A Study of the Vapor Phase Species of Polymeric Sulfur Nitride, $(SN)_x$

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Abstract: Mass spectrometric techniques have been used to study the vapor phase species obtained by heating $(SN)_x$ (polythiazyl), polymeric sulfur nitride, at 100 °C to 160 °C, utilizing direct (collision free) and indirect (multiple wall collision) sampling and electron impact ionization. Field ionization and field desorption mass spectra of $(SN)_x$ are also reported. The results show that $(SN)_x$ vaporizes as a $(SN)_4$ species having a structure different from the "cradle-like" structure of S_4N_4, and probably "linear". Field desorption spectra, obtained by subliming a sample of $(SN)_x$ onto the field emitter, contain only the ion cluster at *m/e* 184 to 186. The heat of sublimation of $(SN)_x$ has been determined to be 29.0 ± 0.5 kcal/mol. Evidence for 1 to 5 atom % hydride impurity in the $(SN)_x$ polymer has been obtained.

Polymeric sulfur nitride (polythiazyl), $(SN)_x$, has recently attracted considerable interest due to its characterization as a strongly anisotropic metal.[2] Mikulski et al.[3a] have prepared analytically pure samples of $(SN)_x$ by the solid state polymerization of S_2N_2 crystals at room temperature. The resulting crystals consist of an ordered array of parallel $(SN)_x$ fibers.[3]

$(SN)_x$ has a number of highly unusual properties:[2,4a] it is highly anisotropic; it is a conductor which becomes a superconductor at 0.3 K; and it may be sublimed to form $(SN)_x$ films with crystal structure identical with the crystals from which it is sublimed. The vapor phase species are of particular interest because of their role in the production of $(SN)_x$ films. While the chemical and physical properties of the $(SN)_x$ crystals and films have been documented,[2,4b] the vapor phase species, which repolymerize as $(SN)_x$ films on cool surfaces, have been a subject of speculation.

Bright et al.[2c,4a] observed that $(SN)_x$ can be sublimed under vacuum at approximately 140 °C to yield $(SN)_x$ films having a structure identical with the $(SN)_x$ crystals. The $(SN)_x$ films were deposited on the cooler surfaces of the apparatus of Bright et al.[4a] and adjacent to the heated $(SN)_x$. The $(SN)_x$ film zone is followed by a zone having no deposit of any type. The vapors issuing from this latter zone may be condensed at liquid nitrogen temperatures to give colored solid material.[5]

We report the results of a study of the vapor species volatilized from $(SN)_x$. A variety of mass spectrometric techniques have been used to obtain spectra of the vapors above $(SN)_x$, as well as those above S_2N_2 and S_4N_4, which are important molecules used in the synthesis of $(SN)_x$. This work has demonstrated that the major vapor phase species of $(SN)_x$ is an $(SN)_4$ molecule having a structure different from the "cradle-like" structure of S_4N_4 and probably "linear".

Experimental Section

All electron impact mass spectra were recorded using a quadrupole mass spectrometer equipped with a molecular beam, high efficiency ionizer (Figure 1). A molecular beam of the volatile $(SN)_x$ vapor species was mechanically chopped to allow phase-sensitive detection. This type of detection eliminates the spectra of background gases and the spectra show peaks due only to $(SN)_x$ vapors and impurities specifically noted in this report. All spectra were obtained using identical instrument settings. The electron energy was 25 eV unless specifically noted.

A number of different techniqes were used to generate $(SN)_x$ molecular beams. The mass spectra of the $(SN)_x$ vapors reported in Table I were measured by evaporating a small sample of the material from a Teflon cell at 140 °C with an orifice that was aligned with the molecular beam skimmer. We will refer to these spectra as "direct method" spectra. Spectra obtained by sampling vapors from an open Teflon chamber and a closed "Knudsen-type" cell were identical within experimental error. The spectra of S_4N_4 were obtained by the "direct method". S_2N_2 was prepared by vaporizing S_4N_4 at 80 °C and passing it over silver wool at 230 °C, following Mikulski et al.[3a] The S_2N_2 vapor was sampled from an orifice located 10 cm past the silver wool. These spectra were identical with S_2N_2 spectra obtained by subliming the vapors of amorphous S_2N_2 at 273 K into the mass spectrometer from a glass tube.

To assess the effect of wall collisions on the $(SN)_x$ vapor species, we recorded spectra using an indirect sampling method. The "indirect method" spectra were obtained by volatilizing $(SN)_x$ at 140-145 °C and passing the vapors through 50 cm of glass tubing in which many wall collisions occurred. In this experiment the $(SN)_x$ vapors form $(SN)_x$ films on glass surfaces a considerable distance before the sampling orifice. Each of the spectra reported in Table I is the average of approximately 20 spectra recorded after heating the $(SN)_x$ for several hours under vacuum at 140 °C. Additional experiments examined the effects of temperature on $(SN)_x$ vapors using both direct and indirect sampling methods.

Experiments undertaken to elucidate the nature of the $(SN)_x$ vapor phase species included measurement of appearance energies (A). Ionization efficiency data (ion current vs. voltage) used to determine the A's were time averaged, using a Nicolet signal averager, over a sufficiently long period to obtain noise-free curves. Approximately 100 curves were used to obtain a time-averaged curve. The A values reported in Table I, in parentheses, are the average obtained from three such time-averaged curves. Since only relative A's are of importance in this work, a linear extrapolation of the straight-line portion of the ionization efficiency curve was used for the A determination. The accuracy for these values is estimated to be ±0.6 eV and the precision is ±0.3 eV.

The technique of phase angle mass spectrometry[6] was used to identify the mass of the major neutral molecular precursor of the various ionic products. The time of flight of the neutral molecules from the chopper to the ionizer is a function of mass and is manifested by different flight times corresponding to different phase shifts in the phase-sensitive detection scheme. All ions (molecular weight ions plus fragment ions) from a given neutral molecular species are characterized by identical phase shifts. Known species, benzophenone, benzil, and salicylic acid, served to calibrate the mass scale and allowed the mass of the neutral species volatilized from $(SN)_x$ to be determined.

Field ionization (FI) and field desorption (FD) mass spectra were obtained on a modified Varian CH7 mass spectrometer. The FI spectrum reported here represents the average of 20 spectra and is

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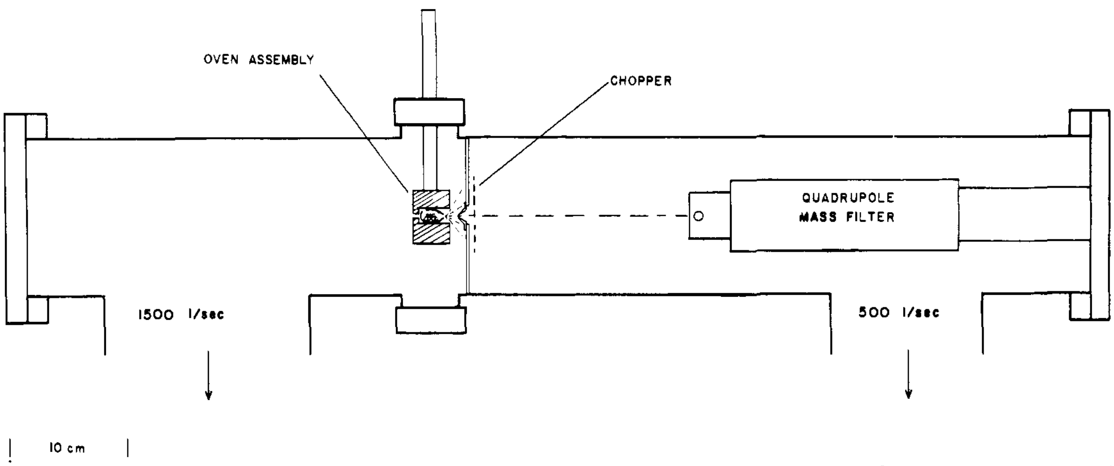

Figure 1. Schematic illustration of the mass spectrometer used in the electron impact (EI) ionization experiments. Species sampled from a Teflon Knudsen cell (or other sampling arrangement) pass through a beam skimmer and are mechanically chopped. This figure shows the configuration used for phase angle spectrometry experiments. For conventional experiments the distance between the chopper and mass spectrometer is decreased to less than 1 cm.

typical of results obtained over the temperature range of 100–160 °C. The FD spectrum is the average of 20 spectra, which were obtained over the temperature range of 30–200 °C and was independent of temperature over this range. The FD field emitter was prepared by subliming a sample of $(SN)_x$ crystals, under vacuum at 180–200 °C, to deposit an $(SN)_x$ film on the field emitter's surface. This type of preparation was necessary since there is no known $(SN)_x$ solvent; thus, the usual "dipping technique" or "microsyringe technique"[7,8] is precluded. The sublimation of $(SN)_x$ onto the field emitter requires special attention to protect surfaces other than the activated field anode from acquiring a conductive coating of $(SN)_x$. We believe this is the first application of a sublimation technique for the preparation of field emitters.

Results and Discussion

Figure 2 shows the data used to determine the heat of sublimation of polymeric sulfur nitride, $(SN)_x$. The logarithm of the product of the ion current (I) and temperature (T) is plotted vs. $1/T$. Since (IT) is directly proportional to pressure,[9] the heat of sublimation was determined directly from the slope, using the Clausius-Clapeyron equation, and is 29.0 ± 0.5 kcal/mol. The linear nature of the data between 80 and 150 °C (Figure 2) strongly suggests that an equilibrium sublimation process dominates over this temperature range. Since the S-N bond energy will undoubtedly be greater than 30 kcal/mol, this suggests that the net number of S-N bonds that are broken during the sublimation process is zero.

The phase angle mass spectrometry results, given in Figure 3, show the phase shifts (Φ) determined for ions in the electron impact mass spectra of $(SN)_x$ vapors, as well as several species used as calibrants. Phase-angle mass spectrometry of $(SN)_x$ ("direct method") indicates that a neutral species having a mass of 190 ± 10 is responsible for greater than 85% of the ions. The only reasonable neutral species in this molecular weight range is $(SN)_4$, mass 184; therefore, we conclude that $(SN)_x$ vaporizes primarily as a single species with a formula $(SN)_4$.

Figure 4 compares the structure of tetrasulfur tetranitride, S_4N_4, with that of a segment of an $(SN)_x$ polymer chain. The well-known "cradle-like" structure[10] of tetrasulfur tetranitride is hereafter referred to simply as S_4N_4.

Table I gives the 25 eV electron impact (EI) mass spectra of S_2N_2 (from direct preparation and from the sublimation of solid S_2N_2), S_4N_4, and the $(SN)_x$ vapors ("direct method" and "indirect method"). These spectra were obtained using identical instrument settings and omit peaks due to isotopic contributions and impurities of $(SN)_x$. The spectra given in Table I are all different allowing one to conclude that neither SN, S_2N_2, nor S_4N_4 is a major vapor phase species of $(SN)_x$. The "indirect method" spectra, obtained by sampling after extensive $(SN)_x$ films are deposited, show a shift toward lighter ions and a large drop in sensitivity because of the relatively small vapor pressure subsequent to $(SN)_x$ film formation. These findings for the "indirect method" spectra are consistent with phase angle mass spectrometry results and show that the $(SN)_x$ vapor is composed primarily of an $(SN)_4$ species.

Comparison of the mass spectra of S_4N_4 and the "direct"

Table I. Electron Impact Mass Spectra[a] and Appearance Energies[b] of S_2N_2, S_4N_4, and $(SN)_x$ Vapors

			$(SN)_x$	
Ion (m/e)	S_2N_2	S_4N_4	Direct[c]	Indirect
SN^+ (46)	47 (13.0)	51 (14.1)	100 (13.0)	100 (13.0)
S_2^+ (64)	1.6	0.8	4.3 (12.9)	19 (12.6)
S_2N^+ (78)	3.2 (12.2)	44	19 (10.1)	32 (10.1)
$S_2N_2^+$ (92)	100 (11.5)	70 (13.7)	60 (11.2)	40 (11.5)
S_3N^+ (110)	0.0	6.6	0.6 (11.5)	2.0
$S_3N_2^+$ (124)	0.0	2.1	3.0 (10.5)	3.0 (8.8)
$S_3N_3^+$ (138)	0.0	100 (12.3)	63 (9.5)	20 (9.6)
$S_4N_2^+$ (156)	0.0	0.0	0.2	0.5
$S_4N_4^+$ (184)	0.0	4.2 (10.4)	0.2 (9.8)	0.0

[a] Mass spectra represent an average of approximately 20 spectra, using 25 eV electrons, and recorded with identical instrumental settings. Isotopic contributions and those due to impurities are not included. [b] Appearance energies, given in parentheses, were measured using H_2O (12.6 eV) and N_2 (15.7 eV) as calibrants and have an estimated accuracy and precision of ±0.6 and ±0.3 eV, respectively. [c] The low A of several of the ions in the "direct" spectra suggest traces of species other than "linear" $(SN)_4$ may be present in the "direct" experiment vapors.

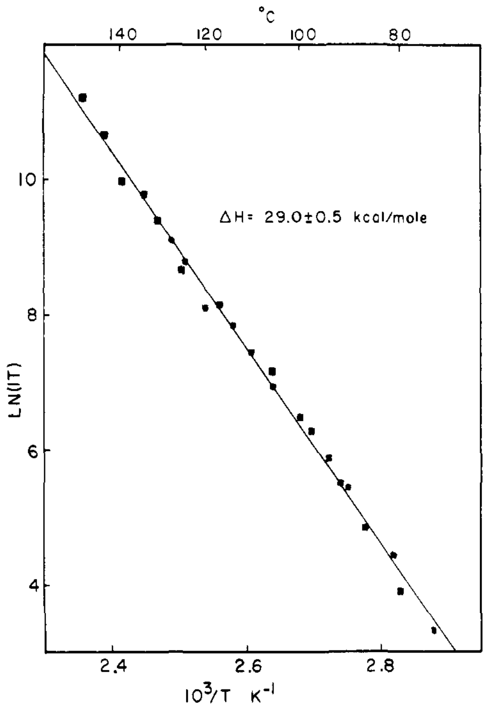

Figure 2. Experimental data used to determine the heat of sublimation of $(SN)_x$

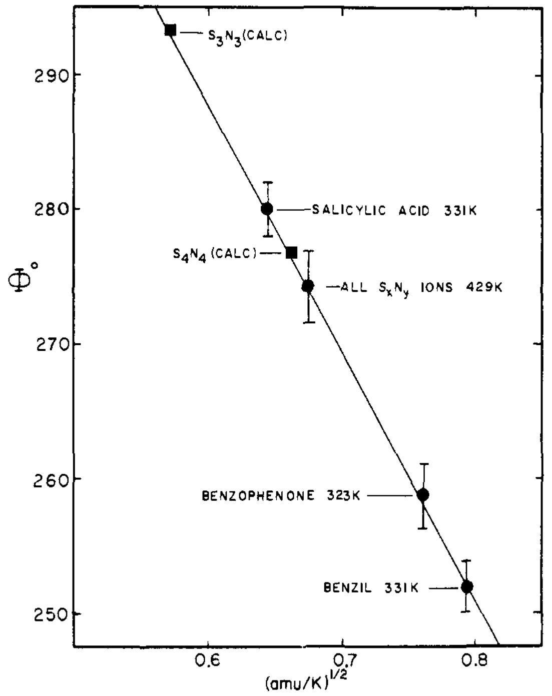

Figure 3. Phase angle mass spectrometry data showing a phase shift for ions in the mass spectrum of $(SN)_x$ corresponding to a neutral species at mass 190 ± 10. Phase shifts observed for salicylic acid, benzophenone, and benzil are used to calibrate the mass scale.

spectra of $(SN)_x$ vapors clearly shows that these are different molecular species. Since the mass spectra (Table I) and chemical properties[2-4] of S_4N_4, and the vapor species from $(SN)_x$ are different, an alternate structure must be postulated for the $(SN)_4$ species from $(SN)_x$. Reasonable choices, considering the $(SN)_x$ crystal structure, are a "linear", bent-chain structure or a cyclic structure (similar to S_4N_4) where the S-S bonds in the "cradle-like" structure have been broken (Figure 4). Field ionization experiments, discussed later, provide evidence for a "linear" structure.

The effect of temperature on the mass spectra of $(SN)_x$ vapors was examined using both direct and indirect sampling techniques. Between the temperatures of 100 and 160 °C, the spectra are independent of temperature. At higher temperatures the spectra show increased contributions of ions due to molecular sulfur (i.e., S^+, S_2^+, S_3^+ ... S_8^+) and molecular nitrogen indicating $(SN)_x$ decomposition.

It is interesting that a similar trend is observed when passing S_4N_4 over heated glass wool at 240 to 300 °C. While the spectra show increased amounts of molecular sulfur at higher temperatures, S_4N_2 is observed as a major product. S_4N_2 is a cyclic species known to result from the thermal cracking of S_4N_4.[11] Our failure to observe a large increase in the $S_4N_2^+$ ion intensity in the $(SN)_x$ vapors at elevated temperatures suggests that $(SN)_4$ does not readily undergo an analogous reaction to form $S_4N_2 + N_2$.

Figure 5 compares the 14 eV electron impact (EI), field ionization (FI), and field desorption (FD) mass spectra obtained for $(SN)_x$ and S_4N_4. The FI and FD techniques are characterized by much simpler spectra than those obtained by conventional electron impact due to the generation of molecular ions with very small amounts of internal energy.[7,8] On progression from EI to FI to FD one generally observes less fragmentation,[8] consistent with the spectra reported in Figure 5. Thus, while the 14 eV EI spectra of $(SN)_x$ does not show the $(SN)_4^+$ ion [Figure 5a′], this species accounts for 10–15% of ionization in the FI spectra of $(SN)_x$ (Figure 5b). In the FD spectra, $(SN)_4^+$ is the only ion which may be attributed to $(SN)_x$. The molecular sulfur (S_8^+) evident in the FD spectra of $(SN)_x$ is the product of a partial decomposition of the $(SN)_x$ at the temperatures (180–200 °C) used in field emitter preparation. The peaks at *m/e* 56–58 result from impurities and the gaseous acetone used for tuning by field ionization prior to field desorption.[7]

As noted above, the EI spectra of $(SN)_x$ vapors and the well-known S_4N_4 species are quite different, suggesting that an isomeric $(SN)_4$ species is formed on sublimation of $(SN)_x$. The FI spectra of S_4N_4 and $(SN)_x$ vapors are in greater contrast; the FI spectra of S_4N_4 (dashed lines, Figure 5b) contain only the molecular ion, $S_4N_4^+$, whereas approximately 85% of the FI $(SN)_4^+$ ions from $(SN)_x$ vapors (solid lines, Figure 5b) fragment to $S_3N_3^+$. These observations provide support for the existence of an isomer of S_4N_4. Ring opening of a cyclic compound followed by fragmentation requires breaking of at least two bonds, making FI fragmentation unlikely. For example, little or no fragmentation involving the ring structure of cyclic hydrocarbon or heterocyclic compounds under field ionization conditions has been reported.[8] These observations support the electron impact and phase angle mass spectrometry results and lead us to postulate that $(SN)_4$ has a "linear" structure, and not the "cradle-like" or cyclic structures.

In contrast to the FI spectra the FD spectra of $(SN)_x$ vapors and S_4N_4 are identical (solid and dashed lines respectively in Figure 5c); both spectra contain only the ion cluster at *m/e* 184–186. While the FD spectra of $(SN)_x$ are consistent with our conclusions regarding the vapor phase species of $(SN)_x$, the results should be interpreted with caution since surface related phenomena may complicate interpretation. Since $(SN)_x$ exists as a polymer on the field emitter surface, presumably with all S-N bonds of approximately equal strength, the observation of only the $(SN)_4^+$ ion suggests that its formation is a uniquely favored process (that is, no other ions such as $S_3N_3^+$, $S_8N_8^+$, etc., are observed). This is especially interesting since $(SN)_4$ is the major gas phase species formed on sublimation of $(SN)_x$. One may rationalize that $(SN)_4$ and $(SN)_4^+$ are the favored products of sublimation and field desorption, respectively, in several ways: a coincidence of energy requirements; a distinct neutral linear $(SN)_4$ entity is desorbed or exists on the emitter surface prior to ionization; or every

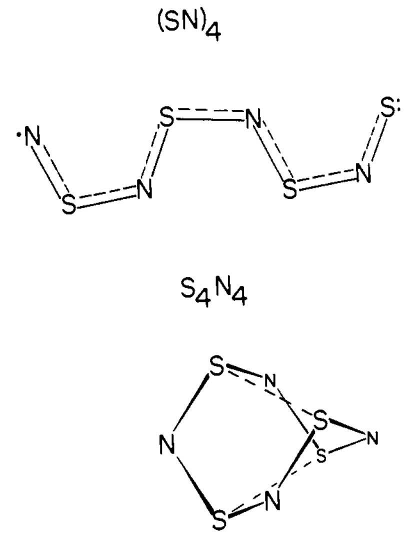

Figure 4. Comparison of the "cradle-like" S_4N_4 structure, with a segment of an $(SN)_x$ polymer chain.

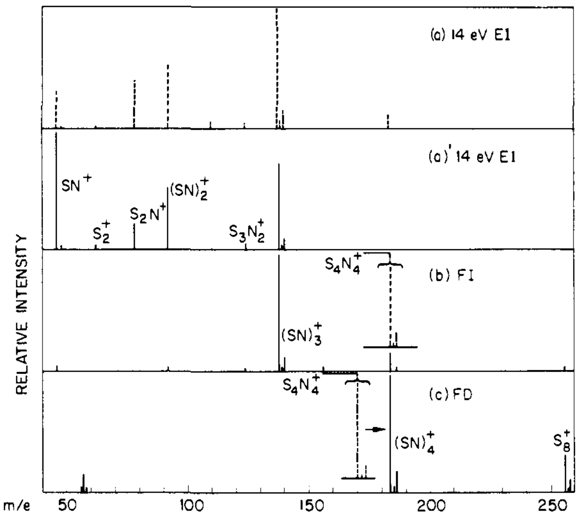

Figure 5. Comparison of low energy 14 eV electron impact (EI), field ionization (FI), and field desorption (FD) mass spectra of the vapors of $(SN)_x$ (—) and S_4N_4 (- - -). EI spectra of S_4N_4 and $(SN)_x$ vapors are given in (a) and (a′), respectively. The FI and FD spectra of S_4N_4 and $(SN)_x$ are compared in (b) and (c).

eighth bond in the $(SN)_x$ polymer chains is weaker than the other S–N bonds; or perhaps that the "cyclic" structure is produced upon vaporization. The last two possibilities appear to be less likely in view of x-ray structure data and the field ionization results.

The FI and FD results support the observation that $(SN)_4$ is the major vapor phase species of $(SN)_x$. The strikingly different spectra observed for the $(SN)_x$ vapors and the S_4N_4 imply that the $(SN)_x$ vapor species is an isomer of S_4N_4, which we believe is a linear species. The existence of a linear species is consistent with observation of highly colored, chemically unstable species, possibly free radicals, which can be condensed from the $(SN)_x$ vapors at liquid nitrogen temperature.[5]

Comparison of the spectra in Table I provides evidence for the existence of other species in the $(SN)_x$ vapors. The low A (8.8 eV) of $S_3N_2^+$ observed in the $(SN)_x$ (indirect method) experiments suggests that molecular S_3N_2 may be formed when "linear" $(SN)_4$ undergoes wall collisions. The A's of *m/e* 92 in both "direct method" and "indirect method" $(SN)_x$ spectra agree with that found for S_2N_2, suggesting S_2N_2 is produced in the vaporization of $(SN)_x$. Comparison of "direct method" and "indirect method" spectra of the $(SN)_x$ vapors suggests S_2N may be a minor component of the vapor in the "direct method" experiment. Evidence for a S_2N species comes from the A of S_2N^+. S_2N^+ has an A of 10.1 eV from $(SN)_x$ vs. 12.2 eV from S_2N_2. Comparison of the $S_4N_2^+$ ion beam intensities suggests that neutral S_4N_2 may be a minor component of the vapor in the "indirect methods" experiment. These observations suggest that S_2N, formed in the "direct method" experiment, may dimerize upon wall collisions in the "indirect method" experiments.

The FI spectra, taken in conjunction with the phase angle mass spectrometry results, allow one to estimate upper limits to the mole fractions of other neutral vapor phase species of $(SN)_x$ ("direct method"). These are S_4N_2 1.5%, S_3N_3 15%, S_3N_2 1%, S_2N_2 2%, S_2N 0.05%, and SN 3%. In addition both the FI and EI spectra suggest an upper limit to the amount of S_4N_4 of approximately 10%. This is further supported by the similarity on the A of *m/z* 184 for both S_4N_4 and $(SN)_x$ vapors.

The possibility that as much as 10% of the $(SN)_x$ vapor sampled from the Knudsen cell exists as S_4N_4 is not unreasonable. More direct (collision free) sampling techniques, using an open Teflon chamber, suggest a slightly reduced upper limit of 5% for S_4N_4. While the "indirect method" spectra suggests even lower limits one expects S_4N_4 to deposit on cool surfaces prior to the sampling orifice. Visual examination of the orifice revealed a small amount of orange crystals indicative of S_4N_4. On the basis of these observations we suggest that a "linear" $(SN)_4$ species is the predominant species sublimed. On collision with walls, or possibly other molecules, "linear" $(SN)_4$ can rearrange, or decompose, to form other S_xN_y species. Gaseous "linear" $(SN)_4$ is very reactive and spontaneously polymerizes on cool surfaces to give $(SN)_x$ films. S_4N_4 either condenses on the walls or is "pumped away" depending on the wall temperature and the rate of S_4N_4 formation. Other species with higher vapor pressures are evacuated. The formation of the above species is consistent with the results of the present study as well as with a matrix isolation study[12] which identified S_4N_4 in the vapor of $(SN)_x$ and suggested the existence of other species, at least one having a "linear" structure. The S_4N_4 may undergo thermal cracking[11] at higher temperatures to produce S_4N_2, which is observed in increased amounts in the $(SN)_x$ "indirect method" spectra.

Since trace impurities markedly affect the behavior of anisotropic metals, and may play an important role in the low-temperature polymerization of S_2N_2, a careful analysis of the spectra of directly vaporized $(SN)_x$ was made. An impurity producing $S_xN_yH^+$ ions was found in both the "direct method" and "indirect method" spectra amounting to approximately 1–5 atom % of the $S_xN_x{}^+$ intensities. This impurity, corresponding to an impurity level on the order of 0.02 to 0.1% hydrogen by weight, is independent of sample temperature or time the sample was heated under vacuum.

The hydride impurity is not found in either S_4N_4 or S_2N_2. When $(SN)_x$ crystals are wetted for approximately 1 min the excess water removed and the crystals quickly put in the mass spectrometer, the initial mass spectra obtained at 120 °C showed 8–10 atom % hydrogen. The level of hydride impurity dropped over a 2-h period until it was typical of uncontaminated crystals. Another experiment was undertaken to determine the possibility of a gas phase reaction between $(SN)_4$ and H_2O. A diffuse molecular beam of H_2O was crossed with the diffuse $(SN)_4$ beam from the Knudsen cell. Species undergoing gas phase collisions are sampled through the "beam skimmer" and are mechanically chopped and ionized in the conventional manner. Under conditions in which more than 80% of the $(SN)_4$ molecules undergo at least one collision with H_2O molecules no change in the hydride impurity level was observed. This experiment rules out a fast bimolecular gas-phase reaction as the source of the hydride impurity. Thus, we conclude that the hydride impurity originates in reactions involving water and probably occurs during the slow (48 h) $(SN)_x$ crystal growth–solid state polymerization process used in the synthesis of $(SN)_x$ crystals.[3a] This is supported by our failure to observe a hydride impurity from amorphous S_2N_2 at 273 K.

In addition to the hydride impurities, at least two other impurities are observed. Ions at *m/e* 62 and 63 (possibly $SNOH^+$) in the "direct method" and "indirect method" spectra are observed. These ions are much more intense in the "indirect method" spectra and the ion currents decrease with the time the sample is heated under vacuum. Another species at *m/e* 140 (possibly $N_2S_3O^+$) was observed in the "indirect method" spectra but decreased at a different rate than *m/e* 63 when $(SN)_x$ was heated under vacuum. Both impurities were not detectable after 10–15 h under vacuum at 140 °C. These facts suggest that the *m/e* 140 impurity originates from a reaction involving the glass surfaces available in the "indirect method". We conclude that, in contrast to the hydride impurity, these impurities are not inherent to the $(SN)_x$ crystals.

In summary, the present work provides evidence for a new gaseous $(SN)_4$ species, of possibly "linear" bent-chain structure, as the predominant component of $(SN)_x$ vapor. The heat of sublimation of $(SN)_x$ has been determined to be 29.0 ± 0.5 kcal/mol and the gas-phase chemistry of $(SN)_x$ vapor has been discussed. Evidence has been presented for the existence of other species, including at least two impurities in the $(SN)_x$ crystals.

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Far-Ultraviolet Circular Dichroism of *N*-Acetylglucosamine, Glucuronic Acid, and Hyaluronic Acid

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Abstract: Circular dichroism spectra are reported for *N*-acetylglucosamine in solution (above 175 nm), glucuronic acid in solution (above 185 nm) and in films (above 175 nm), and hyaluronic acid in solution (above 180 nm) and in films (above 150 nm). The observed features are assigned to n–π^* and π–π^* transitions of the amide and carboxyl chromophores. There is a nonadditivity in the optical features of the polysaccharide relative to the monomer spectra, and possible sources of this nonadditivity are discussed. The amide π–π^* transition has large negative rotational strength in hyaluronate films, the origin of which is attributed to a decreased rotational freedom of the acetamido group when it participates in an intramolecular hydrogen bond in the solid state helical structure. That transition is only weakly optically active in solution indicating that the acetamido groups are not involved in stabilizing the stiff domains of the polysaccharide chain.

Hyaluronic acid is a linear polysaccharide of the form $(G-N)_n$ where G is glucuronic acid (D-glucopyranosyluronic acid) and N is *N*-acetylglucosamine (2-acetamido-2-deoxy-D-glucopyranose). The G–N linkage is $\beta(1 \rightarrow 3)$ and the N–G linkage is $\beta(1 \rightarrow 4)$. The polysaccharide is found in the intercellular matrix of the connective tissues of most vertebrates and in some bacterial capsules.

X-ray studies[2] indicate the presence of helical structure in stretched films of hyaluronates. The detailed structure in solution is not known, but the rheological behavior of solutions is rather unusual and depends on pH as well as concentration.[3,4] Helical structure probably does not persist in solution[5] and a recent NMR study[6] indicates that in solution the chain can be described as having two domains, one of which is flexible and the other stiff. The structure of the stiff domain is as yet uncharacterized.

A previous CD[7] study[8] indicated that the magnitude of the ellipticity at 210 nm, per disaccharide, is larger in hyaluronic acid than in its tetramer and hexamer degradation products. Whether this nonadditivity in the optical property has any relation to the presence of stiff domains in the chain, or reflects purely localized perturbations in the ring conformation or the