückel method of Hoffman and the crystal structure of Boudeulle, and for both a single chain calculation and for the 3D band structure found that the Fermi level lies at the center of an antibonding π band. They conclude that $(SN)_x$ is a semimetal, that quasi-one-dimensional behavior should *not* be observed, and that the observed anisotropy of the material is due to its fibrous nature rather than to microscopic one-dimensionality of the electronic properties.

The Cavendish laboratory group[54] performed a three-dimensional, nonempirical calculation using a tight-binding approximation on the Boudeulle model. They argue that two overlapping conduction bands are required to represent the electron energies near the Fermi level for a single helical $(SN)_x$ chain, implying metallic behavior at all temperatures, with no tendency to distortion of the chain at low temperature. The crucial factor in determining the band structure near the Fermi level for a single chain is the degree of s–p mixing, *not* the crystal structure.

Berlinsky has presented evidence to indicate that the existence of two overlapping conduction bands which cross the Fermi surface should lead to a Peierls instability.[55] He concludes that the lack of a Peierls distortion in $(SN)_x$ is the result of stabilization by three-dimensional interactions. However, the prime reason for a lack of a Peierls distortion in $(SN)_x$ is probably the strength, or relative inflexibility to compression, of the covalent bonds of the $(SN)_x$ chain structure.

Schlüter et al.[56] performed a three-dimensional, semiempirical pseudo-potential calculation on $(SN)_x$ using the Boudeulle structure. Interchain interactions were found to be important, but states close to the Fermi energy are strongly localized along $(SN)_x$ chains and show strong anisotropy. They calculate the density of states, Fermi surface, and optical spectrum, with results in reasonable accord with experiments. Charge-transfer from sulfur to nitrogen is estimated at about 0.9 electron per molecule. However, this is not in accord with the X-ray photoemission results. Features of their calculation allow the conclusion that superconductivity involves the standard BCS electron–phonon coupling mechanism.

Using the Penn structure,[38,43] Bright and Soven[57] performed a band structure calculation using extended-Hückel methods and found little difference from the band structure calculated by Friesen et al.[53] discussed above. Rudge and Grant[58] performed a three-dimensional band structure calculation using the orthogonalized plane wave method on *both* the Boudeulle and Penn structure, and tried to assess how the difference in interchain coupling (3.48 Å S–S distance in the Penn structure, 3.10 Å in the Boudeulle structure) affects the band structure. They obtain a conduction band width of ~2–3 eV. The magnitude of the Fermi level density of states is ~0.13 states/eV spin molecule for both structures; although there are differences in some band widths, in the relative *Z*-point splittings and in the nature of the electron and hole pockets in the Fermi surfaces, it is not possible to choose between them by comparing the calculations to experiment. They conclude that the absence of a Peierls transition in $(SN)_x$ derives from closed Fermi surfaces introduced by interchain coupling, i.e., that $(SN)_x$ is really *not* one-dimensional.

Other band structure calculations have also been made. Chelikowsky et al. have made a semiempirical pseudo-potential calculation for the electronic structure of $(SN)_x$.[59] They calculate with good results the density of states and optical reflectivity both parallel and perpendicular to the *b* axis. These authors obtain a value of the density of states at the Fermi level, $N(E_F)$, of 0.12 state/(eV spin molecule). They suggest the use of an effective mass of $1.3m_e$ in order to obtain a density of states closer to the experimental value. These authors also discuss the change of the superconducting transition temperature, T_c, in terms of a change in the phonon spectrum with pressure rather than due to a change in $N(E_F)$.

Suhai and Ladik have reported the results of an ab initio LCAO–Hartree–Fock calculation in which a double-ζ-type atomic basis set was used.[60] They obtain a value of $N(E_F) = 0.14$ eV/(spin molecule), an effective mass of $1.7m_e$, and the charge transfer from sulfur to nitrogen of ca. 0.4 e.

By use of an LCAO calculation, Ching et al. have made a band structure calculation on both a single $(SN)_x$ chain and three-dimensional crystals.[61] They calculate a value of $N(E_F)$ of 0.01 states/(eV spin molecule) for three-dimensional crystals. They also conclude that a small change in interatomic distances as a result of a pressure increase would cause a large increase in $N(E_F)$.

Yamabe et al. have calculated the band structure of $(SN)_x$ and $(SCH)_x$ in terms of an SCF-tight-binding MO theory in which they use a CNDO/2 approximation.[62] These authors calculate a value of $N(E_F)$ of 0.04 and 0.06 states/(eV spin molecule) for $(SN)_x$ and $(SCH)_x$, respectively.[62] They conclude that $(SCH)_x$ may be metallic providing a Peierls transition does not occur in this system.[62]

Wudl has discussed the synthetic problems associated with variants of $(SCH)_x$,[23] and has reported preparation of the

TABLE II. Analyses of Exposed and Unexposed Crystals and Films of $(SN)_x$[a]

	composition, %				
condition	S	N	O	C	H
unexposed crystals	69.60	30.11			
	69.68	30.50			
	70.11	30.42			
exposed crystals	66.4 ± 0.2	30.2 ± 0.1	3.0 ± 0.4	0.17	0.23
	68.12	29.68	1.66	0.30	0.24
	66.10	28.96	4.93	0.13	0.42
exposed film	63.06	27.24	7.95	1.32	0.53
theory	69.60	30.40			

[a] Analyses performed by Huffman Laboratories, Inc., Wheatridge, Colo., or Galbraith Laboratories, Inc., Knoxville, Tenn. For the unexposed crystals, specific analyses were performed for O, C, and H and <0.1% were found.

somewhat related amorphous $(CH_2Te_2)_x$[21b] which has a room temperature conductivity of ~2000 Ω cm.

6. Chemical Stability

Crystals of high purity $(SN)_x$ prepared and maintained in vacuo at room temperature appear to be stable indefinitely. Although "analytically pure" crystals of $(SN)_x$ have been reported,[35a] a recent mass spectrometric study by Smith et al. on high-quality crystals obtained from several different laboratories has shown hydride species content typically on the order of 5–10%.[63] Some samples have hydride content as high as 20%.[63] Evidence was obtained to show that hydride incorporation results from reaction with water.[63] These observations are to be contrasted with the work of Mikulski et al. which indicates a lack of hydride formation and a lack of reactivity with water for at least 7 days on fully polymerized "analytically pure" crystals.[64] Mikulski et al. state, however, that tarnishing of crystals and reaction with water occur with incompletely polymerized $(SN)_x$ crystals.[64]

Cyclic voltammetric studies in which $(SN)_x$ is used as an electrode material in aqueous media support the conclusion that $(SN)_x$ is stable in the presence of water.[65] Mikulski et al. also state that analytically pure crystals of $(SN)_x$ are stable to both dry and moist air and oxygen for at least 7 days at room temperature.[64] These authors note that incompletely polymerized crystals of $(SN)_x$ are less stable in this respect.[64] Kaneto et al. have shown quite conclusively that exposure of high-quality $(SN)_x$ crystals to atmospheric oxygen at temperatures of ca. 360 K significantly decreases the conductivity and results in a conductivity maximum in the 30–40 K range.[66] Less pronounced but comparable results were obtained by heating $(SN)_x$ crystals above 330 K in an argon atmosphere.[66]

As is emphasized below, particularly in discussing the conductivity and superconductivity of $(SN)_x$ in sections II.C.9a and b, physical perfection of crystals is obviously very important in determining their properties. Inherent in the topochemical polymerization is the generation of some defect structure. Furthermore, some S_2N_2, low molecular weight oligomers of $(SN)_x$, and/or traces of impurities can be physically occluded as $(SN)_x$ polymerizes. It is not clear whether it is better to grow large crystals of S_2N_2 and polymerize them slowly, or grow $(SN)_x$ by allowing S_2N_2 to polymerize as small crystal nuclei form. The annealing process, if carried out too rapidly, may cause additional physical voids to be established in the crystals.

As to chemical purity and properties, there has been some dispute as to the stability of $(SN)_x$ crystals in air. Walatka, Labes, and Perlstein[9] found considerable oxygen contamination and smaller C, H contamination. Other groups[11,15] prepared higher purity crystals and presented analytical data which indicated no such contamination. Mikulski et al.[35a] presented some preliminary data to indicate that $(SN)_x$ is much more stable in air than the results of the Temple group imply.

Table II indicates the analyses of exposed and unexposed crystals by the Temple group,[67] where crystals were of the size typically used in measurement (1–2 mm long, cross-sections of 0.2–0.5 × 0.2–0.5 mm, weighing ~1 mg). If this variability in reactivity between various groups of crystals is real, it is probably associated with traces of unpolymerized monomer, chemical impurities, and various degrees of physical perfection as indicated by Mikulski et al.[64]

7. Other Modes of Preparation

Metallic high-quality samples of $(SN)_x$ can be prepared by several alternative methods to the thermal polymerization of vapor phase grown crystals of colorless S_2N_2, designated as "normal" $(SN)_x$.

a. Polymerization of Red Monomer

Polymerization of crystals of a red paramagnetic monomer which is formed in the pyrolysis of S_4N_4 yields golden lustrous $(SN)_x$ crystals on the order of hours at room temperature.[33] Comparable polymerization of colorless S_2N_2 occurs on the order of days. On the basis of its paramagnetism as determined by EPR, the mass spectrometric molecular weight of 46, and its greater volatility relative to S_2N_2, the SN· structure is assigned. This is reasonable even though Heal considered that the SN· species is too reactive to be isolated.[20] The saturation pressure of the red monomer is ca. 0.035 Torr/0 °C.[33]

The red paramagnetic monomer is not S_4N_2 as it differs from the latter compound in volatility and magnetic and physical properties. The compound tetrasulfur dinitride, S_4N_2, is well known.[19] It has a melting point $\lesssim$23 °C and is reported to be diamagnetic. The SN· monomer is more volatile than S_2N_2, whereas S_4N_2 has a volatility greater than but comparable with that of S_4N_4.[28] The red monomer is a crystalline solid at 25 °C which polymerizes rapidly at this temperature. The compound S_4N_2 is a dark red unstable liquid at room temperature which slowly evolves gas. However, S_4N_2 can be formed under some conditions in the pyrolysis of S_4N_4.[15a]

The $(SN)_x$ crystals obtained by polymerization of the red monomer are also golden lustrous in appearance. This material, which has unit cell parameters comparable to those of normal $(SN)_x$, is designated as "red" $(SN)_x$.[33] High-quality crystals of red $(SN)_x$ are stable in air at room temperature for periods of ca. 5 months.[68] By comparison, crystals of normal $(SN)_x$ are stable in air for a period on the order of a week.[64] Elemental analysis of red $(SN)_x$ corresponds to the designated formula. The conductivity and superconducting transitions of this material are comparable to those of normal $(SN)_x$.[33]

b. Polymerization of Brown Monomer

Crystals of a dark brown $(SN)_2$ monomer, which has a mass spectrometric molecular weight of 92, polymerize at room temperature in a time on the order of 15 min to form golden lustrous $(SN)_x$ crystals.[33] This material is designated as "brown" $(SN)_x$. The X-ray unit cell parameters of brown $(SN)_x$ are comparable to those of normal $(SN)_x$. However, the a parameter is ca. 4% higher than the comparable value for normal $(SN)_x$.[33] The stability of brown $(SN)_x$ in air at room temperature is on the order of 2 days or less,[68] but the crystals isolated thus far are quite impure.

The intermediate blue-black paramagnetic solids obtained from the polymerization of the red and brown monomers yield distinctly different EPR spectra with respect to line width at half-intensity and line shape from that obtained from the colorless S_2N_2 intermediate.[33,69] The EPR spectra are characteristic of the paramagnetic polymers and are not due to paramagnetic monomer species.

c. Photopolymerization of S_2N_2

Photopolymerization of crystals of S_2N_2 grown from tetrahydrofuran solution at temperatures of ca. −25 to −60 °C yields high-quality crystals of $(SN)_x$.[33,70] The $(SN)_x$ obtained by this method is comparable to normal $(SN)_x$ with respect to elemental analysis, crystal structure, conductivity, and superconductivity.

d. Sublimation of $(SN)_x$

Sublimation of $(SN)_x$ crystals in vacuo at ca. 135 °C yields a volatile red-purple monomer, which is considered to be a linear $(SN)_4$ tetramer.[48,71] When condensed at temperatures of ca. 0 °C this monomer rapidly polymerizes to form a golden lustrous film of $(SN)_x$. Condensation on oriented substrates such as stretched films of Mylar, Teflon, or polyethylene yields epitaxially oriented $(SN)_x$.[46] By using Mylar film rubbed with Kimwipe, Bright et al. obtained good optical uniaxiality of $(SN)_x$ films condensed on this substrate.[46] The red-purple monomer formed by the sublimation of $(SN)_x$ appears to be diamagnetic[28] and is distinctly different from the red paramagnetic monomer obtained in the pyrolysis of S_4N_4, and from S_4N_2 as described previously.

Sublimation of $(SN)_x$ at temperatures of ca. 135 °C yields other volatile products in addition to linear $(SN)_4$, which was characterized by field desorption mass spectrometry.[48] Upon high-vacuum fractionation of the sublimate one can also isolate colorless S_2N_2 and a yellow condensate, among other products.[28] An infrared and UV-visible spectroscopic study by matrix isolation of $(SN)_x$ sublimate has shown the presence of SN, S_2N_2, and S_4N_4, together with other unidentified products.[72]

Low molecular weight oligomers of $(SN)_x$ with $x \lesssim 4$ have been prepared.[73] These molecules may be useful in the further elucidation of the nature of $(SN)_x$.

e. Orthorhombic Sheared $(SN)_x$

Baughman et al. have shown that a shear induced orthorhombic form of $(SN)_x$ can be formed from the normal monoclinic phase.[74] The deformation mechanism of this transition has been studied by Young and Baughman.[75] By use of the shear transformation theory of Bevis and co-workers,[76] Young and Baughman find that the calculated transformation with the third lowest shear strain corresponds most closely to the experimentally determined value.[75] The shear induced transformation in $(SN)_x$ is comparable to that observed in polyethylene.

f. Additional Approaches

In an attempt to incorporate $(SN)_x$ into clathrate structures, Hsu and Labes[10] investigated several clathrating hosts, including benzophenone. Although no clathrates were isolated, single crystals of $(SN)_x$ were obtained by slow evaporation of a solution of tetrahydrofuran saturated with benzophenone at room temperature. Shiny, well-formed $(SN)_x$ crystals were obtained, whose surfaces were covered with polycrystalline benzophenone, which was washed away with acetone.

Another approach to the preparation of $(SN)_x$ which *might* yield an alternative method involves a large number of flame reactions of atomic nitrogen with sulfur compounds. Yields in all of these reactions are low, but conceptually they represent an inexpensive way of synthesizing $(SN)_x$. For example, H_2S reacts with atomic nitrogen to form $(SN)_x$ as well as H_2, NH_3, S_7NH, and S.[77,78] CS_2 and COS react with atomic nitrogen and the only nitrogen-containing product is $(SN)_x$.[78] Finally, atomic nitrogen reacts with sulfur to yield S_4N_4, S_4N_2, and $(SN)_x$.[78-80]

8. Thin Films, Epitaxial $(SN)_x$

Thin films of $(SN)_x$ can be prepared in any of four known ways: by the pyrolysis of S_4N_4 through Ag wool,[4] by pyrolysis of S_4N_4 over Pyrex or quartz wool at ca. 275 °C,[81] by polymerization of the red SN· monomer,[28] and by sublimation in vacuo of $(SN)_x$.[46] The conditions for the pyrolysis were discussed in section II.B. The major difference is that substrates such as glass, quartz, sapphire, printed circuit boards, or polymer films are attached to a cold finger in a sublimation apparatus.

Typical conditions are given by Hsu and Labes,[10] and by Bright et al.[46] This involves heating $(SN)_x$ at ca. 135–150 °C in vacuo of $\gtrsim 10^{-5}$ Torr. Condensation of the sublimate on a substrate held at temperatures between 0 and 25 °C leads to quite rapid formation of $(SN)_x$ films. Condensation of the red-purple volatilized condensate on an oriented substrate such as stretched Mylar film yields epitaxially oriented crystalline $(SN)_x$.[46]

Bright et al. claim the preparation of completely oriented films of crystalline $(SN)_x$ on stretched substrates such as Mylar, Teflon, and polyethylene.[46] These authors state that the crystal structure of the epitaxially oriented film thus obtained is identical with that of the precursor material.[46] It is pointed out by de la Cruz and Stolz that even though optical reflectivity measurements indicate complete chain alignment in the epitaxial lattice, the anisotropy of the electrical resistivity, ρ, is several orders of magnitude less in this material than that determined for single crystals of $(SN)_x$.[82] The perpendicular to parallel resistivity ratio, $\rho_\perp/\rho_\parallel$, is on the order of 1000 in single crystals of $(SN)_x$ and is ca. 5 and essentially temperature independent for epitaxial $(SN)_x$.[82] Furthermore, Temkin and Fitchen note that the Raman peaks in $(SN)_x$ single crystals are sharper than those obtained from thin films.[83] These observations suggest that there is more complete chain ordering in $(SN)_x$ single crystals than in the corresponding epitaxially oriented films.

The electrical resistance of epitaxial crystalline films of $(SN)_x$ has been measured by de la Cruz and Stolz over the temperature range 0.07 to 300 K.[82] A superconducting transition in the film was not detected by these authors[82] as has been found for single crystals of $(SN)_x$.[14] It is noted by de la Cruz and Stolz that the temperature dependence of $\rho_\perp$ is essentially the same for single crystals and epitaxial $(SN)_x$.[82] They suggest that the values of $\rho_\parallel$ and $\rho_\perp$ are determined by the same temperature dependent mechanism in epitaxial films. The conductivity, σ, in the temperature range 0.07 to 2 K was found[82] to follow the equation

$$\sigma(T) = \sigma(0) + \alpha \exp(-\Delta/kT) \qquad (1)$$

These authors conclude that σ in epitaxial $(SN)_x$ films is primarily determined by an intrinsic conduction mechanism which produces a finite conductivity at 0 K.[82]

Electrical resistance measurements of epitaxially oriented $(SN)_x$ films have also been made by Soulen and Utton over the temperature range 0.03 to 8.9 K.[84] These authors note that below 0.25 K the resistance approaches a constant value. This they interpret as being suggestive of superconducting fluctuations of small particles in the $(SN)_x$ film lattice. The absence of conclusive evidence of a superconducting transition in highly oriented epitaxial films of $(SN)_x$ is a further indication of lattice orientation differences between epitaxial and single crystals of $(SN)_x$.

Soulen and Utton attempted without success to fit their conductivity results to an equation of the form[84]

$$\sigma(T) = \sigma(0) = C \exp(DT^{-b}) \qquad (2)$$

where C, D, and b are constants. This is comparable to eq 1 found to be useful by de la Cruz and Stolz.[82]

It should be noted as discussed in section II.C.7.d that sublimation of $(SN)_x$ actually yields a number of volatile products. Condensation and polymerization of these materials can result in an epitaxially oriented lattice of questionable homogeneity. In view of this, and the problem of achieving a completely oriented epitaxial lattice structure as noted above, it is not surprising that Soulen and Utton did not find a simple temperature dependence of conductivity for their samples. The theory of the for-

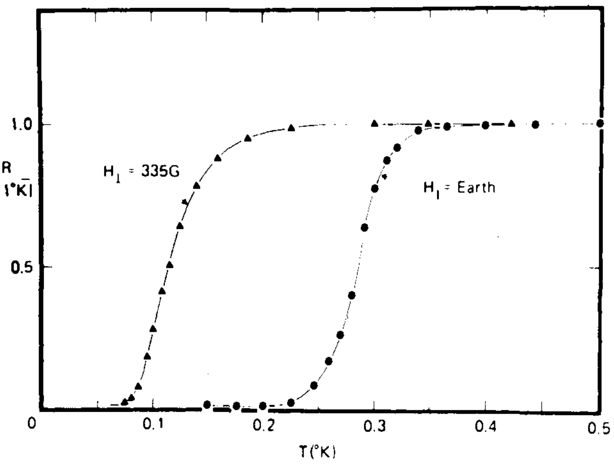


Figure 5. Normalized temperature-dependent resistance of crystalline $(SN)_x$ over superconducting region with earth's and 335 G magnetic field applied perpendicular to fiber axis (from ref 14).

mation of epitaxially oriented $(SN)_x$ has been discussed by Mauritz and Hopfinger.[85]

9. Conductivity

a. Normal State Conductivity

Walatka, Labes, and Perlstein[9] reported the first single crystal conductivity data on $(SN)_x$ from 4.2 to 300 K. Along the polymer chains ($\sigma_\parallel$), the data showed the material to be metallic over the entire temperature range studied, with a small conductivity maximum at ca. 33 K (3–5 times the room temperature conductivity of ~1000 Ω^{-1} cm^{-1}). Data were also gathered in this temperature range to determine the Seebeck coefficient. These data had a small negative value with no critical behavior. Further studies by Hsu and Labes[10] indicated this maximum was moving to lower temperatures as crystal samples with greater physical perfection were prepared, and that the low-temperature conductivity was becoming significantly larger. Attributing the weak temperature dependence of the conductivity beyond this observed maximum to impurity scattering, Hsu and Labes implied that further control of chemical purity and physical perfection might "continue this trend". Greene, Grant, and Street[11] confirmed these results reporting average room temperature conductivities of ca. 600 Ω^{-1} cm^{-1} increasing 10–25 times at 4 K.

The IBM group subsequently has reported crystals whose conductivities increase by a factor of >100 down to helium temperatures, with no maximum observed in the conductivity, but simply an increase down to the superconducting transition (see section II.9.b).[37] Since that time all groups working in the field have observed typical room temperature conductivities between ca. 1000 and 3000 Ω^{-1} cm^{-1} with increases at liquid helium temperature by a factor of ca. 200 to 250. The room-temperature conductivity of currently prepared high quality $(SN)_x$ crystals is ca. 4000 Ω^{-1} cm^{-1}.[15b] The exact values seem to depend mainly on physical perfection, which in turn depend on the success in growing more nearly perfect S_2N_2 crystals, and allowing more controlled polymerization to minimize crystalline lattice defects.

More recent results from the IBM group indicate that crystals can be grown where $\sigma_{\parallel 4\,K}/\sigma_{\parallel RT}$ can reach ca. 1000; these crystals seem to result from slower growth and completion of the polymerization at 25 °C rather than an annealing procedure.[15a]

Fewer measurements have been done perpendicular to the polymeric chains because of the obvious fibrous nature of the sample. Hsu and Labes[10] reported the anisotropy of the conductivity ($\sigma_\parallel/\sigma_\perp$) to be ~50 at room temperature and ~500 at 20 K. $\sigma_\perp$ displays a weak conductivity maximum between 45 and 70 K. Grant et al.[86] report a conductivity maximum in $\sigma_\perp$ at ~40 K and $\sigma_\parallel/\sigma_\perp$ of ~10^3 in the low-temperature region.

The metallic conductivity down to very low temperatures and the absence of a Peierls distortion, a metal–insulator transition characteristic of some one-dimensional systems studied to date, are striking features of the behavior of $(SN)_x$. Not only the possibility of superconductivity but also the understanding of the reasons for stabilization of this system against distortion triggered a wave of intense investigation which would reveal aspects of the dimensionality and behavior of this first example of a polymeric metal.

b. Superconductivity

Greene, Street, and Suter[14] observed that $(SN)_x$ becomes superconducting with a transition temperature T_c of 0.26 ± 0.03 K by measuring the conductivity along the fiber axis; they observed a decrease in T_c with increasing magnetic field as shown in Figure 5. The three crystals studied all had σ_{RT} of ca. 1000 Ω^{-1} cm^{-1}, σ_{RT}/σ_{1K} of ca. 0.2, and a small conductivity maximum between 20 and 30 K. The depression of T_c by a magnetic field, H, was significantly less with H parallel to the fiber axis than when H is perpendicular to the fiber axis. Later, when the IBM group prepared crystals of improved quality, where the conductivity maximum at 20 to 30 K was absent and where σ_{40K}/σ_{RT} was >100, T_c increased to 0.33 K, and the width of the transition decreased from 0.08 to 0.06 K. In the better quality crystals, there is no measurable residual resistance in the superconducting state, which seems to indicate that the transition temperature might increase more in "perfect" crystals.[37]

Measurements of the complex a.c. susceptibility in $(SN)_x$ at ca. 0.2 K also have shown superconductivity in this material. No change in sample magnetization was observed at the superconducting transition.[87] That a superconducting transition does occur in $(SN)_x$ crystals has been further verified by observation of the Meissner effect in this polymer.[88]

i. Effect of Crystal Quality. Civiak et al.[89] examined several crystals of variable quality where considerable surface tarnishing of $(SN)_x$ crystals could be observed. Even with crystals showing a considerable residual resistance below T_c, and with normal state conductivities varying over two orders of magnitude, T_c always fell between 0.26 and 0.28°. It appears that *individual* fibers undergo a true superconducting transition, and that residual resistances depend on the density of the fiber segment junctions. By carefully studying measured excess conductivity *above* the superconducting transition temperature, Civiak et al.[90] conclude that this excess conductivity can be attributed to fluctuation conductivity of the Aslamazov–Larkin type, i.e., thermodynamic fluctuations into the superconducting state (see Figure 6). The temperature dependence of the fluctuation conductivity is that of a 0-D or 1-D superconductor with respect to the temperature-dependent coherence length. The coherence length is several times the interchain separation. This means that the observed dimensionality is not likely a function of weak interchain coupling. Rather, the coupling is a direct result of interactions among bundles of many individual fibers. This result is consistent with respect to the band structure calculations which indicate that $(SN)_x$ is a highly anisotropic 3-D metallic polymer.[54]

Azevedo et al.[91] studied the temperature and angular dependence of the upper critical magnetic field, H_{c2}. A large anisotropy is observed at all temperatures with $H_{c2_\parallel} \cong 8.1$ kOe and $H_{c2_\perp} = 870$ Oe with respect to the polymer axis at 0 K. Their results are interpretable in two ways: an intrinsic effect of the particular quasi 1-D structure of $(SN)_x$, or as an extrinsic consequence of $(SN)_x$ consisting of bundles of fibers, i.e., that the critical field anisotropies result from size effects. The size effects would require that the average fiber diameter would be <300 Å; electron microscopy visualizes fibers as small as 1500 Å. The authors conclude that this critical field behavior is probably an intrinsic effect.

c. Effect of Pressure

Gill et al.[92] have studied the pressure dependence of both the superconductivity and normal conductivity of $(SN)_x$. The pressure dependence of the normal conductivity at room temperature has also been reported by Kamimura et al.[51] This effect is unique among nontransition metal superconductors. A qualitative argument is presented which attributes this increase to a pressure induced band structure change. It should be noted that Douillard[26] reports $(SN)_x$ exploding at ca. 18 kbar at room temperature. The effect of pressures up to 50 kbar on the conductivity, and up to 17 kbar on the superconductivity of $(SN)_x$ has been determined by Müller et al.[93] At 293 K the resistivity ratio, ρ_p/ρ_0, decreases from unity at atmospheric pressure to ca. 0.1 at 20 to 50 kbar. The resistivity decrease with increasing pressure is attributed by these authors to a decrease in the effect of crystal imperfections with increasing pressure.

The value of the superconducting critical temperature, T_c, was found to increase *linearly* from ca. 280 mK at atmospheric pressure to ca. 520 mK at 8 kbar. At ca. 9 kbar pressure T_c decreased abruptly. However, only traces of superconductivity could be detected at this and higher pressures. In commenting on the linear increase of T_c as a function of temperature as compared to the quadratic temperature dependence of T_c found by Gill et al.,[92] Müller et al.[93] note that they measured pressure directly by use of an internal manometer, whereas Gill et al. estimated pressure from room-temperature measurements. Müller et al. suggest that the rapid decrease of T_c above 9 kbar may be due to the formation of another metallic phase of $(SN)_x$.[93]

Clarke has studied the effect of hydrostatic pressure on the X-ray diffraction pattern and conductivity of $(SN)_x$ single crystals at pressures up to 22 kbar.[94] The x-ray diffraction patterns showed no indication of a change in crystal structure for pressures up to 22 kbar as was suggested by Müller et al.[93] The compressibility along the *b*-axis direction, K_b, was found to be 2.2 ± 0.2 and 0.31×10^{-12} cm^2/dyn at 1 and 20 kbar, respectively. The values of compressibility along the a and *c* axes, K_a and K_c, were found to be essentially identical, ca. 5.5 ± 0.5 and 0.70×10^{-12} cm^2/dyn at 1 and 20 kbar, respectively. Clarke attributes the relatively high *b*-axis compressibility at low pressure to the somewhat flexible S-N-S and N-S-N bond angles in the $(SN)_x$ chain.[94] He notes that the *b*-axis compressibility is significantly less at pressures greater than 10 kbar than the comparable values along the a and *c* axes. By comparison the value of K_b for $(SN)_x$ is ca. 0.5 that of K_b for TTF-TCNQ at 1 bar.[94] The value of K_c of $(SN)_x$ is ca. two times the corresponding value for TTF-TCNQ.[94]

Clarke[94] notes that the conductivity in the *b*-axis direction, $\sigma_\parallel$, as a function of pressure is directly proportional to K_b^{-1}. However, $\sigma_\perp$ does not have a comparable dependence on K_c^{-1}. This Clarke suggests is the result of $\sigma_\perp$ being dependent on interfiber interactions rather than being an intrinsic property of $(SN)_x$. Clarke concludes that these results are further evidence of the three-dimensional bonding character of $(SN)_x$.[94]

Epstein and Lipari have calculated the electrostatic interactions between polymer chains in $(SN)_x$.[95] From calculations of the crystalline Madelung energies and molecular Coulomb potentials obtained by the use of a modified Evjen summing procedure, these authors conclude that the net electrostatic potential between polymer chains is small. They note, however, that the total electrostatic potential at any atomic site with regard to all crystal interactions with the site may be large. Comparable calculations and conclusions on S_2N_2 and S_4N_4 were also made by these authors.[95] These calculations were made with the assumption that a full unit of electronic charge was transferred from sulfur to nitrogen.[95] However, Epstein and Lipari note that the experimentally determined values of charge transfer in $(SN)_x$ are 0.5 or less.

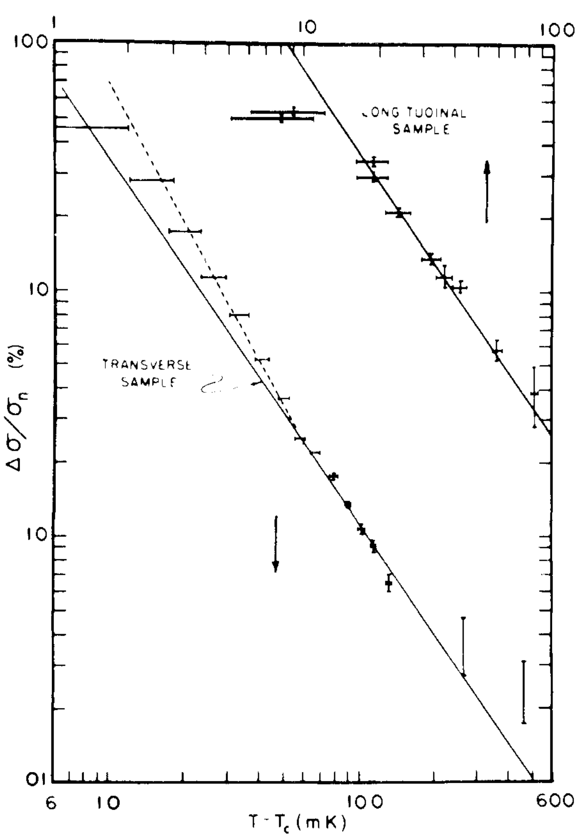


Figure 6. Log–log plot of normalized conductivity vs. T–T_c of $(SN)_x$ crystals mounted parallel and perpendicular to highly conducting axis. The solid line slope is −(3/2) and the dashed line slope is −2. Note that upper and lower temperature scales are different for the respective curves (from ref 90a).

Chelikowsky et al. have made a semiempirical pseudopotential calculation of the band structure of $(SN)_x$.[96] Their calculated pressure simulation yielded no significant change in the density of states at the Fermi level, $N(E_F)$. Their calculated density of states spectrum compares favorably with X-ray photoelectron spectroscopy (XPS) results, with the exception of the lower energy bands. Chelikowsky et al.[96] conclude, not having Clarke's[94] compressibility data, that the increase in T_c with pressure is not likely to be due to a change of $N(E_F)$, but is probably the result of phonon spectrum changes. The reflectivity spectrum parallel to the *b* axis calculated by these authors agrees well with experiment.[96] The calculated reflectivity spectrum perpendicular to the *b* axis shows qualitative agreement with experiment.[96]

The conductivity in the *b*- or chain-axis direction in $(SN)_x$ crystals as a function of pressure, $\sigma(p)_\parallel$, up to 80 kbar has also been studied by Friend et al.[97] The value of $\sigma(p)$ was found to increase with an increase in pressure up to ca. 9 kbar.[97] The value of $\sigma(p)/\sigma(0)$ approaches a constant value of ca. 10 at pressures greater than 30 kbar. A T^2 temperature dependence of the resistivity, which was attributed to electron-electron scattering, was found for $(SN)_x$ crystals at atmospheric and higher pressures. In the pressure range studied two different T^2 temperature-dependent modes were observed.[97]

d. Effect of Stress

Chiang et al. have studied the effect of uniaxial stress in $(SN)_x$ crystals on conductivity parallel, $\sigma_\parallel$, and perpendicular, $\sigma_\perp$, to the chain axis.[98] The conductivity was found to decrease as the stress increased. The change in $\sigma_\perp$ was greater than that in $\sigma_\parallel$. The changes in σ were considered to be the result of stress induced band structure changes, and/or lattice defects.

In a similar study of $(SN)_x$ Davidson and Yoffe found that the stress–strain relationship in $(SN)_x$ crystals depends on the method of polymerization and on crystal perfection.[99] The values

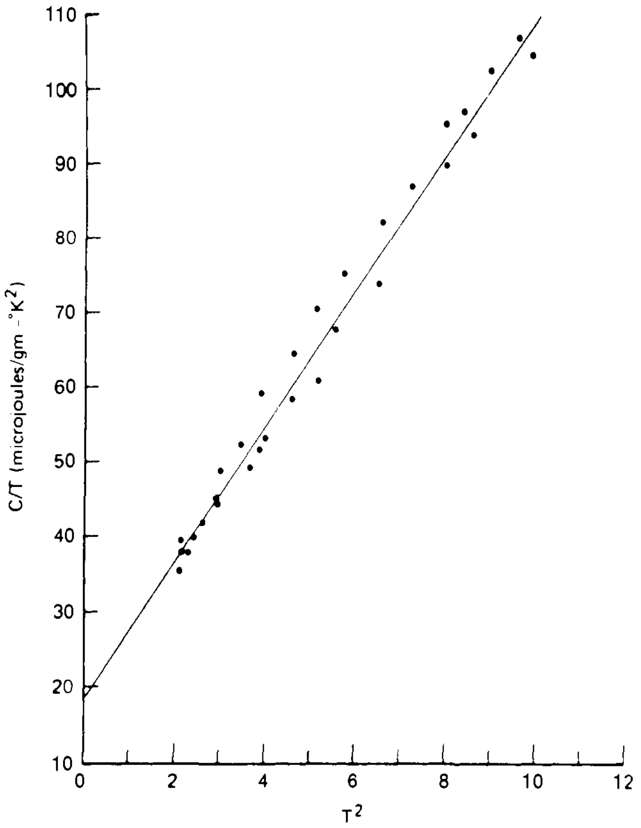


Figure 7. Plot of the specific heat of $(SN)_x$ below 3.2 K (from ref 11).

of Young's modulus and the yield and breaking stresses were found to increase with a slower rate, and longer time of polymerization. For the highest quality crystals studied by these authors, values of Young's modulus, the yield stress, and breaking stress were found to be 3.09 × 10^{-10}, 14.50 × 10^7, and 36.60 × 10^7 N·m², respectively.[99] They noted that the crystal which was strongest along the chain axis direction was comparatively weak transversely.[99]

10. Specific Heat

Greene, Grant, and Street[11] performed detailed measurements of the specific heat, *C*, in the region 1.5 to 10 K. From a plot of C/T vs T^2, a linear region is found below 3.2 K (Figure 7). Above this temperature the departure from a T^3 dependence is evidence of anisotropy in the lattice dynamics of $(SN)_x$. The data allow an estimate of the conduction-band width to be ca. 1 eV, and of an electronic state density of 0.18 state/(eV spin molecule). An extension of the specific heat measurements over the range 1.5 to 80 K has been made by Harper et al.[100] This had led to a revised value of the electron band structure density of states at the Fermi level of 0.14 state/(eV spin molecule).[100] The value of *C* was found to deviate from a T^3 dependence at ca. 3 to 4 K. In the temperature range 4 to 20 K the temperature dependence is ca. 2.7. Above 20 K it was found that *C* is proportional to *T*. These results are discussed in terms of several models of the lattice specific heat.[100]

11. Magnetoresistance

Magnetoresistance measurements by Beyer et al. of $(SN)_x$ have been made for conductivity both parallel and perpendicular to the polymer or *b* axis.[101] From this study calculated electron (*n*) and hole (*p*) mobilities in the crystalline *b*-axis direction of 430 ± 40 and 610 ± 60 cm²/V·s, respectively, were obtained.[101] However, thermoelectric power measurements on $(SN)_x$ indicate it to be *n* type.[15b] Charge carrier densities of $n = p = 3 \times 10^{21}$ cm^{-3}, which were derived from band structure calculations, were assumed in the calculations. This yielded a scattering time of 1.5 × 10^{-13} s, which corresponds to a mean free path ~700 Å along the *b* axis.[101] Beyer et al.[101] conclude that transverse conductivity via interfiber transport appears to be limited by tunneling as postulated for granular metals.[102] Beyer et al. found that bending $(SN)_x$ crystals led to negative magnetoresistance values.[101] These authors suggest that this is due to defect formation in the fibrous structure.

A comparable small positive magnetoresistance in $(SN)_x$ crystals has also been determined by Möller et al.[103] These authors note that the magnetoresistive behavior of $(SN)_x$ is quite different from that of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ (KCP) and $K_{1.64}[Pt(C_2O_4)_2]\cdot H_2O$ (KO_xP).[103] Möller et al. found a strong positive behavior for KCP and a negative magnetoresistance for the latter.[103] These two latter materials are considered to be essentially one-dimensional conductors.

12. Magnetic Susceptibility

The magnetic susceptibility, χ, of $(SN)_x$ single crystals has been determined by Kaneto et al.[66] A temperature-independent value of $\chi = (0.2 \times 0.1) \times 10^{-6}$ emu/g (~9 × 10^{-6} emu/mol) was obtained.[66] This yielded a calculated density of states, $N(E_F)$, at the Fermi level of ca. 0.14 ± 0.06 state/(eV spin molecule).[66] A comparable value of $N(E_F)$ was obtained from specific heat measurements.[11,100] Kaneto et al. noted that this value of χ for $(SN)_x$ is small as compared to that for TTF–TCNQ, which they gave as ca. 0.7 × 10^{-4} emu/mol.[66] These authors also noted that the magnetic dipole density is ca. 1% of the itinerant electron density.[66]

Whereas the conductivity of high quality $(SN)_x$ crystals is a monotonic function of temperature down to the superconducting transition temperature, Kaneto et al. found a resistivity minimum at ca. 30 to 40 K for $(SN)_x$ crystals irradiated with γ-rays from a ^{60}Co source.[66] This minimum is comparable to that found in low quality $(SN)_x$ single crystals. The ^{60}Co-irradiated crystals yielded an essentially linear increase in magnetic susceptibility with an increase of T^{-1}. Kaneto et al. suggest that the resistivity minimum is related to radiation-induced paramagnetic centers.[66]

The paramagnetic susceptibility of single crystals of $(SN)_x$ has also been determined by Scott et al. as $\chi_p = (5.5 \times 1.0) \times 10^{-6}$ emu/mol.[104] The value of χ_p was found to be temperature independent.[104]

13. Optical Properties

Chapman et al.[7] were the first to study the infrared and optical absorption spectra of a thin film (<0.5 μ) of $(SN)_x$ obtained by depositing S_2N_2 vapor on to a quartz window. In a more recent work, Kamimura et al.[51] have, however, claimed that these spectra are of an "unidentified blue nonmetallic SN compound". Figure 8 gives the reflectivity of a thick film of $(SN)_x$ and the transmission of a thin film, as well as the earlier spectrum of Chapman et al.[7] Kamimura et al. analyze their data by a Drude model; their results will be compared with others below.

Bright et al.[12] prepared films of $(SN)_x$ a few microns thick by sublimation of $(SN)_x$ at 130 to 150 °C and <10^{-4} torr to a 27 °C cold finger on which were mounted glass substrates. Indications were observed of preferential orientation of the films with the ($\bar{1}$02) plane parallel to the glass surface. Reflectance measurements were carried out; in the infrared the spectrum is relatively structureless aside from 995- and 685-cm^{-1} bands related to S–N stretching modes (differing from Chapman et al.[7] results) with a sharp decrease in reflectance corresponding to a band edge at 22 000 cm^{-1}. The data were analyzed with a Drude–Lorentz model, and the results will be discussed below after presenting other recent data.

Pintschovius, Geserich, and Möller[105] and Grant, Greene, and Street[106] reported reflectivity measurements on $(SN)_x$ single crystals. Both groups carefully probed the band edge region (visible to near-infrared) in detail. For light polarized perpen-

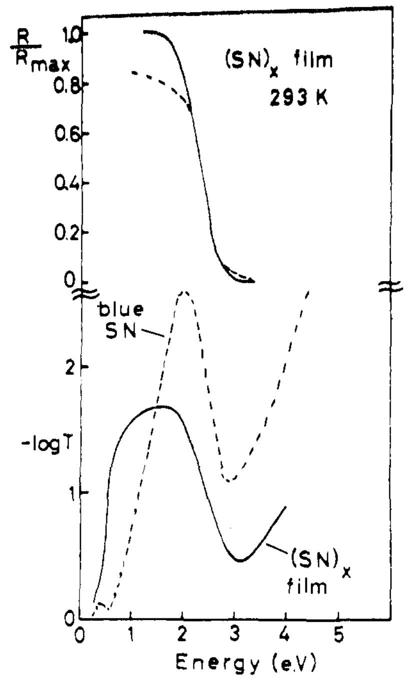


Figure 8. Upper: The normalized reflectivity of a thick film on $(SN)_x$. The dashed curve shows a Drude-type fit. Lower: The optical transmission spectrum measured through a thin film. The dashed spectrum is that of an unidentified blue nonmetallic SN compound (from ref 51).

dicularly to the polymer chain axis, the reflectivity was nearly constant in Pintschovius et al.'s sample[105] and showed only slight structure in the Grant et al.'s measurements[106] (see Figure 9). For light polarized parallel to the chain axis a pronounced plasma edge is exhibited terminating at 2.72[104] to 3 eV.[105] Both of these papers criticize aspects of the Bright et al.[12] interpretation of their reflectivity data.

For metallic behavior, reflectivity data can be analyzed in terms of a Drude dielectric function $\epsilon(\omega)$

$$\epsilon(\omega) = \epsilon_1 + i\epsilon_2 = \epsilon_{core}\left(1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)}\right) \tag{3}$$

with

$$\omega_p = (Ne^2/m^*\epsilon_0\epsilon_{core})^{1/2} \tag{4}$$

where ϵ_{core} is the high frequency dielectric constant arising from the core polarizability, ω_p the plasma frequency, m^* the effective mass, N the density, and τ the relaxation time of free carriers. The reflectance R is related to the real and imaginary parts of the dielectric constant through the optical constants n and k, by the formulas:

$$\epsilon_1 = n^2 - k^2; \qquad \epsilon_2 = 2nk \tag{5}$$

$$R = (n - 1)^2 + k^2/(n + 1)^2 + k^2 \tag{6}$$

Thus the experimental parameters ϵ_{core}, ω_p, and τ can be determined by fitting the experimental reflectivity data. The effective mass, m^*, can be estimated, and the static conductivity $\sigma_{\parallel}$ can be calculated at room temperature:

$$\sigma_{\parallel} = [n_1/m^*(1) = n_2/m^*(2)]e^2\tau \tag{7}$$

It seems likely that the Bright et al.[12] estimates of ϵ_{core}, the plasma energy $\hbar\omega_p$ and the Drude lifetime are incorrect, and Grant et al.'s[106] reevaluation of their data indicated better agreement with single-crystal reflectivity data. As can be seen from Table III, it is likely that $\epsilon_{core} > 5$, $\hbar\omega_p$ is in the range 2.6–4.6 eV, τ is $\sim 1 \times 10^{-15}$ s, and m^*/m is 1–2.

More recent optical property measurements on $(SN)_x$ single crystals[107] and of oriented films[108] have been determined. Geserich et al.[107] have shown that the intrinsic transverse conductivity is ca. $10^3\ \Omega^{-1}\ cm^{-1}$. These authors also show that adjacent fiber boundary layers determined or limit transverse single crystal conductivity. From both polarized and unpolarized Raman and IR data on crystalline and film samples of $(SN)_x$ Stolz et al. have made vibrational frequency assignments.[109] These authors also determined the longitudinal, v_L, and transverse, v_T, velocity of sound in $(SN)_x$. For example, in the 020 direction the values of v_L and v_T were determined as 8300 ± 800 and 2000 ± 100 (also 1200 ± 100) m/s, respectively.[109] For the 102 direction the values of v_L and v_T were found to be 4000 ± 500 and 2400 ± 300 (also 1350 ± 150) m/s, respectively.[109]

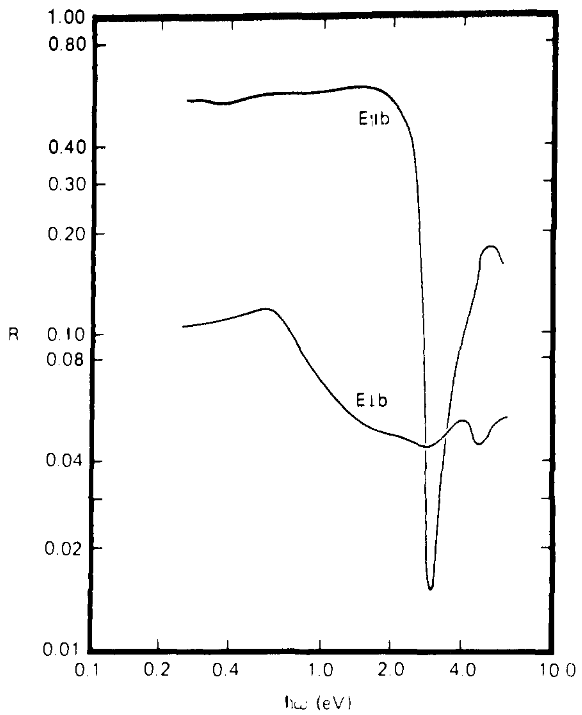


Figure 9. Room-temperature polarized reflectivity of single crystals of $(SN)_x$ with light polarized parallel and perpendicular to the b axis (from ref 106).

TABLE III. Experimental Parameters Deduced from Optical Reflectivity Data

	ϵ_{core}	$\hbar\omega_p$, eV	τ, s	σ, $\Omega^{-1}\ cm^{-1}$	m^*/m
Pintschovius[105]	6.5	2.72	3.5×10^{-15}	3.4×10^4	0.9
Kamimura[51]	6.8	2.6	1.5×10^{-5}	1.5×10^4	
Bright[12]	1.46	2.36	1.9×10^{-15}	3.0×10^3	5.2
Grant[106]		4.6 ± 1	$1 \pm 0.25 \times 10^{-15}$		2.0
Bright[106] (reevaluated by Grant)	4.1	5.1	1.2×10^{-15}		
Möller[108]	6.5	2.7	2.6×10^{-15}	2.5×10^4	0.9
	4.0	1.6	2.6×10^{-16}	5.4×10^2	4.0

The temperature dependence of the reflectance spectrum of $(SN)_x$ at 300, 77, and 4.2 K has been studied by Kaneto et al.[110] The plasma edge in the reflectance spectrum for $E \parallel b$ was found to undergo a blue shift with a decrease in temperature.[110] These authors found that the relaxation time of the itinerant electrons as estimated from the reflectance spectrum, τ_{opt}, at 4.2 K is increased by a factor of ca. 1.5 of the value determined at 300 K. By comparison, the relaxation time determined from dc conductivity measurements, τ_{dc}, increases by ca. two orders of magnitude in going from 300 to 4 K. These anomalous results led Kaneto et al. to conclude that there is a significant difference between the behavior of bulk and surface itinerant electrons.[110]

14. Plasmon Dispersion

Plasmon dispersion by $(SN)_x$ single crystals with 75-keV inelastic electron scattering energy-loss spectroscopy has been studied by Chen et al.[111] These authors found a sharp dispersion peak at ca. 2.5 eV, which corresponds to plasma excitation as determined from optical reflectivity measurements, weak peaks at 6.6 and 8.7 eV, and a broad dispersion peak at ca. 23 eV, which corresponds to interband transitions.[111] The variation of the plasma energy, $\hbar\omega_p$, as a function of the angular deviation away from the *b* axis, θ, is significantly less than that expected from the equation

$$\hbar\omega(\theta) = \hbar\omega(0) \cos \theta \qquad (8)$$

which should hold for a one-dimensional metal.[111] One-dimensional materials such as TTF–TCNQ and $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ yield values of $\omega/\omega_p = 0$ for $\theta = 90°$, where ω_p is the plasma frequency. For $(SN)_x$ at 90° $\omega/\omega_p \sim 0.6$.[111] This is an interesting experiment which shows that $(SN)_x$ is a highly anisotropic three-dimensional metal rather than a true one-dimensional conductor.

Ruvalds et al. have considered plasmon dispersion in $(SN)_x$ in terms of an electron gas model which has an anisotropic effective mass ratio.[112] Ruvalds et al.[112] calculated the deviation of the angular anisotropy of the plasmon energy spectrum for ω_p away from the theoretical one-dimensional equation as found by Chen et al.[111] with very good agreement by assuming an electron effective mass ratio, $R = m_\perp/m_\parallel = 1.9$. The excellent agreement between the calculated and experimental plasmon energy as a function of θ in terms of $R = 1.9$ is additional convincing evidence that $(SN)_x$ is effectively an anisotropic three-dimensional material.[112]

Plasmon dispersion and optical properties of epitaxially grown $(SN)_x$ films have been studied by Stolz et al.[113] By using a 30-keV electron beam, energy loss spectrum peaks for $(SN)_x$ at room temperature at 1.7, 2.4, 4.4, 6.2, 8.2, 12.0, and 22.3 eV were obtained for *k* parallel to the *b* axis, $k \parallel b$.[113] The plasmon energy for $k \perp b$ found by Stolz et al. is ca. 2.4 eV. Stolz et al. note that the plasmon energy for $k \perp b$ obtained from optical measurements on single crystals of $(SN)_x$ is about 1.5 eV. Plasmon energy values obtained by reflectivity are ca. 0.15 eV lower for epitaxial films than those determined from $(SN)_x$ single crystals.[113] Stolz et al. also found that the plasmon energy values derived by electron energy-loss spectroscopy on $(SN)_x$ epitaxial films are lower than the comparable values for single crystals.[113] This work also indicates differences between the lattice and/or defect structure of $(SN)_x$ single crystals and epitaxial films.

15. X-Ray and Ultraviolet Photoemission

The IBM group has performed X-ray photoemission spectroscopy (XPS) measurements on a nonoriented $(SN)_x$ film deposited on a gold substrate.[114] Despite some problems with oxygen and carbon contamination, and degradation of the polymer in air or the X-ray beam, it was possible, from an analysis of the core level spectra, to estimate the amount of charge transfer in $(SN)_x$ to be between 0.30 and 0.42 of an electron from S to N. Study of XPS spectra in the valence band region confirms the metallic nature of $(SN)_x$ by virtue of a small electron yield observed at the Fermi level, and the results were compared with band structure calculations. The electronic structure of $(SN)_x$ as determined by XPS has also been reported by Ley.[115]

Ultraviolet photoemission (UPS) induced by He I and He II resonance radiation of single-crystal and polycrystalline films of $(SN)_x$ has been studied by Koch and Grobman.[116] The results are similar for the two forms of $(SN)_x$ and are comparable to those obtained by XPS. The authors found good agreement between the experimental and theoretical electron state density obtained from band structure calculations.

16. Conclusions

The evidence that has accumulated regarding the physical properties of $(SN)_x$ indicates that it is to be regarded as a highly anisotropic three-dimensional semimetal. Band structure calculations clearly indicate that there is a density of states at the Fermi level of ca. 0.1 state/(eV spin molecule). Conductivity, specific heat, magnetoresistance, optical properties, plasmon dispersion, critical magnetic field effects on the superconducting transition, and pressure effects on both the superconductivity and normal conductivity are all consistent with this three-dimensional view of the material. However, because of the fibrous nature of $(SN)_x$ crystals, the system behaves as a group of decoupled superconducting fibers of the order of 250 Å in diameter. The fluctuation-induced conductivity above the superconducting transition fits a 1-D model of the Aslamasov–Larkin type.

Although there are some problems (for example, the critical magnetic field behavior perpendicular to the fiber axis is very anomalous and is not thoroughly understood), further progress in understanding $(SN)_x$ is probably a materials problem. If less fibrous crystals can be grown (perhaps under pressure?) or if polymorphic forms of $(SN)_x$ can be prepared, or if intercalation of $(SN)_x$ or clathration of $(SN)_x$ can be achieved, then some variation in properties may result, particularly if the dimensionality or interactions with other materials are altered.

Several groups are examining the possibility of structural variations—substitution or partial substitution of selenium for sulfur—and other isoelectronic structures, but no progress has been as yet reported. There is no reason to assume the uniqueness of $(SN)_x$. Therefore, the search for other polymeric materials which may be metallic and superconducting is a problem which is being intensively investigated by many laboratories throughout the world.

In a study of the electronic structure of NO, N_2O_2, SN, and higher homologs Salahub and Messmer conclude that the stability of $(SN)_x$ is enhanced by the ca. 0.5 electron transfer from S to N.[117] The reverse type of transfer occurs in isoelectronic NO, since O is more electronegative than S. Such electronegativity difference considerations lead these authors to conclude that polymers comparable to $(SN)_x$ formed from NO, or other group 5B and 6B elements, with the possible exception of $(SeN)_x$, are unlikely.[117] The published accounts to date on attempts to form $(SeN)_x$ have not shown success.[15a] The lack of stability of Se_4N_4 and Te_4N_4 add little encouragement in this respect.[118]

III. Halogenated Polysulfur Nitride

Halogenated derivatives of $(SN)_x$ are an additional class of polymeric materials which have been found to have metallic properties. Preparation of brominated $(SN)_x$ has recently been reported by three groups. Brominated $(SN)_x$ has been prepared by Bernard et al.[119] Street et al. at IBM have prepared blue–black single crystals of $(SNBr_{0.4})_x$ and obtained a room-temperature conductivity for this material of ca. $2 \times 10^4\ \Omega^{-1}\ cm^{-1}$.[120] This is an order of magnitude higher than that of crystals of normal $(SN)_x$. Synthesis of brominated $(SN)_x$ has also been reported by the University of Pennsylvania group.[121] However, as with $(SN)_x$, brominated $(SN)_x$ is not a new material. Goehring mentioned this material in a 1956 review[32] in which she cites a reference to $(BrS{\equiv}N)_x$ of Clever and Muthmann from 1896.[122]

Whereas the IBM group reports that the *b* unit cell parameter, i.e., along the polymer chain axis, is doubled on bromination, as shown by electron diffraction,[120] Akhtar et al. state that there is no significant change in this parameter.[121] There is agreement that the volume of $(SNBr_{0.4})_x$ increases by ca. 50% upon bromide absorption by $(SN)_x$ crystals.[120,121] The stability in air of this material is significantly lower than that of $(SN)_x$.[121] Halogenation of $(SN)_x$ by I_2 and ICl have also been reported.[120] Direct bromination by Br_2 of S_4N_4 at room temperature with ICl, IBr, and with I_2 at ca. 125 °C has also been reported by this group.[123]

Raman scattering and X-ray diffraction studies of brominated $(SN)_x$ of compositions $(SNBr_{0.55})_x$, blue-black $(SNBr_{0.4})_x$, and copper-colored $(SNBr_{0.25})_x$ have been made by Iqbal et al.[124]

They interpret their results as showing that bromine is present in interfibrillar regions as Br_3^-, and as Br_2 inserted in the $(SN)_x$ lattice. They note that the unit cell volume of solid Br_2, 68.1 Å^3, is essentially the same as that of $(SN)_x$, 66.3 Å^3.[124]

The paramagnetic susceptibility of $(SNBr_{0.4})_x$ has been studied by Scott et al.[125] At temperatures <30 K a small Curie-like behavior was found which yields an upper limit of $S = \frac{1}{2}$ species, such as Br_2^- or Br_3^- of 2×10^{-4} M.[125] At higher temperatures the value of χ_p was found to be essentially linear, and follow the equation, $\chi_p = \chi_0 + \alpha T$ where $\chi_0 = (16.9 \pm 1.2) \times 10^{-6}$ emu/mol and $\alpha = (1.1 \pm 0.1) \times 10^{-8}$ emu/mol·K.[125]

IV. Comparable Low-Dimensional Materials

A. Organic Compounds

A general review of conductivity of high polymers was written by Goodings.[126] There are several books with extensive treatments of the subject.[127-129] However, in view of the often large effect of impurities and polymer chain anisotropies on conductivity as noted by Baughman,[18] we found that the majority of this literature is virtually impossible to interpret. Noncritical surveys have already been published by several authors. We will therefore restrict ourselves to a few brief comments regarding this work.

Increasing the conductivity of polymer systems by involving donor–acceptor interactions—creating polymeric analogs of metallic charge-transfer salts such as tetrathiofulvalenium 7,7,8,8-tetracyanoquinodimethane (TTF–TCNQ)—has been one dominant theme.[21-23] Even a monomeric acceptor added to a polymeric donor should cause some increase in chain–chain interactions, and the earliest examples of this type of interaction involved adding the well-known acceptors iodine or TCNQ to poly(phenylene)[130] or poly(vinylpyridines).[131,132] Lupinski and Kopple's[132] complexes contained a mixture of a poly(vinylpyridine)–TCNQ complex with neutral TCNQ, and conductivities of the order of 10^{-4} Ω^{-1} cm^{-1} were achieved in materials that could be cast as homogeneous thin films from solution. Goodings[126] discusses several other more recent examples of such complexes; in general, these polymeric complexes have lower conductivities than their monomeric analogs. This is probably due to packing considerations.[133] The counter polymer, i.e., monomeric donor and polymeric acceptor, has yet to be produced.

B. Polyacetylene and Polydiacetylene

Another approach to achieving high conductivity in polymers involves the preparation of conjugated molecules in which π-electron delocalization might lead to high conductivity.

The fully conjugated isomeric hydrocarbon polymers, *cis*- and *trans*-polyacetylene, $(CH)_x$, have recently been studied intensively.[134] The conductivities of the cis and the thermodynamically more stable trans isomers are reported to be 1.7×10^{-9} and 4.4×10^{-5} Ω^{-1} cm^{-1}, respectively. Polyacetylene was synthesized by use of a Zeigler catalyst.[134c] Isomer content in these materials can be varied by thermal isomerization.[134c]

The conductivities of these materials were found to be very sensitive to small traces of impurities. For example, when a trans $(CH)_x$ film was exposed to NH_3 vapor, the conductivity decreased from 4.4×10^{-5} to $<10^{-9}$ Ω^{-1} cm^{-1} without a detectable change in weight.[134b,c] The conductivity of *trans*-$[CH(AsF_5)_y]_x$ increased from ca. 10^{-5} to 10^2 Ω^{-1} cm^{-1} when y was increased from 0 to 0.05.[134c] These observations have led Chiang et al. to conclude that the intrinsic conductivities of the pure $(CH)_x$ isomers are probably considerably lower than the above reported values.[134b]

The polydiacetylenes studied to date are insulators which have conductivities at room temperature of ca. 10^{-16} to 10^{-12} Ω^{-1} cm^{-1}.[135] These materials are of interest as photoconductors.[18] The polydiacetylenes, which are obtained by solid-state polymerization, have highly dichroic optical properties and a metallic luster. They are examples of systems where some electron-localizing mechanism leads to an insulating state. Thus, even though one can formally write a partially filled band model for such a polymer, one cannot necessarily expect a conducting system to exist.

C. Halogenated Polyacetylene

Halogenation of polyacetylene with Br_2 and I_2 results in dramatic increases of the room-temperature conductivity from 4.4×10^{-5} to ca. 0.5 and 160 Ω^{-1} cm^{-1}, respectively, for the trans isomers.[134b] Halogenation of cis $(CH)_x$ with ICl and IBr yields *cis*-$[CH(ICl)_{0.14}]_x$ and *cis*-$[CH(IBr)_{0.15}]_x$ with conductivities of 50 and 400 Ω^{-1} cm^{-1}, respectively.[134b] The conductivities of *cis*-$(CHI_{0.25})_x$ and *cis*-$[CH(AsF_5)_{0.14}]_x$ are reported to be 360 and 560 Ω^{-1} cm^{-1}, respectively.[134b] The conductivity of *cis*-$[CH(AsF_5)_{0.14}]_x$ calculated in terms of the density is comparable to that of some metals.[134b]

Plots of ln σ vs. $T^{-1/4}$ or $T^{-1/2}$ were found to be essentially linear.[134c] Chiang et al. found metal-to-insulator transitions in these materials at dopant concentrations of ca. 1%.[134c] The stoichiometry of the brominated material was found to vary from $(CHBr_{0.05})_x$ to $(CHBr_{0.23})_x$ with a slight decrease in conductivity. These conductivities are reportedly the highest room temperature values of any currently known covalent organic polymers.[134a] These materials are postulated to be charge-transfer π complexes of the polymer and halogens.

"Single crystals" of $(SN)_x$ and the exfoliated bromination product consist of strands or fiber bundles of essentially linear chains of the polymer in highly oriented form. By contrast $(CH)_x$ films consist of a highly entangled polymer lattice.[136] Even stretched $(CH_x)_x$ films, which were studied by scanning electron microscopy, show only partial ordering of the highly disordered crystalline lattice.[136] This leads one to be highly optimistic about the conductivity of such polymers if polymer orientation comparable to that in $(SN)_x$ could be achieved.

Formation of n-type and p-type semiconductors by doping $(CH)_x$ with NH_3 or alkali metals, and halogens or AsF_5, respectively, has led to the preparation of covalent organic polymer semiconductor junctions by Chiang et al.[137]

In both brominated $(CH)_x$ and $(SN)_x$ Raman spectral studies show the presence of ordered Br_3^- ions.[138] In the case of the iodinated analogs the nature of the iodine species is not as well established. The presence of iodine as I_2 and I^- or I_5^- in a partially ordered state is inferred.[138b,c] A similar study of iodine derivatives of $(CH)_x$ also indicates the presence of I_3^- and possibly I_5^-.[139] From X-ray diffraction studies of this system it was concluded that the iodine species form sheets of intercalated layers in the $(CH)_x$ lattice.[139]

Speculation about the mechanism of conductivity in the polyacetylene complexes has largely been based on analogy with the interpretation of the enhanced conductivity in halogenated $(SN)_x$. The presence of the acceptor is viewed as modifying the band structure of the parent polymer. In many charge-transfer complexes of intermediate conductivity, however, conductivity is enhanced by π complexing between donor and acceptor molecules. The most conducting direction in such structures is perpendicular to the hydrocarbon plane. Until structural information becomes available on the polyacetylene complexes, this interesting mechanistic question cannot be resolved.

V. Comments on the Future

There is no reason to believe that other highly conducting systems will not be found. Several papers have been written on the design of high conductivity low-dimensional materials.[140] Yet most of the advances in this field have been of an empirical nature, or have relied on "rediscovery" of observations in the early literature of compounds with metallic lusters.

If one simply looks at the dramatic increase in activity in this field, one must anticipate that further advances will occur by either purposeful design or trial and error. Hardly anyone expected ten years ago that polymeric metals would be found. It is unlikely that one can accurately gauge what the next few years of discoveries will be. The field is open to imaginative suggestions from both chemists and physicists.

VI. Addendum

Several additional relevant summaries of recent research on $(SN)_x$, halogenated $(SN)_x$, and polyacetylene have been written since the submission of this manuscript. Some will appear as part of the Les Arcs, France, NATO Conference Proceedings.[141] Street and Clarke have made a comparison of the properties of $(SN)_x$ and $(CH)_x$, and their halogenated derivatives.[142] The infrared spectra of $(SN)_x$ and brominated $(SN)_x$ scanned to frequencies as low as 60 cm^{-1} have been reported by Macklin et al.[143] This work corroborates previous Raman studies on these materials[124] which show the presence of ordered intercalated Br_2 and Br_3^-, together with these species adsorbed or coated on $(SN)_x$ fibers.

Heger et al. have determined the crystal structure of $(SN)_x$ by neutron diffraction.[144] These authors obtained results which are in good agreement with the Penn structure.[43] They found that the $(SN)_x$ chains are planar within experimental error. The planes are tilted with respect to the $(\bar{1}02)$ plane by 2.0(5)° around the [010] direction. An average of one defect site to nine normal atomic sites is typical of the crystals studied. Defect density was found to vary markedly with crystal perfection.

Batra et al.[145] have calculated the electronic structure, total density of states, and orbital density of states for $(SN)_x$ and S_2N_2 by use of an extended tight-binding method. The energy states near the Fermi level in $(SN)_x$ were found to be derived from S 3p and N 2p orbitals. These authors conclude that $(SN)_x$ does not undergo a Peierls distortion owing to the strong interchain interactions and the resulting three-dimensional character. X-ray emission spectra have been calculated by Friesen et al.[146] The electron density of states calculated by these authors agree quite well with those calculated by Batra et al.[145] and by Ching et al.[61]

Work on polyacetylene is continuing at a brisk pace.[141] It is of interest to note that initial measurements of the electrical properties of doped polyacetylene were reported by Berets and Smith in 1968.[147] Polyacetylene itself has been known for many years.[148] Ziegler–Natta catalysis as a polymerization method was reported in 1958.[149] Hatano et al.[150] studied the electrical properties of both crystalline and amorphous $(CH)_x$ and noted that oxygen sorption caused a marked decrease in the conductivity. Polysulfur nitride, $(CH)_x$ and their halogenated products thus have in common, in addition to their high conductivity, the fact that they all were known before the dawn of the current search for molecular metals and one-dimensional systems.

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