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Preparation and Properties of $(SN)_x$

Abstract: The chain compound $(SN)_x$ is the first example of a superconducting polymer. In this paper we review the chemistry, structure, and physical properties of $(SN)_x$ and describe how the electrical properties of this novel material depend upon the crystal growth technique. The thermal properties of S_2N_2 and $(SN)_x$ are discussed with particular reference to the crystal growth process. The fibrous nature of the polymer is described and evidence is presented showing that interchain coupling plays a significant role in determining the physical properties of this material. Finally we summarize our attempts to prepare analogous polymeric metals.

Introduction

Most known polymers have a high electrical resistivity at room temperature, which increases still further as the temperature is lowered. Furthermore, such polymers often form solids that are structurally poorly crystalline or even amorphous. Polymers of higher conductivity [1] would be of great interest, and several organic polymers have been prepared which are, in fact, semiconducting. In the last two years experimental studies of the inorganic polymer sulfur nitride, $(SN)_x$, have shown that this material is a unique exception to conventional polymeric behavior [2–4]. Crystals of $(SN)_x$ exhibit the properties of a highly anisotropic metal with a resistivity along the polymer chain which decreases with decreasing temperature [2, 3] and eventually vanishes at a superconducting transition temperature around 0.3 K [4]. This represents the first report of superconductivity in a polymer. As such there is considerable interest in achieving a fundamental understanding of the chemical and physical properties of this material in order to gain insight into the design of other polymeric metals and superconductors, perhaps with higher transition temperatures.

In this paper we emphasize the chemistry of $(SN)_x$; the physics will be discussed at length elsewhere [5]. We briefly review the history and structure of $(SN)_x$ and describe in detail our current technique for the preparation of high quality material, showing how this technique has improved the electrical properties of the polymer. The thermal properties of $(SN)_x$ and its precursor S_2N_2 are described in terms of their significance to the polymerization and crystal growth processes. The evidence relating to the dimensionality of crystalline $(SN)_x$ is summarized and we show how the fibrous nature of the polymer crystals results in apparent one-dimensional behavior of certain properties. Finally, we describe potential modifications of $(SN)_x$.

History of $(SN)_x$

Though there has been a great deal of work on $(SN)_x$ in the last two years it is not a new material; it was first prepared prior to 1910 in the form of a transparent thin blue film by Davis [6]. Later, in 1910, Burt [6] prepared both films and crystals by the thermal pyrolysis of S_4N_4 and he showed that the pyrolysis can be catalyzed by the presence of hot silver wire. Initially the silver reacts with the S_4N_4 to give silver sulfide and nitrogen. It is the silver sulfide which acts as catalyst but even today little is known about the mechanism. The principal product of the pyrolysis is S_2N_2 [7] which spontaneously polymerizes in the solid state to give $(SN)_x$. This reaction is shown schematically in Fig. 1. On the basis of its total insolubility in known solvents, Burt characterized $(SN)_x$ as a polymer consisting of sulfur-nitrogen chains, but no further characterization of this unusual material took place for 43 years. At this time Goehring and Voigt [7, 8] began an extensive study of its structure and properties and they found pellets of $(SN)_x$ to be semiconducting. This observation was confirmed by other workers [9, 10] and it was not until 1973 that Walatka, Labes, and Perlstein [2] measured individual crystals of the polymer and showed them to be metallic down to 4.2 K. Subsequent specific heat and conductivity measurements [3] showed that $(SN)_x$ remained metallic to 1.5 K. On cooling to 0.26 K, Greene, Street,

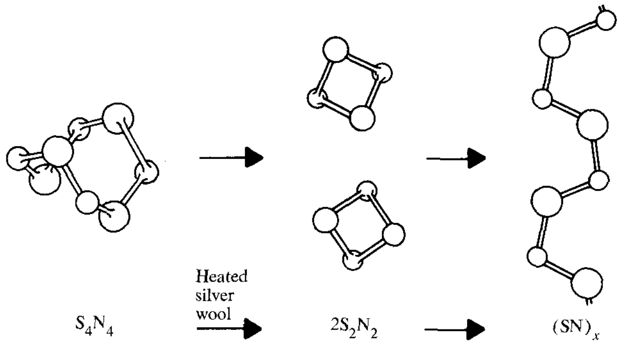


Figure 1 Schematic representation of the preparation of $(SN)_x$ by the pyrolysis of S_4N_4 and the solid state polymerization of the resulting S_2N_2.

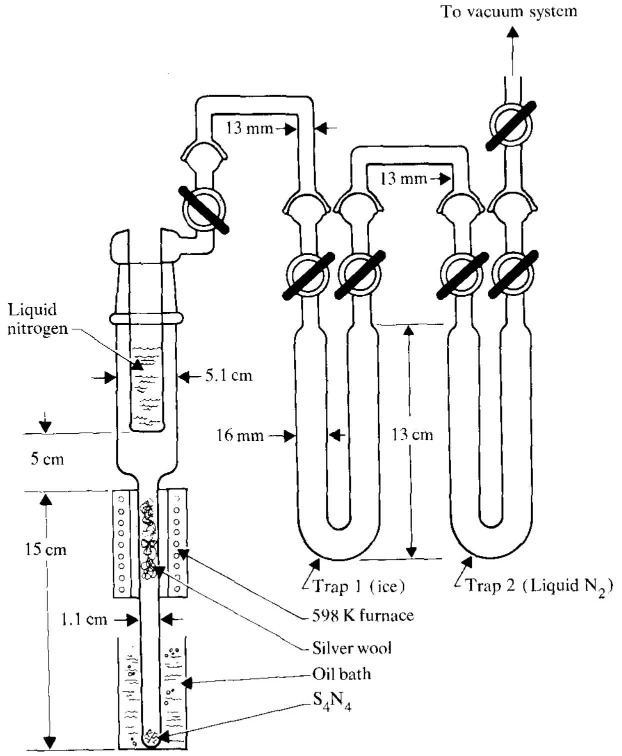


Figure 2 Apparatus for the preparation of $(SN)_x$ crystals.

and Suter [4] found that this highly anisotropic, pseudo-one-dimensional polymer became superconducting. This result was of considerable interest because it showed that highly anisotropic solids could exhibit superconductivity and led to the hope that the polymeric structure of $(SN)_x$, with suitable modification, could allow one to test the excitonic theory of superconductivity proposed by Little [11]. However, it should be emphasized that the superconductivity observed in $(SN)_x$ is not due to the Little mechanism.

Since their first preparation by Davis and Burt, films of $(SN)_x$ have been studied extensively. They are prepared both by the pyrolysis of S_4N_4 [12] and also by the evaporation of $(SN)_x$ [13]. Douillard [13] showed that these films were oriented with the $\bar{1}02$ plane in the film plane. Recently more highly oriented films have been prepared [14]. All these films have a semiconducting (not metallic) conductivity behavior and do not superconduct [15], and we do not discuss them further.

Preparation of crystals of $(SN)_x$

Since the first experiments of Davis and Burt, the conditions for the pyrolysis of S_4N_4 and the subsequent solid state polymerization have been widely studied [16, 17] but it was not until 1973, apparently, that crystals of quality appropriate to demonstrate the intrinsic metallic and superconducting behavior of the polymer were prepared [2]. Since that time considerable improvements in the electrical properties of the crystals have been achieved by us [18] and by others [19]. In an earlier publication [18] we briefly described our method of crystal growth. We now describe in more detail our current techniques, which have led to the further improvements in crystal quality described later in this paper.

S_4N_4 prepared by the standard process in the literature [20] is carefully purified by recrystallization from dioxane or benzene, followed by fractional sublimation until its melting point is at least 462 K. This latter step is particularly important if hydrocarbon impurities in the final $(SN)_x$ product are to be avoided. The S_4N_4 is heated in vacuum to about 350 K and the vapor passed over silver wool at about 600 K. The product of the resulting pyrolysis, which is mainly S_2N_2, is collected on a liquid nitrogen cold finger. In order to reduce the contamination of the $(SN)_x$ by side products of the pyrolysis, our initial apparatus has been modified by the addition of a second trap as shown in Fig. 2. When all the S_4N_4 has evaporated, the cold finger is allowed to warm to room temperature and the volatile products distill into the two traps. The first trap is maintained at ice temperature and the second at liquid nitrogen temperature. The apparatus is open to the pump throughout this process. Only S_2N_2 appears to stop in the first trap, whereas a ring of the remaining S_2N_2 (and also some byproducts which were not characterized) forms at the entrance to the second trap just above the liquid nitrogen level. After approximately three hours the traps are isolated and the liquid nitrogen in the second trap is immediately replaced by ice, causing the ring of S_2N_2 to warm up and slowly sublime into the cooler parts of the ice-cooled U-tube. The S_2N_2 crystals in both U-tubes are allowed to grow and poly-

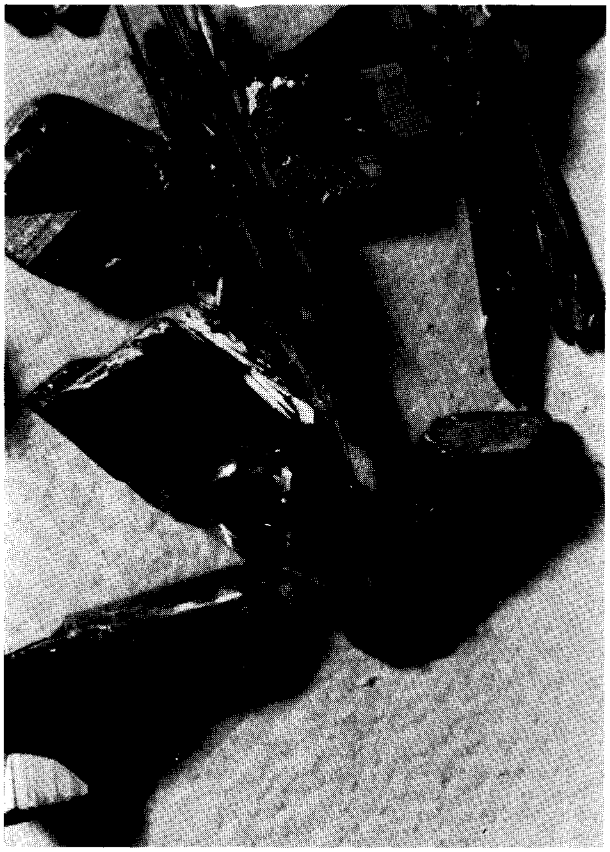


Figure 3 Needles and more equidimensional crystals of $(SN)_x$.

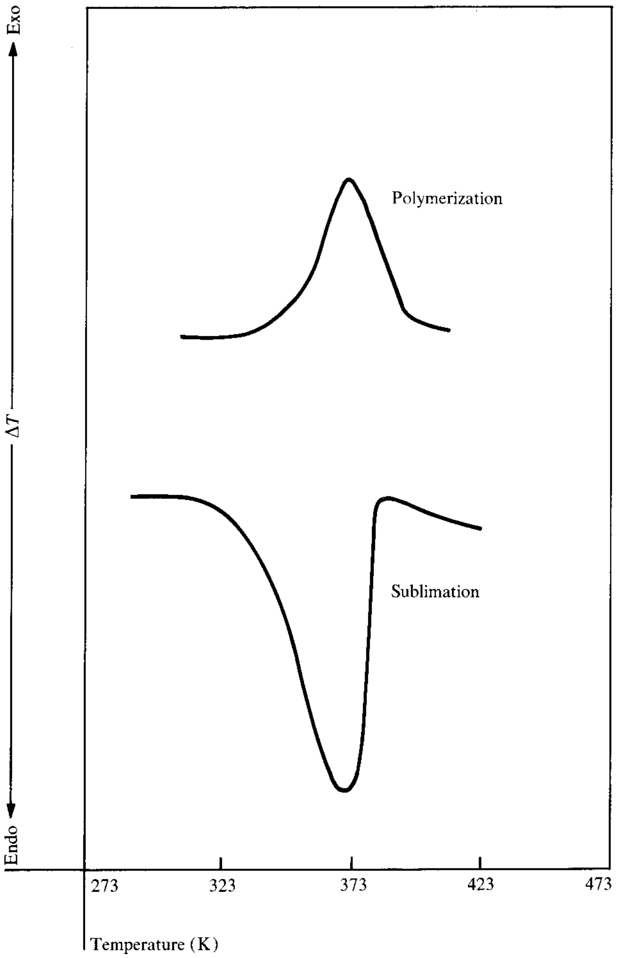


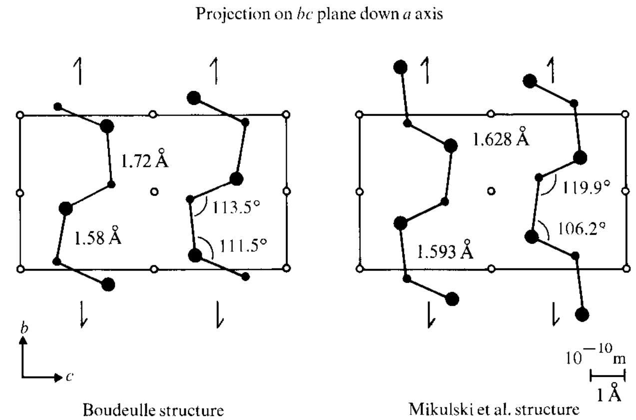
Figure 4 Differential thermal analysis (DTA) of S_2N_2 in helium atmosphere showing exothermic polymerization in a closed system and endothermic sublimation in an open system; heating rate, 15°/min.

merize at ice temperature for two days. They are then warmed to room temperature and the polymerization process is continued at room temperature for at least 14 days and preferably longer. Though we believe that the first trap initially contains only S_2N_2, during the course of polymerization a narrow orange ring of S_4N_4 appears in the trap, which suggests that a small amount of vapor phase dimerization of S_2N_2 takes place at the same time as the solid state polymerization. The $(SN)_x$ crystals formed in this first trap are approximately equidimensional, whereas the second trap always contains some needles. Examples of both types of crystals are shown in Fig. 3. The needles presumably result from temperature gradients produced during the transition from a liquid nitrogen to an ice bath. Their dimensions are 5 to 8 mm long and approximately 1 mm wide.

The optimum amount of silver wire (0.025 mm diameter) used for the catalyst is about half the weight of S_4N_4 [17]. In a typical experiment, about 0.6 g of S_4N_4 is used. Care must be exercised to avoid contamination of the silver during the tedious procedure of forming it into a plug that effectively fills the heated zone of the furnace. Contamination of the silver or the inside of the apparatus can lead to as much as 4 to 5 atomic percent of hydrogen in the resulting $(SN)_x$ [21]. Though we heat the silver to a measured temperature of 598 K, we do not believe that temperature is critical [16]. According to the Law of Mass Action, the yield of S_2N_2 is favored by low pressures. The measured pressure in our system after the initial reaction,

$$2Ag + \tfrac{1}{4}N_4S_4 \rightarrow Ag_2S + \tfrac{1}{2}N_2,$$

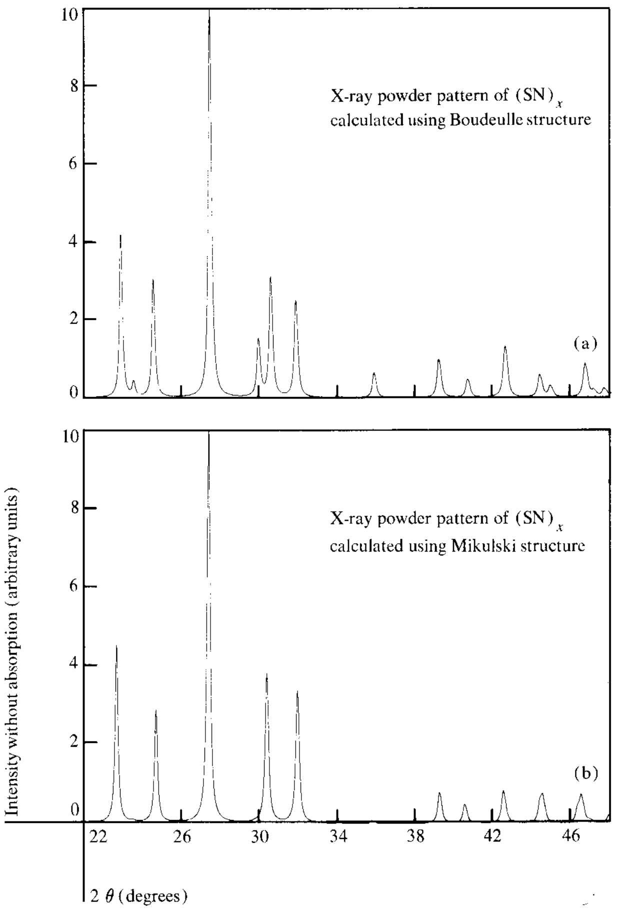
has abated is $\approx 10^{-6}$ torr (1.3×10^{-4} Pa). We have observed that higher pressures favor increased amounts of side products, particularly S_4N_2. This is especially noticeable if one attempts to speed the evaporation of S_4N_4 by raising the temperature much above 360 K.



Space group $P2_1/c$
Lattice constants
$a = 4.153$ Å (4.153×10^{-10}m)
$b = 4.439$ Å $\beta = 109.7°$
$c = 7.637$ Å

Figure 5 Comparison of Boudeulle structure [23] and Mikulski et al. structure [19, 25] of β phase $(SN)_x$.

Figure 6 Calculated x-ray powder patterns for (a) Boudeulle structure of β phase $(SN)_x$; and (b) Mikulski et al. structure [19, 25] of β phase $(SN)_x$.



For good quality crystals it is necessary to ensure that all the S_2N_2 is polymerized before exposing them to air. Walatka, Labes, and Perlstein [2] remove the unpolymerized S_2N_2 by extraction with benzene and Mikulski et al. [19] heat their crystals to 348 K under vacuum. We believe that these techniques are not ideal, since they leave voids in the crystals where the S_2N_2 is removed. Thermal analysis of S_2N_2 in an inert atmosphere, as shown in Fig. 4, demonstrates that when S_2N_2 is heated in a closed system, spontaneous exothermic polymerization takes place. The measured heat of polymerization is 3.7 kcal/mole of SN. However, if the S_2N_2 sample is heated under the same conditions in an open system, endothermic sublimation takes place rather than polymerization. Figure 4 shows the sublimation endotherm displaced to slightly lower temperature from the polymerization exotherm. In view of these results, we are very cautious about attempting to accelerate the polymerization process by raising the temperature above room temperature, particularly in vacuum, but we have found that good crystals of $(SN)_x$ can be obtained by polymerizing S_2N_2 for two days at 348 K under 70 atmospheres of nitrogen.

Structure of $(SN)_x$

Though Burt [6] recognized that $(SN)_x$ was a polymer, it was Goehring and Voigt [8] who first investigated the structure suggesting a zig-zag chain geometry. Douillard [22] showed that this chain geometry was incorrect, and he demonstrated another chain configuration which has proved to be basically correct. He also showed that $(SN)_x$ appeared to exist in two phases. These phases were further characterized by Boudeulle [23], who described the normal phase of $(SN)_x$ as a crystalline β phase and the other phase as a poorly crystalline or small-grain-size α phase. She also stated that the two phases could exist in the same crystal. Douillard suggested that this phase conversion was effected by x-ray irradiation—a suggestion which Boudeulle discounts, though she does not state clearly the conditions under which she did obtain the α phase. Nevertheless, she did show the α phase to be monoclinic with lattice constants $a = 4.04 \pm 0.05$Å ($4.04 \pm 0.05 \times 10^{-10}$m), $b = 4.43 \pm 0.05$Å, $c = 7.84 \pm 0.05$Å, and $\beta = 110 \pm 1°$. These lattice constants are very similar to those of the β phase given in Fig. 5. In order to account for two irreproducible lines in the x-ray powder patterns of some $(SN)_x$ samples Boudeulle defined a third and larger monoclinic cell. This α' phase has not yet been observed by other workers. The crystals of the β phase available to Boudeulle were not of sufficient quality for x-ray structural analysis but she was able to determine their structure using electron diffraction techniques [23, 24]. Later, when better crystals permitted x-ray studies, Mikulski et al. [19, 25] suggested modifications to the Boudeulle structure of the β phase. A comparison of these two suggested structures for the β phase is given in Fig. 5. The lattice constants are the same for both structures. The main differences between the two structures are that the chains are shifted relative to one another along the *b*-axis such that the interchain interaction appears to be less in the x-ray structure. In addition, the bond alternation is no longer present in the x-ray structure and the angles at the nitrogen and sulfur atoms are changed. In her thesis Boudeulle herself questions whether the bond alternation she reports is real. Both structures have rather high residual factors (Boudeulle, 19 percent; Mikulski, 16.5 percent). This latter residual factor is reduced to 11 percent in a refinement model which includes the main $(SN)_x$ chain at 73 percent occupancy and the sulfur atoms of three minor $(SN)_x$ chains, arising from the defect structure, with an occupancy factor of nine percent each. Comparison of the experimental x-ray powder diffraction data tabulated by Boudeulle [23] with that calculated for the two proposed structures (Fig. 6), using Smith's program [26], suggests that the x-ray-determined structure is, in fact, more correct. However, this comparison could be confused by preferred orientation effects often present for x-ray powder samples of $(SN)_x$. Further confirmation of the x-ray structure comes from recent neutron diffraction studies [27]. Figure 7 shows a view down the *b* axis of the x-ray structure depicting how the centro-symmetrically related, translationally inequivalent chains in Fig. 5 alternate in the $\bar{1}02$ plane. The shortest interchain bonds are tabulated in Table 1. Comparison of these bond lengths with the corresponding van der Waals radii suggests that the interaction between the chains is weak, particularly between $\bar{1}02$ planes. This is further emphasized if one considers the Bondi [28] value for the van der Waals radius of sulfur, 3.8×10^{-10} m, rather than Pauling's value used in Table 1. On this basis it was initially thought that this highly anisotropic material was perhaps quasi-one-dimensional. However, as we discuss later, other evidence indicates that the interchain interactions are more significant than is suggested by the rather large interchain spacings, and thus $(SN)_x$ is not pseudo-one-dimensional but is a highly anisotropic three-dimensional semimetal.

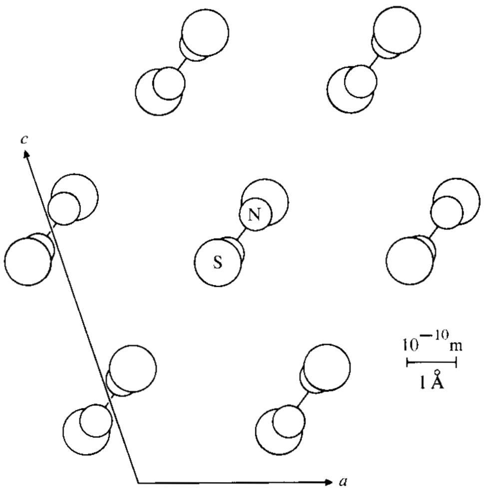


Figure 7 View down the *b*-axis of the Mikulski et al. structure [19, 25] of β phase $(SN)_x$.

Table 1 Comparison of shortest interchain bonds in the Mikulski et al. structure [19, 25] of β phase $(SN)_x$ with the corresponding van der Waals radii.

Shortest separation	*Interchain distance* (10^{-10} m)		*van der Waals radius* (1^{-10} m)
	Within ($\bar{1}02$) *plane*	*Between* ($\bar{1}02$) *planes*	
S—S	3.48	3.72	3.70
N—N	3.35	3.37	3.15
S—N	3.26	3.40	3.35

Very recently Baughman et al. [29] have shown that on shearing or grinding the β phase of $(SN)_x$, partial conversion to a new orthorhombic phase takes place. Simultaneously, the lattice constants of the residual β phase change slightly from the values given in Fig. 5 to $a = 4.040(2)$ Å [$4.040(2) \times 10^{-10}$m], $b = 4.429(8)$ Å, $c = 7.849(3)$ Å, and $\beta = 109.3°$. The authors believe this is a consequence of internal strain fields due to structural defects, such as stacking faults, which are introduced during the shear deformation. They also point out that these lattice constants agree almost exactly with those determined by Boudeulle for the α phase. The new orthorhombic phase (probable space group $P2_12_12_1$) has lattice parameters $a = 6.251 \times 10^{-10}$ m, $b = 4.429 \times 10^{-10}$ m, and $c = 4.807 \times 10^{-10}$ m. The *b* axis or chain axis is the same as the β phase and the chain geometry is also believed to remain the same. The differences in the packing of the chains are shown in Fig. 8. For convenience in comparing the two phases, the equivalent monoclinic axes for the orthorhombic phase are shown. Note that for the orthorhombic phase the chains are rotated from their positions in the β phase and the mode of stacking of the two translationally in-

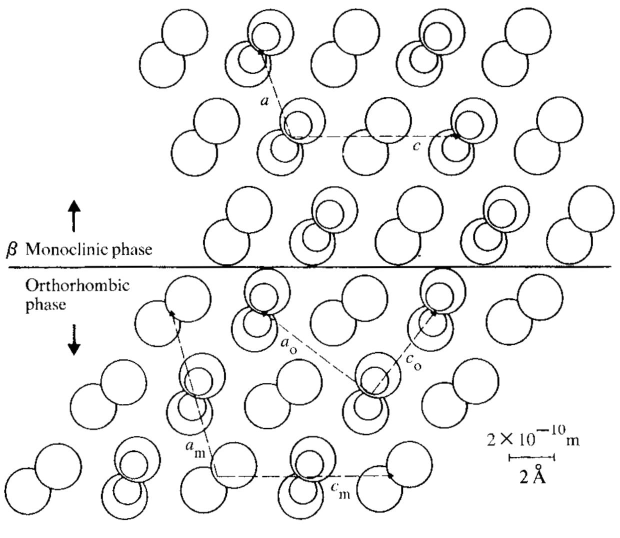
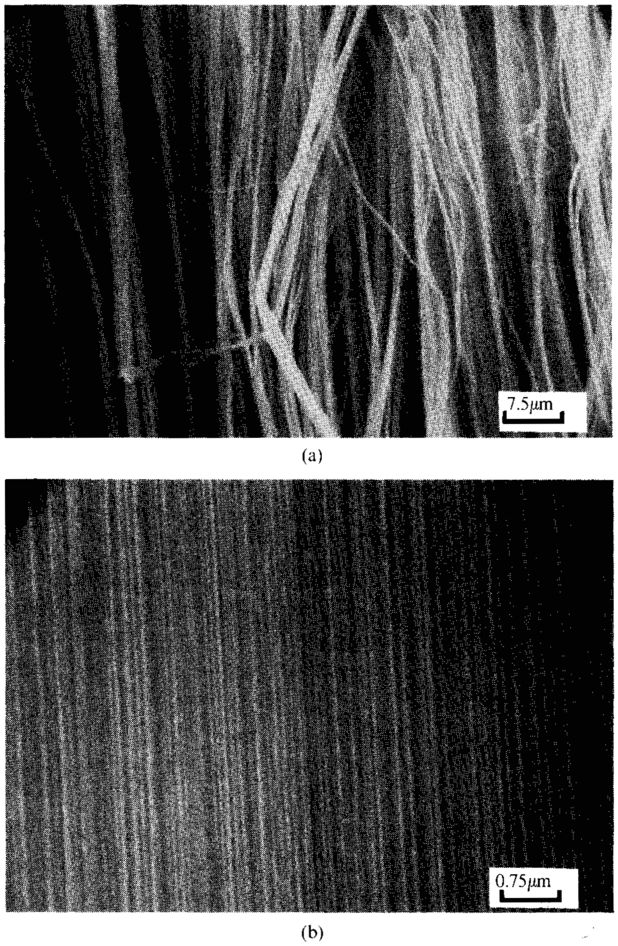


Figure 8 Comparison of the β monoclinic phase and the orthorhombic phase of $(SN)_x$ as viewed down the chain axis [29]. For the orthorhombic phase the equivalent monoclinic cell constants a_m and c_m are shown for reference.

Figure 9 Scanning electron micrographs of $(SN)_x$ crystals: (a) fibrous crystal; and (b) less fibrous crystal.



equivalent chains has changed. These changes may lead to significant differences in the interchain interactions. However, a clear evaluation of the properties of this orthorhombic phase may be hindered unless it can be prepared phase-pure. Similar remarks apply to the α phase.

Fibrous nature of the polymer crystals

All the crystals of the polymer prepared to date have a striated appearance parallel to the chain axis, which reflects the fibrous structure that Boudeulle [23] suggested was the result of extensive twinning. Baughman et al. [30, 31] have investigated the polymerization of S_2N_2 and they have demonstrated that this twinning is a consequence of the non-unique dimer to polymer transformation. It seems likely that the mechanism of fiber formation in $(SN)_x$ is similar to that discussed by Wegner et al. [32] for poly(oxymethylene) prepared by solid state polymerization of 1,3,5-trioxane. Polymerization probably starts at nuclei originating at defects in the S_2N_2 monomer. Polymer growth proceeds rapidly in the chain direction, but in the lateral directions crystal growth soon stops because the chains become out of register due to differences in the lattice constants of the monomer and the polymer. Meanwhile, crystal growth in the chain direction can continue until a defect in this direction is encountered. In this way fibrous rather than homogeneous crystals are obtained. In poor quality crystals the fibers are very apparent, but in other crystals they are not so obvious because there is no discontinuity between them; this is illustrated in Fig. 9. Even in these better quality crystals, ready cleavage takes place along planes parallel to the fiber axis. Using scanning electron microscopy and transmission electron microscopy we have attempted to determine the diameter of these fibers and we obtain values from 120 to 25 nm. Though these values are in good agreement with the short range order perpendicular to the fiber axis observed by Boudeulle [23] from x-ray line broadening, the ultimate fiber diameter may be even smaller. No satisfactory measurement of the chain length of $(SN)_x$ is available although the mass spectrometric data of Smith et al. [21] can be interpreted in terms of a short chain length $(SN)_4$ in the solid. They report that the dominant species in the vapor phase is a linear $(SN)_4$ species. Similar conclusions were reached by Siedle and Hertz [33]. The low heat of sublimation (29.0 ± 0.5 kcal/mole) of this linear tetramer, compared to the expected S—N bond strength, led Smith et al. to conclude that no S—N bond was broken during the sublimation, which, in turn, implies that every eighth bond in the solid is either very weak or the chain length corresponds to $(SN)_4$. Such a short chain length seems unlikely, and it is obvious that more work is required before the chain length in $(SN)_x$ can be established.

Stability of $(SN)_x$ and S_2N_2

There have been reports that S_2N_2 is explosive [16, 17]. We have not found this to be the case, nor does the differential thermal analysis (DTA) of S_2N_2 shown previously suggest explosive behavior either on sublimation or polymerization. However, we have had explosions with $(SN)_x$ itself when grinding, compressing, or heating in the presence of air. This explosive behavior is consistent with the thermal analysis data shown in Fig. 10. When heated in air, $(SN)_x$ shows a very strong exotherm at 513 K. The violent nature of this exotherm is also demonstrated by the excessive self-heating apparent in the thermogravimetric analysis (TGA) data in Fig. 10. When heated in helium, with air carefully excluded, the DTA data change considerably. There is a major endotherm at 513 K which is due to decomposition to entirely volatile products. Impure samples frequently leave a white residue at this stage. There is also a minor endotherm at 496 K, the significance of which is not yet understood. Though this region is not shown in Fig. 9, $(SN)_x$ is thermally inert between liquid nitrogen and room temperatures. These observations are not consistent with the work of Douillard [22] who reported that above 413 K, $(SN)_x$ converts to S_4N_4; we have never observed this.

When $(SN)_x$ is heated in vacuum to temperatures above 373 K, it begins to dissociate. As mentioned in the previous section, Smith et al. [21], using mass spectrometric techniques, have investigated the vapor obtained by heating the polymer to 373 to 433 K. They report that the major species volatilizing is a linear molecule $(SN)_4$ which, on collision with walls, can rearrange to the familiar cradle-structure S_4N_4 molecule. At temperatures above 433 K, molecular sulfur and molecular nitrogen become more important.

Mikulski et al. [34] have investigated the reactivity of $(SN)_x$ to moisture and oxygen and they report it to be chemically inert. However, Mengel et al. [35], using x-ray-photoelectron spectroscopy, have shown that the surface of completely polymerized $(SN)_x$ oxidizes on exposure to air in about six hours. This surface oxidation was also observed in the mass spectroscopic work of Smith et al. [21], which showed the presence of several oxygen species on the surface of $(SN)_x$ crystals but not in the bulk. Consistent with these latter observations we find films to be much less stable in air than bulk crystals.

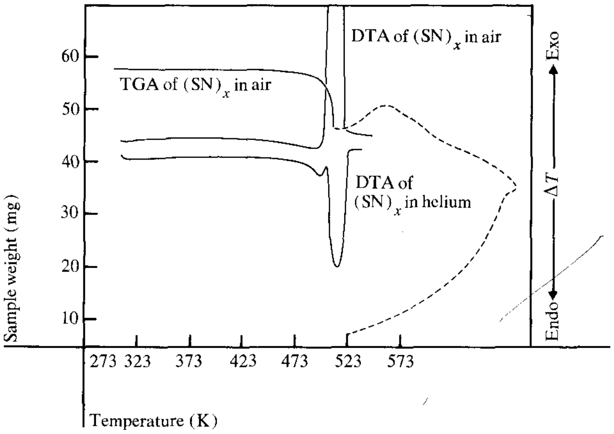


Figure 10 Differential thermal analysis (DTA) data and thermogravimetric analysis data for $(SN)_x$ in helium and in air.

Electronic properties of $(SN)_x$

The possibility that metallic conduction occurs in $(SN)_x$, as suggested by the experiments of Labes and coworkers [2], and its subsequent confirmation by the superconductivity experiments of Greene et al. [4], has led to a rapid increase in the number of experimental and theoretical papers on this compound. These papers have been the subject of two recent reviews [5, 36]. In simple chemical terms this conductivity can be thought of as arising from delocalization along the polymer chain of the unpaired electron in the $\pi^*_{p_z}$ antibonding level of each SN unit. Obviously, in the polymer, appreciable rehybridization of the SN molecular orbitals takes place, but band structure calculations seem to agree that this does not involve the sulfur *d* orbitals. In this section we show that the electrical properties of the $(SN)_x$ crystals are very dependent on crystal growth technique. The resistivity ρ of $(SN)_x$ crystals obtained by our preparative technique is compared with that of crystals from other sources in Fig. 11. This figure shows the fiber or *b*-axis electrical resistivity of $(SN)_x$ normalized to the room temperature value. For comparison, curve (a) shows the semiconducting behavior of $(SN)_x$ pellets [9], and curve (b) shows some of the original data of Walatka, Labes, and Perlstein [2]; curve (c) is for a crystal grown in our laboratories using the technique of [2].

There are two main problems with this technique which limit the quality of the crystals. First, the by-products of the pyrolysis and unpyrolyzed S_4N_4 are not adequately separated from the $(SN)_x$. Second, the polymerization time is too short for complete polymerization, making it necessary to remove the unpolymerized S_2N_2, which leads to voids as discussed earlier. Extrinsic effects associated with this growth technique lead to the minimum observed in the resistivity curves (b) and (c) and also to the low resistivity ratio [ρ(300 K)/ρ(4 K)]. In contrast to Civiak et al. [37], we believe that even the superconducting transition is influenced by these extrinsic effects. Curves (d), (e), and (f) show crystals grown by our own technique and annealed in vacuum at

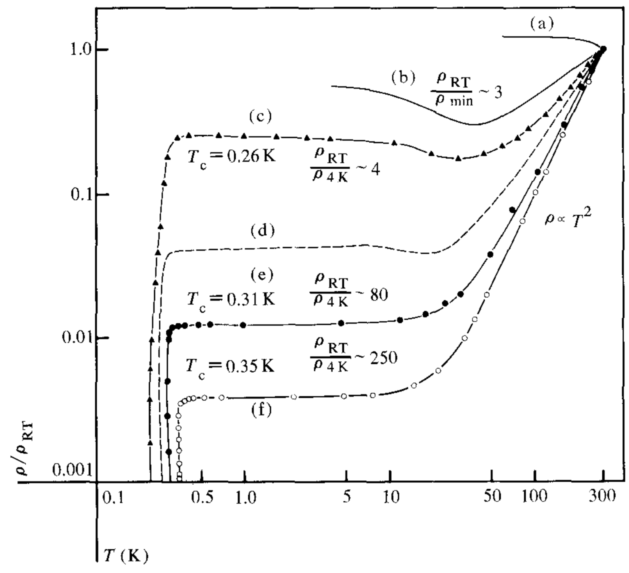


Figure 11 Temperature dependence of the resistivity of $(SN)_x$ crystals from various sources: (a) $(SN)_x$ pellets [9]; (b) crystals from original data of [2]; (c) crystals grown in this laboratory using technique of [2]; and (d), (e), and (f) crystals grown by the technique described in this paper.

room temperature for increasing lengths of time. As annealing time increases, the resistivity minimum becomes less pronounced and shifts to lower temperatures. At the same time the resistivity ratio increases to about 250. In addition, the room temperature conductivity increases from 1000 to 4000 $(\text{ohm}-\text{cm})^{-1}$ and the superconducting transition temperature from 0.26 to 0.35 K. These results were reported previously and the normal state properties have subsequently been verified by the work of Chiang et al. [38]. These observations confirm that the resistivity minimum is due to extrinsic contributions such as chain breaks and defects. The annealing process apparently allows more complete polymerization of the $(SN)_x$ chains. The best samples have a small low-temperature residual resistivity as found in ordinary metals. However, the temperature dependence of ρ between 20 and 250 K is not typical of that found in ordinary metals. We find $\rho(T) = AT^2$ when corrected for the residual resistivity. This result is also found by Chiang et al. [38] and Geserich and Pintschovius [36], who have suggested that electron-electron scattering is responsible for the unusual T^2 behavior. Given the semimetallic Fermi surface of $(SN)_x$ [39], this is a very plausible hypothesis; however, more experiments are necessary to prove the matter conclusively. Similarities may exist with the layered material TiS_2 [40] and with tetrathiofulvalene tetracyanoquinodimethane (TTF-TCNQ) and its derivatives [41] where a T^2 dependence of the resistivity over a wide temperature range has been observed and electron-electron scattering has been proposed. Although our own techniques and those of others [19] have achieved considerable improvement in the electrical properties of $(SN)_x$ crystals, we expect further progress as developments in the crystal growth process lead to crystals of even greater purity and perfection. In confirmation of these expectations we have occasionally obtained crystals with much lower resistivities at 4 K and resistivity ratios of approximately 1000.

Some of the thinner needles prepared by this technique exhibit a twisted morphology. Kahlert and Seeger [42] have recently shown that these thin twisted needles have very high conductivities, indicating a low concentration of defects. The highest conductivity measured along the chain was 10^6 $(\text{ohm}-\text{cm})^{-1}$ at 4 K (c.f. 5.5×10^5 $(\text{ohm}-\text{cm})^{-1}$ for the best crystal of Chiang et al. [38]) and 1700 $(\text{ohm}-\text{cm})^{-1}$ at room temperature. On deformation of these crystals by bending at right angles and returning to their original shape, the chain conductivity at 4 K decreases from 10^6 to 10^4 $(\text{ohm}-\text{cm})^{-1}$. The authors ascribe this effect to a sharp increase in the density of chain breaks. It seems likely that such severe bending in these fibers causes macroscopic damage and perhaps locally induces orthorhombic phase $(SN)_x$. This could also explain the observed change in electrical properties. Kahlert and Kundu [43] report that their needles show no conductivity maximum; however, the data of Kahlert and Seeger show conductivity maxima for some of these needles, the magnitude of the maximum becoming more pronounced as their cross sectional area increases. By a modification of our technique, Kahlert and Kundu have prepared large crystals of $(SN)_x$ weighing up to 180 mg. Currently, these crystals are of poor quality compared to the needles, with surface cracks and macroscopic twinning, presumably due to twinning in the original S_2N_2 crystals. Such large crystals should also be checked for inclusions of S_4N_4.

Our crystals, like those reported by Smith et al. [21], contain up to five atomic percent of hydrogen. Though the mechanism for the incorporation of this large amount of hydrogen is not established, it appears to be uniformly distributed throughout the $(SN)_x$ crystals and is presumably bonded to the nitrogen. Unless it is present as a second phase, which seems unlikely, this means that ten percent of the nitrogen atoms are bonded to hydrogen—which, in turn, could lead to hydrogen bonding between chains. The influence of this hydrogen on conductivity and superconductivity remains to be determined.

Dimensionality of $(SN)_x$

When the structure of $(SN)_x$ was first reported by Boudeulle [23, 24], comparison of interchain distances with van der Waals radii suggested that the material was pseudo-one-dimensional with strong bonding along the chains but only weak van der Waals interaction between the chains. This early viewpoint was apparently supported by the anisotropy in the measured electrical conductivity [12, 44] shown in Fig. 12. Over much of the temperature range between 4 K and room temperature, the conductivity was a factor of 10^3 greater along the chain direction than in the perpendicular direction. However, it is now believed that the measured perpendicular conductivity is extrinsic and very low owing to the fibrous nature of the crystals. In addition, there is other evidence suggesting that $(SN)_x$ is not one-dimensional but has important three-dimensional interchain coupling. Perhaps the first such evidence was the absence of a Peierls transition at low temperatures, which characterizes other one-dimensional systems such as [$K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$] (KCP) and the TTF-TCNQ charge transfer complexes [1, 45, 46]. Moreover, the optical properties [14, 36, 47], although strongly anisotropic, were indicative of a three-dimensional interaction, as were the electron energy loss experiments [48]. A direct measure of the anisotropy which can be obtained from these experiments is the ratio of the parallel and perpendicular transfer integrals. This ratio is about eight for $(SN)_x$ compared with 100 or more for KCP and TTF-TCNQ. Indirect chemical evidence for the strength of the interchain forces comes from the complete insolubility of $(SN)_x$ in all known solvents and also from our inability to insert host species between the chains. Theoretical information about the dimensionality of $(SN)_x$ comes from band structure and Fermi surface calculations [39], which show conclusively that $(SN)_x$ is an anisotropic three-dimensional semimetal and not a quasi-one-dimensional metal. The coupling responsible for the metallic properties of $(SN)_x$ is believed to involve both sulfur-nitrogen and sulfur-sulfur bonding [49].

Analogs of $(SN)_x$

Since the discovery of superconductivity in $(SN)_x$, there has been intensive effort in many laboratories to synthesize analogous compounds. It seems appropriate to start by considering compounds analogous to S_2N_2 and S_4N_4, the precursors of $(SN)_x$. The only compound suggested to have a structure similar to S_2N_2 is N_2O_2 [50], which does not polymerize to give $(NO)_x$. More recent work [51] indicates that N_2O_2 has a planar cis or trans structure, not a cyclic structure. The literature also contains several reports of a material As_2S_2; these reports are misleading and actually refer to As_4S_4 [52].

There are several compounds formally analogous to S_4N_4 in which isoelectronic substitutions have been made for nitrogen or sulfur. Realgar, or As_4S_4 [52, 53], exists in nature and, though its molecular structure is very similar to that of S_4N_4 [54], there are important differences—the arsenic occupies the sulfur positions and the sulfur occupies the nitrogen positions. The same type of difference presumably applies to As_4Se_4 [55]. The molecular structure of P_4S_4 [56] is the same as As_4S_4; again the larger atom forms a tetrahedron around an approximately square planar arrangement of the smaller atoms (see Fig. 1). The remaining elements of Group V do not appear to form compounds analogous to S_4N_4. Replacement of the sulfur by other Group VI elements gives Se_4N_4 [57] and possibly Te_4N_4 [58]. Messmer and Salahub [59] have discussed these materials and they conclude that $(SeN)_x$ is the most probable analog of $(SN)_x$.

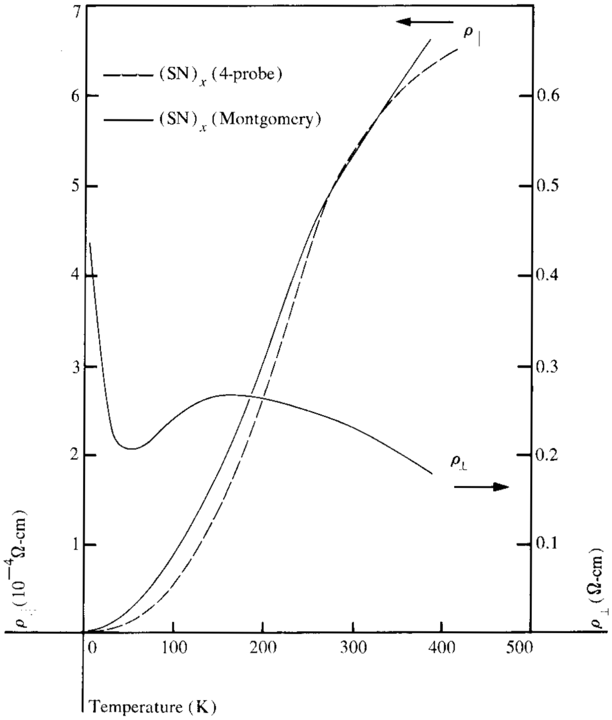


Figure 12 Anisotropy in the dc conductivity measured along the fiber or *b*-axis ($\rho_\parallel$) and in the perpendicular direction ($\rho_\perp$).

Several compounds are known in which only two of the sulfur atoms in S_4N_4 are replaced by isoelectronic groups, giving $R_2S_2N_4$ where R = $(CH_3)_2Si$ [60], or CH_3As [61]. The latter compound is known only as an oil, but we have also prepared the corresponding phenyl compound which is crystalline [62]. However, from preliminary x-ray studies of this compound it appears likely that these materials do not possess the cradle structure of S_4N_4 but have, instead, the crown structure of the S_8 ring. These materials would give rise to polymers of the type $(RSN_2)_x$ which, if they were isostructural with $(SN)_x$, would have no two-fold screw axis along the polymer chain axis. This should lead to insulating rather than metallic properties [44].

Attempts to polymerize these precursors and to prepare others are in progress. However, it is already apparent that in no case do they polymerize as readily as S_4N_4 or S_2N_2. For example, polymerization of Se_4N_4 by the methods used for S_4N_4 has not been successful, despite the fact that Se_2N_2 is observed in the mass spectrum of Se_4N_4. However, it is not formed in significant amounts on heating Se_4N_4, in vacuum, to as high as 493 K. Instead, it appears that the Se_4N_4 slowly decomposes in the solid state to the elements before a significant vapor pressure of Se_4N_4 develops. An analogous solid state decomposition to the elements also takes place for S_4N_4, but in this case the higher vapor pressure also facilitates vapor phase reactions. Preliminary x-ray-photoelectron spectroscopy (XPS) data on Se_4N_4 [63] suggests that there is less charge transfer from selenium to nitrogen than from sulfur to nitrogen in S_4N_4 [35]. This is contrary to what one would expect from electronegativity differences and may also partly explain the apparent instability of Se_2N_2. At this point it seems that if polymers analogous to $(SN)_x$ are to be prepared, new synthetic routes will have to be found.

Summary

We have found that $(SN)_x$ is a relatively stable fibrous crystalline polymer which exists in at least two modifications, the usual β monoclinic form and the orthorhombic form, and possibly a third modification—the α monoclinic phase. The fourth modification, the α' monoclinic phase, requires confirmation. In air, $(SN)_x$ suffers fairly rapid surface oxidation and, on heating or vigorous grinding, it is explosive. Experiments on improved quality crystals have confirmed that, electrically, $(SN)_x$ presents a unique exception to normal polymeric behavior by exhibiting metallic conductivity and superconductivity. Its normal state and superconducting properties have been shown to be sample dependent but the role of hydrogen remains to be evaluated. Though its chain structure is highly anisotropic it appears that the chains of sulfur and nitrogen atoms interact sufficiently strongly that the early description of $(SN)_x$ as pseudo-one-dimensional material is not appropriate but was, in fact, partly a reflection of its fibrous nature. It is more accurate to think of the fibrous $(SN)_x$ as an anisotropic three-dimensional semimetal, which explains why it does not undergo a Peierls transition. Attempts to decrease the interchain coupling by inserting small molecules between the chains have not been successful. The existence of a variety of compounds analogous to S_4N_4 initially encouraged the synthesis of chain compounds isoelectronic with $(SN)_x$. However, it now appears that new approaches must be tried because the procedure for the preparation of $(SN)_x$ does not seem to be general. Nevertheless, certain analogs, $(SeN)_x$ for instance, are not obviously thermodynamically unattainable. Clearly, much more interesting work remains to be done in this novel field of chemistry.

Acknowledgments

Many of our colleagues have contributed to the work discussed above. In particular, we thank P. M. Grant, W. D. Gill, W. E. Rudge, L. J. Suter, H. Arnal, C. Brulet, J. Mayerle, and D. Miller for helpful discussions and experimental input through the course of this work. In addition, the technical assistance of R. Bingham has been much appreciated.

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Received June 7, 1976; revised October 1, 1976

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