

Poly(sulphur nitride): an Assessment of the Synthesis from Trichlorocyclotri(azathiene) and Trimethylsilyl Azide †

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An improved synthesis and purification, and some properties, of powdered $(\text{SN})_x$ are reported. Gram quantities can be prepared by reacting $(\text{NSCl})_3$ and Me_3SiN_3 (molar ratio 1:7.5) in acetonitrile, followed by the liquid- SO_2 extraction of impurities. The product polymers are fine black powders; surface areas ($14\text{--}22\text{ m}^2\text{ g}^{-1}$) were measured by the B.E.T. method. Freshly prepared and purified samples readily converted to S_4N_4 both photolytically and by thermal activation; a rapid solid-state conversion to S_4N_4 occurred at ca. 120°C (under N_2). Differential scanning calorimetry gave $\Delta H(\text{conversion}) = -(20 \pm 1)\text{ kJ mol}^{-1}$ of S_4N_4 . Aged samples of powdered polymer were sublimed *in vacuo* at 110°C to give gold-bronze conductive layers, $\sigma(\text{bulk}) \approx 5\ \Omega^{-1}\text{ cm}^{-1}$. A new mode of growth of $(\text{SN})_x$ single crystals during high-vacuum sublimation was observed.

Since the discovery of the superconductivity of $(\text{SN})_x$ in 1975 this quasi-one-dimensional polymer has been studied in great detail.¹ Unfortunately, the classical route to $(\text{SN})_x$ (pyrolysis of S_4N_4 to S_2N_2 , then polymerisation of the S_2N_2) suffers from several serious disadvantages: tedious preparation, explosive intermediates² (hence hazardous purification steps), and the high concentration of structure defects, especially multiple twinning, in the crystalline product. Consequently several alternative methods have been developed;^{3–16} the solution reactions between S_2Cl_2 , $\text{S}_3\text{N}_2\text{Cl}_2$, $\text{S}_6\text{N}_4\text{Cl}_2$, or preferably $(\text{NSCl})_3$, and an azide³ are the simplest. In these reactions no intermediate is isolated and the polymer precipitates rapidly.

The only practically important alternative routes to bulk $(\text{SN})_x$ are based on either the solid polymerisation of S_2N_2 prepared by other methods,^{4–7} or the electrolysis of S_5N_5^+ salts.^{8,9}

Disulphur dinitride is prepared by passing S_4N_4 ⁴ or $\text{S}_4\text{N}_3\text{Cl}$ ⁵ over heated $\text{Ag}/\text{Ag}_2\text{S}$ catalyst, by the thermolysis of $\text{Ph}_3\text{As}=\text{NS}_3\text{N}_3$,⁶ or more recently⁷ by the gentle thermolysis of a mixture of S_4N_4 and $\text{S}_2\text{N}_2 \cdot 2\text{AlCl}_3$. Small single crystals of $(\text{SN})_x$ have been grown directly from the 'red monomer' (SN) isolated in very small quantities from the products of decomposition of S_4N_4 vapour at an $\text{Ag}/\text{Ag}_2\text{S}$ catalyst.¹⁰ $(\text{SN})_x$ can also be prepared from S_4N_2 ,¹¹ and $[\text{S}_5\text{N}_5][\text{FeCl}_4]$,¹² or by low-pressure plasma reactions (of S_4N_4 vapour¹³ or $\text{H}_2\text{S}/\text{NH}_3$ ¹⁴ or $\text{H}_2\text{S}/\text{N}_2$ ¹⁵). $(\text{SN})_x$ is one of the multitude of products from the reaction between SO_2 and NH_3 .¹⁶

The aims of this investigation of the route using $(\text{NSCl})_3$ and Me_3SiN_3 to powdered poly(sulphur nitride) (abbreviated to ppsn) were: (i) to optimise yield and purity, (ii) to gain some insight into the reaction mechanism, (iii) to correlate physico-chemical properties of the ppsn with reaction conditions, and (iv) to compare the properties of $(\text{SN})_x$ films obtained by high-vacuum sublimation, from (a) ppsn and (b) the 'standard polymer' $(\text{SN})_x$ crystals (abbreviated to cpsn) obtained by the solid-state polymerisation of S_2N_2 .⁴ A preliminary summary of some of this work has been reported as a note added in proof in ref. 3.

† Supplementary data available (No. SUP 56623, 8 pp.): detailed description of apparatus and synthesis of $(\text{SN})_x$. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx.

Non-S.I. units employed: Torr $\approx 133\text{ Pa}$, eV = $1.60 \times 10^{-19}\text{ J}$, bar = 10^5 Pa , in $\approx 2.54 \times 10^{-2}\text{ m}$.

Experimental and Results

Moisture sensitive materials and $(\text{SN})_x$ were handled in a Vacuum Atmospheres Corporation glove-box (HE43-2) fitted with an HE-493 Dri-Train. I.r. spectra were recorded using a Perkin-Elmer 577 grating spectrophotometer; X-ray photographs (Cu- K_α radiation) were obtained using a standard Debye-Scherrer camera (114 mm diameter) and a fully focusing Guinier-De Wolff camera (Nonius, Delft) with a quartz crystal monochromator. $(\text{SN})_x$ single crystals were examined by the 114-mm diameter camera with Gandolfi randomiser, precession camera, and by a Picker FACS-I diffractometer. Thermogravimetric analysis (t.g.a.) and differential scanning calorimetry (d.s.c.) were carried out with a Stanton Redcroft Thermobalance (model TG 750) and a Mettler FP800/FP85 Thermo-system. Mass spectra were recorded by an AEI MS9 spectrometer interfaced to a VG2025F data processor. M.s.–g.l.c. data were obtained using a V. G. Micromass 12B spectrometer connected to a Pye-Unicam 104 gas chromatograph and VG2025F data system. Core-level photoelectron spectra were obtained using an AEI ES 200B spectrometer with Mg- $K_{\alpha 1,2}$ source.

Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 240 Elemental Analyser. Nitrogen analysis was by the micro-Kjeldahl method, sulphur was determined as BaSO_4 , and chlorine by potentiometric titration as AgCl after combustion of samples in oxygen. Silicon was determined by atomic absorption spectroscopy. The free surface area of the $(\text{SN})_x$ powder was measured by the Brunauer–Emmett–Teller (B.E.T.) method using nitrogen.

The starting materials $\text{S}_3\text{N}_2\text{Cl}_2$ (1) and $(\text{NSCl})_3$ (2) were prepared by the usual methods.¹⁷ In the synthesis of (1) (from NH_4Cl and refluxing S_2Cl_2), particular care was taken to avoid contamination of the product (formed in the reflux condenser) with sulphur and NH_4Cl , by terminating the reaction before total consumption of S_2Cl_2 . Compound (2) was prepared from finely powdered (1) by repeated (three or four times) chlorination, followed by recrystallisation of (2) from dry CCl_4 [2.5 cm^3 per gram of (2)] under an atmosphere of dry chlorine.

The same procedures were used for the preparation of (1) and (2) labelled with ^{15}N . The starting material, $[\text{NH}_4]_2[\text{SO}_4]$ enriched to 5.1 atomic % ^{15}N ,[†] was converted to NH_4Cl ,

† ^{15}N -Enriched (5.1 atomic %) ammonium sulphate supplied by Physico-Chemical Measurement Unit, Harwell, Analytical Services, Didcot, Oxfordshire OX1 10RE.

Table 1. Synthesis of (SN)_x by the solution reactions of S₃N₂Cl₂ and (NSCl)₃ with Me₃SiN₃ in acetonitrile

Synthesis sample no. ^a	Reactant A ^b Compound, weight (g), solution volume (cm ³)		Reactant B ^b Weight of Me ₃ SiN ₃ (g), solution volume (cm ³)		Excess factor <u>reactant B</u> reactant A	Reaction temperature ^c (°C)	Reaction time (h)	Reactant A/B purity code ^d	Yield of (SN) _x ^e (%)		Extraction solvent	S:N atomic ratio of purified sample	
	Crude	Purified											
1	I	1.5	60	5.3	26	3.0	-13 ± 2	48	H(JTB)/PS	71	42	CS ₂ , SO ₂	1.41
2	II	1.5	60	5.3	26	2.5	-10 ± 2	48	H(JTB)/PS	53	30	SO ₂	1.00
3^f	II	1.5	60	5.3	26	2.5	-16 ± 3	120	H(JTB)/PS	71	26	SO ₂	1.01
4	II	2.5	60	8.83	30	2.5	-10 ± 2	48	H(JTB)/PS	78	42 ^g	MeCN	0.96
5	II	3.0	120	10.60	60	2.5	-18 ± 0.2	72	H(Fis)/PS	74	53	SO ₂	1.05
6	II	1.54	60	5.21	26	2.5	-19	24	PG/PS	74	36	SO ₂	
7	II	4.97	200	17.36	90	2.5	-10	40	PG/PS	66	53	SO ₂ , C ₆ H ₆	1.59
8	II*	1.46	60	5.21	26	2.5	-10	64	PG/PS	64	45	SO ₂	1.3
9	II	1.55	60	5.21	26	2.5	-16	40	PG/Sy	74	43	SO ₂	1.06
10^h	II	1.48	55	2.08	10.4	1.0	-17	24	PG/Sy				
11	II	1.48	60	5.21	26	2.5	-16	40	H(Fis)/Sy	78	45	SO ₂	0.97
12	II	1.49	60	5.21	26	2.5	-17	40	H(Fis)/PS	74	51	SO ₂	0.99
13ⁱ	II	1.5	60	5.21	26	2.5	-14	40	PG/PS	71	44	SO ₂	0.90

^a Synthesis sample numbers in bold type indicate the recommended procedure. ^b I, S₃N₂Cl₂ (1 g = 5.13 mmol); II, (NSCl)₃ (1 g = 4.089 mmol); II*, (NSCl)₃ labelled with ¹⁵N (5.1 atomic %); for Me₃SiN₃, 1 g = 6.68 mmol. ^c Temperature controlled by Haake F2-C bath circulator with an external cooling loop; for syntheses 1—4 a less accurate cooling device was used. ^d Reagent purity coding: acetonitrile, H = h.p.l.c. grade (JTB = J. T. Baker, Fis = Fisons); trimethylsilyl azide, PS (Petrarch Systems, Inc.), PG = acetonitrile of polarographic grade purity, Sy (synthesized, free of silyl ether contamination). ^e Yields of purified (SN)_x based on I and II (cf. equations relating to routes I and II). ^f This synthesis was carried out without stirring; the addition rate of reactant B to A was ca. 0.04 cm³ min⁻¹. In all other tabulated syntheses the reaction mixtures were vigorously and continuously stirred and the addition rate was ca. 0.2 cm³ min⁻¹. The stirring continued for typically 24 h at room temperature in addition to the reaction times given here. ^g The purified product contained ca. 14% (w/w) S₄N₃Cl. ^h No polymer was obtained. ⁱ The PG acetonitrile contained 50 p.p.m. of water deliberately added.

by reaction with aqueous BaCl₂, and then *via* S₃N₂Cl₂ to (NSCl)₃.¹⁷ Trimethylsilyl azide was obtained,¹⁸ for (SN)_x preparations 9—11, from SiMe₃Cl and NaN₃; preparations 1—8, 12, and 13 (see Table 1) used unpurified Me₃SiN₃ (Petrarch Systems Inc., U.S.A.). The purity of Me₃SiN₃ was established by m.s.-g.l.c. Acetonitrile (h.p.l.c. grade, J. T. Baker, U.S.A., and Fisons, U.K.) for preparations 1—5, 11, and 12 was refluxed and distilled over P₄O₁₀ then refluxed with CaH₂ and finally distilled through a column (30 cm) packed with Fenske helices. Acetonitrile for preparations 6—10 and 13 was h.p.l.c. grade (Fisons, U.K.) purified to a polarographic grade standard according to Walter and Ramalay (method B).¹⁹ A voltammogram showed a practically zero background current within the range +1.5 to -1.5 V vs. s.c.e. (saturated calomel electrode). The liquid SO₂ (B.D.H.) was dried over P₄O₁₀ for several days then distilled and stored over CaH₂.

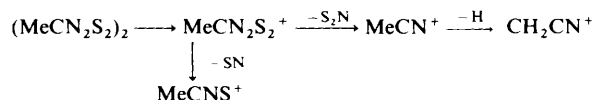
All operations for the synthesis and purification of (SN)_x were carried out under dry nitrogen using oven-dried (500 °C) glassware.

Preparation of (SN)_x*—Reactions were carried out in a 250 (or 500) cm³ three-necked flask with a pressure-equalised dropping funnel. The preparation of (SN)_x from S₃N₂Cl₂ (*i.e.* sample 1, Table 1) was unsatisfactory (see Discussion section). The optimised procedure for synthesis from (NSCl)₃ was as follows. (Further details for the preparation of samples 2—13 are also given.)

A vigorously stirred suspension of (NSCl)₃ (1.5 g, 6.13 mmol) in acetonitrile (60 cm³, 1.5 mol) was quickly cooled to ca. -18 °C and trimethylsilyl azide (6 cm³, 46.3 mmol) in acetonitrile (20 cm³, 0.38 mol) was added dropwise (2 h). The suspension of (NSCl)₃ in acetonitrile changed colour rapidly: yellow, orange, brown, dark brown, and eventually (in ca. 10 min) blue-black. After the addition, the mixture was stirred at -18 °C (24 h) and then at room temperature (for 24 h,

during which time nitrogen evolution ceased). When the (SN)_x particles were allowed to settle, the solution appeared dark orange-brown in transmitted light. The (SN)_x was vacuum filtered (grade 3 glass frit) and dried (ca. 6 h) at room temperature *in vacuo* (ca. 10⁻² Torr). The main contaminant was S₄N₄ (typically 30—50%).

Isolation of (MeCN₂S₂)₂ from the Filtrates.—Filtration removed solvent and unreacted Me₃SiN₃. Gentle heating of the dark solid obtained after evaporation gave a residue of almost pure S₄N₄, and a purple volatile component (vapour pressure ca. 10⁻¹ Torr at 0 °C) which was sublimed (over 6 h) at room temperature into a sealable trap at -78 °C. Fractionation *in vacuo* gave [cf. (PhCN₂S₂)₂²⁰] dark purple crystals with a green metallic sheen. The sharp melting point (95.5 ± 0.3 °C, without decomposition under nitrogen) and the e.s.r. and mass spectra confirmed that the compound was (MeCNSSN)₂.²¹ It is more conveniently prepared from [MeCNSSN]Cl by electrolytic reduction.²¹ The mass spectrum was obtained at 70 eV ionising potential: MeCN₂S₂⁺ *m/e* 119 (98%), S₂N⁺ 78 (100), MeCNS⁺ 73 (46), MeCN⁺ 41 (64), SN⁺ 46 (30), and CH₂CN⁺ 40 (23) and indicated the fragmentation pattern given below.



Purification of Crude (SN)_x by Solvent Extraction.—Impurities were extracted (0—15 °C) using a fully sealed glass extraction unit,²² a thoroughly out-gassed low-boiling solvent (*e.g.* SO₂, CS₂, C₆H₆, or MeCN), and a copious reflux rate (several litres per day).

The extraction apparatus containing crude (SN)_x was evacuated and adsorbed gases on the polymer surface were largely removed by a brief 'soak' in solvent vapour followed by evacuation (procedure repeated 3—5 times). This treatment

* A more detailed description of the synthesis is provided in SUP 56623.

Table 2. Chemical analyses of purified (SN)_x powders

Synthesis sample no.	S ^a	N ^b	Cl	C	Si	Total	S:N atomic ratio
1	71.20	22.15	0.75	0.75	6.95	101.80	1.41
2	64.80	28.35	0.50	0.15	0.40	94.20	1.00
3	66.30	28.15		0.85		95.30	1.01
4	62.25	28.35	2.55	0.45	0.60	94.20	0.96
5	68.80	28.40	0.00	0.00	1.10	98.30	1.05
6		28.55		0.45	1.30		
7	76.75	21.00		0.95	2.45	101.15	1.59
8	72.90	24.45		0.35	1.50	99.20	1.30
9	53.60	22.00	12.95	1.05	6.30	95.90	1.06
10	No polymer obtained						
11	62.30	28.15	0.30	0.00	1.10	91.85	0.97
12	62.00	27.30	0.00	2.25	0.75	92.30	0.99
13	61.30	29.70	0.00	0.00	0.60	91.60	0.90
Theory	69.60	30.40				100.00	1.00

^a Mean value of at least two analyses. ^b Mean value of at least four analyses (two by the Kjeldahl method and two with a Perkin-Elmer 240 Elemental Analyser).

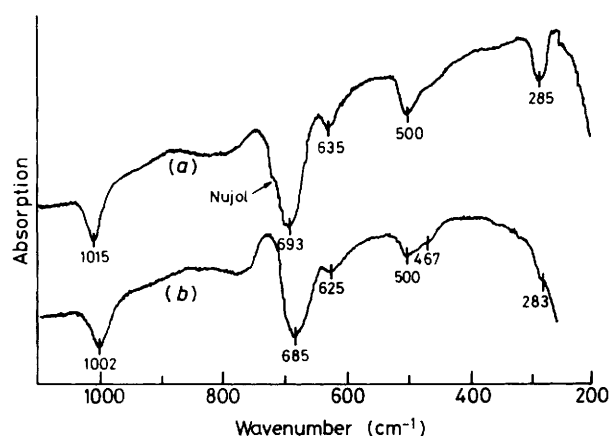


Figure 1. Infrared spectra of (SN)_x. (a) Concentrated Nujol mull of ppsn (samples 2, 3, 5, 6, 12, and 13); (b) vacuum-deposited film of (SN)_x on a KBr plate from a ppsn source (sample 5) [cf. I.r. spectra of standard (SN)_x deposited on CsI plate: ν_{\max} . 1 001, 689, 629, 500, and 278 cm^{-1} ; J. W. Macklin, G. B. Street, and W. D. Gill, *J. Chem. Phys.*, 1979, **70**, 2425]

improved the subsequent rate of reflux. Liquid SO₂ (ca. 25 cm³) was condensed in, the extractor was tightly sealed (Rotaflo tap), and the flask portion was immersed in a water-bath (ca. 30 °C). The cooling fluid was either water from the mains supply or ethanol from a refrigerated-bath circulator (HAAKE, model F2-C). After extraction and evaporation of the solvent, the (soluble) residue was almost pure S₄N₄.

Samples 4 and 9 also contained some S₄N₃Cl (extracted more slowly than S₄N₄). Other likely impurities [S₈ (rhombic) and NH₄Cl] were not found by i.r. and Guinier-De Wolff powder diagrams; the detection limits are ca. 1% by the latter method.

The freshly extracted and outgassed ppsn (*i.e.* several hours at ca. 10⁻³ Torr) was markedly photosensitive; illumination through the filled water jacket (from a 15-W lamp bulb) caused rapid formation of S₄N₄ at the ppsn surface. However, samples left in the evacuated extractor for several days in darkness lost their photosensitivity, apparently due to an aging process.

Characterisation and Properties of Purified (SN)_x Powder.—Chemical analyses are summarised in Table 2. I.r. spectra [Figure 1(a)] were obtained with concentrated Nujol mulls

(they appeared deep blue by transmitted light). Spectra of the same mull could be taken repeatedly without change. In contrast, (SN)_x in pressed KBr and CsI discs decomposed rapidly in the i.r. beam (loss of the 1 015 cm^{-1} absorption) to give S₄N₄ (growth of the 928 cm^{-1} absorption).

Optical microscope, scanning electron microscope (s.e.m.), and surface area (B.E.T.) examination. Under a stereomicroscope (40 times magnification and incident illumination) ppsn appeared microcrystalline, uniformly black with a bronzy sheen. A small proportion of product from synthesis 3 was present as crystals of length 5–10 μm (perhaps representing the 'large' end of the size distribution spectrum) which appeared very bright gold when reflecting the light source. A further small part of each sample of ppsn was compacted into flakes (effect of the stirring bar against the flask wall).

Under s.e.m. examination at high magnifications (> 500), evaporation of sample 5 occurred with rapid rounding of corners and edges. Coating with gold much improved the stability of the image and thus allowed an assessment of the particle size distribution. The bulk of the ppsn was in the micrometre and submicrometre range with only a small proportion present in the 2–5 μm range. This was confirmed by the B.E.T. data.

Adsorption isotherm measurements on samples 2 (180 mg) and 5 (450 mg) with N₂ at 77 K [interpreted by the B.E.T. equation using $\sigma(\text{N}_2) = 0.162 \text{ nm}^2$ as the projected area of nitrogen molecule] gave surface area values of 22 ± 5.5 and $14.4 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$ respectively.

X-Ray powder diagrams. Samples of ppsn freshly purified by extraction with SO₂ gave Debye-Scherrer powder photographs with up to 11 well resolved diffraction lines (Table 3). All lines were somewhat broadened due to the small particle size. More pronounced broadening and fewer clearly distinguishable lines were observed for samples with a stoichiometric excess of sulphur. For instance, sample 7 (S:N molar ratio 1.59:1) gave eight diffraction lines (numbered 1–8 in Table 3); however, there were neither extra lines nor significant shifts in the 2 θ values, compared with pure stoichiometric samples.

Impurities, such as S₄N₄, S₈, and NH₄Cl were easily detected from their most intense lines (which are also much sharper than the ppsn lines). Hence the powder photographs provided both structural data and a convenient purity test. To enhance the detection limit we used a Guinier-De Wolff camera. By the standard addition method, the detection limit for the three main impurities was estimated as ca. 1% (w/w) using the following diffraction lines: S₄N₄ ($\bar{1}11$), 4.73 (90); (111), 4.61 (70); (200),

Table 3. X-Ray powder photograph of ppsn (sample 3) and its comparison with the diffraction pattern of (SN)_x microcrystals obtained by the polymerisation of the red monomer, SN⁺, and the Gandolfi camera photograph of a single crystal obtained in this work during high-vacuum sublimation of ppsn. All measurements were corrected for film shrinkage

Diffraction line no.	ppsn (sample 3) ^a		(SN) _x microcrystals from red monomer ^b		(SN) _x single crystal, Gandolfi pattern		Calculated pattern ^c				
	<i>d</i> _{hkl}	Relative intensity	<i>d</i> _{hkl}	Relative intensity	<i>d</i> _{hkl}	Relative intensity	<i>d</i> _{hkl}	<i>h</i>	<i>k</i>	<i>l</i>	
1	4.45 ^d	m									
2	3.77 ^e	m	3.99	s	3.91	m	3.91	1	0	0	
3	3.24	vs		3.60	s	3.59	m	3.59	0	0	2
4	2.87 ^e	s (dif) ^f	3.24	vs	3.23	vs	3.24	1	0	2	
5	2.30	w	2.93	s	2.93	s	2.93	1	1	0	
6	2.22	w	2.80	s	2.80	s	2.79	0	1	2	
7	2.14	w	2.30	w	2.29	vw	2.29	1	0	2	
8	2.07	w	2.22	m	2.22	w	2.22	0	2	0	
9	1.82	vw	2.12	m	2.11	m	2.12	0	2	1	
10	1.63	w	2.03	m	2.03	w	2.03	1	1	2	
11	1.38	w	1.82	w		1.94	w	1.94	1	2	1
						1.83	w	1.83	1	2	2
					1.73	vw	1.74	1	4	4	
			1.61	w (dif)			1.62	2	0	4	
			1.37	w (dif)			1.38	1	3	0	

^a Pure, stoichiometric (SN)_x in a black powdery form prepared by electrochemical reduction of S₅N₄Cl in liquid SO₂ gives entirely identical powder pattern (see ref. 8). ^b A random assemblage of ca. 0.1 mm (SN)_x crystals rapidly grown from the red monomer, SN⁺ (A. J. Banister and Z. V. Hauptman, unpublished work). ^c The indexed *d*_{hkl} values were generated by the computer program 'Indexing and Least Square Refinement of Powder Diffraction Data' (D. A. Appleman and H. T. Evans, jun., U.S. Geological Survey, Geologic Division, Washington, D.C., 1973) using the structure data by Mikulski *et al.*:⁴ *a* = 4.153, *b* = 4.439, *c* = 7.637 Å, β = 109.7°, space group P2₁/c. ^d This line corresponding to the diffraction by the {010} set of planes is disallowed for the P2₁/c group (see Discussion section). ^e Probably a superposition of two lines. ^f dif = diffuse.

Table 4. Differential scanning calorimetry of samples 5 and 7 with interruptions and sample characterisations at various temperatures (marked with arrows in Figure 3)

Point no.	Temperature (°C)	Weight loss (%)	Appearance under microscope (magnification 40)	Species observed	
				I.r	T.l.c. (CS ₂)
Figure 3(a), sample 5					
1	110	nil	unconverted ppsn and S ₄ N ₄ crystals	(SN) _x , S ₄ N ₄	S ₄ N ₄
2	130	nil	mostly S ₄ N ₄ crystals	S ₄ N ₄	S ₄ N ₄
3	150	nil	S ₄ N ₄ crystals	S ₄ N ₄	S ₄ N ₄ , S ₄ N ₂ (trace)
4	165	5.8	S ₄ N ₄ crystals turned dark red	S ₄ N ₄ , S ₄ N ₂	S ₄ N ₄ , S ₄ N ₂ , S ₈ (trace)
Figure 3(c), sample 7					
1	125	nil	ppsn and orange-red solidified melt	S ₄ N ₄	S ₄ N ₄ , S ₄ N ₂
2	150	nil	dark red solidified melt	S ₄ N ₄ , S ₄ N ₂	S ₄ N ₄ , S ₄ N ₂ , S ₈ (trace)

4.38 (100); S₈ (222), 3.85 (100); (026), 3.44 (40); NH₄Cl (100), 3.87 (23); (110), 2.74 (100).²³ The figures represent (*hkl*), *d*_{hkl}, and (*I*/*I*₀) respectively.

Mechanical behaviour. Stress-strain characteristics have already demonstrated²⁴ the metal-like behaviour of the cpsn crystals. The powdered polymer also has the properties of a malleable metal. Thus, when pure ppsn is rubbed in an agate mortar it is easily compacted into shiny gold-bronze flakes. Their lustre and colour provide a useful qualitative purity test for the ppsn. Samples with a large excess of constitutional sulphur (e.g. sample 7) or partially hydrolysed samples (e.g. after ca. 10 d exposure to moist air) produce dull dark brown-bronze flakes.

Under 40 kbar pressure, the powdered polymer compressed to a tablet ($\frac{1}{8}$ in diameter) with a coppery metallic lustre (of the flat sides) and a density 2.30 g cm⁻³ (cf.⁶ X-ray density of the

β-phase 2.30 g cm⁻³). Such consolidation is typical of powder metallurgy. **CAUTION:** the compression can be hazardous. Detonation occurred at only 2 kbar with freshly prepared (SN)_x (sample 5) but with the sample after storage for 5 months under dry N₂, detonation occurred at 35 kbar. Thus aged samples and unpurified samples appear to be much less liable to detonate during compression.

Thermogravimetric analysis. T.g.a. (under a flow of nitrogen) of two samples prepared from (NSCl)₃ gave very similar thermograms [Figure 2(a)]. Portions of sample 2 (2.5 mg in each case) heated at 112, 118, 130, and 140 °C gave times of total decomposition of 3.5, 3.0, 1.0, and 0.5 h respectively.

Differential scanning calorimetry. D.s.c. curves (heating rate 4 °C min⁻¹) are shown (Figure 3) for samples of ca. 4 mg, weighed accurately to ±0.02 mg, and encapsulated in cold sealed aluminium crucibles. The well reproducible curves are

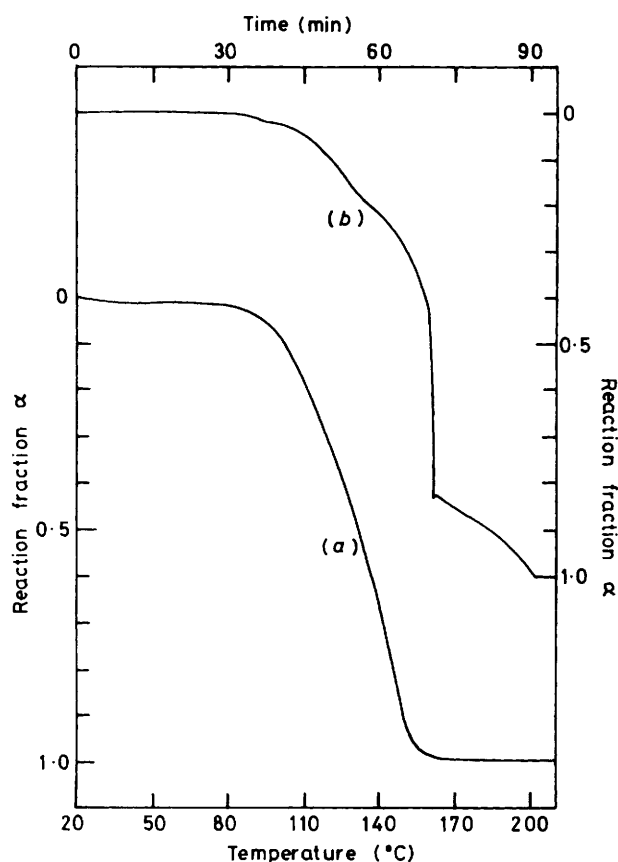


Figure 2. Thermogravimetric analyses of the powdered polymer: (a) samples 2 and 3, (b) sample 1

for three types of ppsn: (a) freshly prepared (sample 5), (b) after storage for 6 months (sample 5), and (c) a product with excess constitutional sulphur (sample 7). The exothermic peak areas for curves (a) and (b) (i.e. using further portions of samples 5 and 7 respectively) were reproducible to within ca. 5%. Intermediates were identified (see Table 4) by interrupting runs at various temperatures (indicated by arrows on curves a and c). Crucibles were cooled quickly, weighed, opened, and the contents were examined (Table 4) under the microscope, by i.r. spectra, and by t.l.c. analysis.

Mass spectral analysis. Mass spectra of ^{15}N enriched $(\text{SN})_x$ established that ca. 15% of the azide nitrogen entered the polymer chain. Labelled $(\text{NSCl})_3$ (5.1 atomic % ^{15}N) was reacted with unlabelled Me_3SiN_3 to give polymer (sample 8 in Table 1). Examination of numerous mass spectra of this sample of ppsn showed that the intensity ratio $^{92}I:^{93}I$ was the most reproducible to determine the ^{15}N content. Unlike the SN^+ peaks, those for S_2N_2^+ (m/e 92) were well clear of background interferences. Three typical mass spectra, showing only the major peaks, are given in Table 5. The S_2^+ peak intensity was also useful diagnostically since an increase correlated with an enhanced S:N ratio in the $(\text{SN})_x$ (sample 8).

The $^{92}I:^{93}I$ ratio was best suited for the estimation of $^{14}\text{N}:^{15}\text{N}$ ratios in $(\text{NSCl})_3$ also. Good agreement was found between the observed and calculated intensity ratios $^{92}I:^{93}I$ (Table 6).

The computations of the relative intensities (I) as a function of isotopic abundances (a) were carried out with the program ISOBUND²⁵ based on standard formulae.²⁶ The relationship between the abundances $^{15}a_i$ (atomic %) and the relative intensities ^{93}I , within a narrow range $3 \leq ^{15}a_i \leq 6$ approxi-

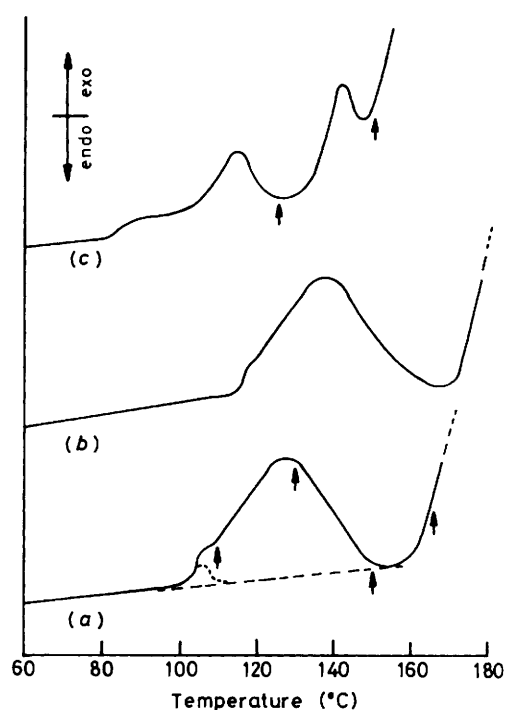


Figure 3. Differential scanning calorimetric curves of the powdered polymer (scanning rate 4°C min^{-1}): (a) sample 5 freshly synthesised and purified, (b) sample 5 after storage for 6 months, (c) sample 7 with an excess of chemically bonded sulphur (S:N = 1.591). Arrows indicate the points of interruption in a succession of repeat runs with a fresh portion of the same sample

Table 5. Mass spectra of $(\text{SN})_x$ powders and $(\text{NSCl})_3$ at 70 eV ionising potential and ca. 80°C

Ion	m/e	Relative intensities		
		$(\text{SN})_x$ (sample 6) S:N ca. 1.0	$(\text{SN})_x$ (sample 8) S:N ca. 1.3	$(\text{NSCl})_3$
SN^+	46	100	100	73
S_2^+	64	12	47	6
S_2N^+	78	2.5	6	5
S_2N_2^+	92	49	60	100
S_3N_3^+	138	12	10	24
S_4N_2^+	156	1	2.5	3
S_4N_4^+	184	1	1	1

mates closely to the straight line: $^{15}a_i = 0.456(^{93}I_i) - 0.54$. The percentage of the azide nitrogen, n_{az} , incorporated into the polymer is as given below, where $^{15}a_1$ (= 5.1) is the abundance

$$n_{\text{az}} = 100(^{15}a_1 - ^{15}a_2)/(^{15}a_1 - ^{15}a_{\text{nat}})$$

in the starting labelled $(\text{NSCl})_3$, $^{15}a_2$ (= 4.4) is the calculated abundance in the product $(\text{SN})_x$, and $^{15}a_{\text{nat}}$ (= 0.37) is the natural abundance of ^{15}N . Substitution of these values into the above formula gave $n_{\text{az}} = 14.8 \pm 2.2\%$ azide nitrogen in $(\text{SN})_x$.

Preparation of $(\text{SN})_x$ Layers.—Since adhesion and stability of $(\text{SN})_x$ are much affected by the quality of the underlying support, the glass slides [$65 \times 16 \times 1$ mm to suit the electron spectroscopy for chemical analysis (e.s.c.a.) sample holder] were freshly cleaned (using a proprietary surfactant, MICRO in an ultrasonic bath, followed by rinses with dilute HCl and distilled

Table 6. $S_2N_2^+$ ($92 + n$) isotope peaks: * observed and calculated relative intensities of the starting compound, $(NSCl)_3$, and the product $(SN)_x$, both ^{15}N -labelled and unlabelled

Isotope ion <i>m/e</i>	Relative intensities					
	(NSCl) ₃ labelled with 5.1 atomic % ¹⁵ N		(NSCl) ₃ unlabelled		(SN) _x (sample 8), labelled	(SN) _x (sample 6), unlabelled
	Calc.	Obs.	Calc.	Obs.	Obs.	Obs.
93	12.35	12.33 (0.34)	2.34	2.1 (0.3)	10.83 (0.28)	2.28 (0.22)
94	9.35	9.51 (0.40)	8.90	9.3 (0.3)	9.36 (0.30)	9.08 (0.25)
95	1.03	1.13 (0.12)	0.14		1.04 (0.20)	

* The *m/e* 92 peak is normalised to 100. The data with standard errors (given in parentheses) are mean values of at least five scans.

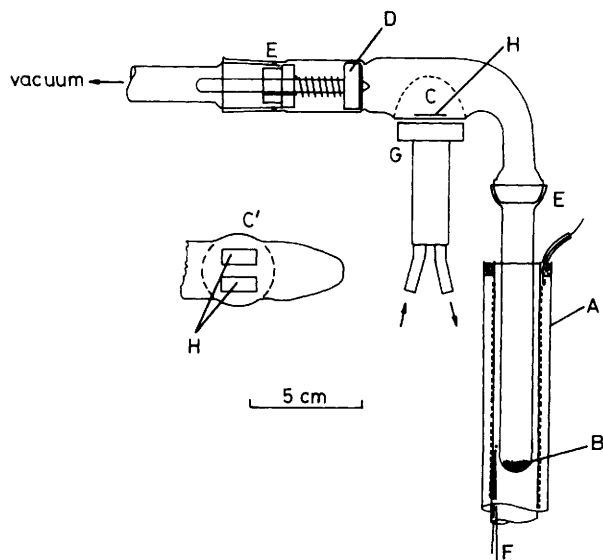


Figure 4. Sublimation apparatus for vacuum deposition of $(SN)_x$ films: A, resistance heater; B, source material; C, deposition chamber (C', plan view); D, spring-loaded poly(tetrafluoroethylene) baffle; E, greaseless joints ('Young'); F, thermocouple; G, cooling block; H, substrates

water) and placed side by side in chamber C of the sublimation apparatus shown in Figure 4. This apparatus was assembled in a glove-box with polymer (sample 2, 3, 5, or 6 or cpsn) at B, and then connected to a high vacuum unit *via* an isolable liquid N_2 trap (to condense light volatiles).

During an outgassing period (16 h) the deposition chamber C was kept at 250 °C (using heating tape) while the source material was maintained at 50 °C for the powder (ppsn) or 80 °C for the crystal (cpsn) respectively. At the end of this period the line vacuum was usually $\leq 2 \times 10^{-6}$ Torr. Optimised conditions for coating are now given.

Source temperatures were 111 °C for ppsn and 150 °C for cpsn; the pressure in both cases was $\leq 5 \times 10^{-6}$ Torr. After outgassing, the temperature at B was raised (to 150 °C) more slowly for the powder (*ca.* 0.05 °C min^{-1}) than for the crystals (*ca.* 2 °C min^{-1}). This minimised the pressure rise due to decomposition. At pressures $\geq ca.$ 10^{-3} Torr, decomposition occurred rapidly with formation of S_4N_4 at B and contamination of the coatings at C (with S_4N_4 , sulphur, species containing Si, *etc.*). The temperature of the deposition chamber C was maintained at 20 °C throughout the coating period except for an initiation period (*ca.* 10 min) during which a copper block G at 10 °C was brought into contact with C to ensure preferential deposition. Subsequent formation of sound uniform layers depended on this initial nucleation. Once the

first coherent layer was formed on the bottom area of C the preferential supply of the nutrient vapour to the substrates continued and less material was wasted on the upper walls of C. Clean substrates became evenly coated on all sides.

Growth of Crystals during High Vacuum Sublimation.—Unexpected crystal growth occurred during two vacuum sublimations of ppsn (from samples 2 and 3) at 110 °C: several well formed bright gold crystals ranging from 0.2 to 0.5 mm³ (0.5 to 1.2 mg) were found in the sublimation residue (at B, Figure 4). Only one crystal had a suitable size for an X-ray structure determination giving sharp, well resolved diffraction spots; however it was twinned along the (100) plane. Its precession photograph appeared to mimic an untwinned crystal: space group $P2_1/c$ with six-fold *a* axis [$a = 24.63(7)$, $b = 4.429\ 5(8)$, $c = 7.61(4)$ Å, $\beta = 108.2(3)^\circ$], an effect that was caused by the extremely anisotropic shape of the diffraction spots. Since slicing or grinding across the fibrils invariably ended in extensive damage, the remaining crystals were reduced in size, for X-ray work, by vacuum sublimation (150 °C, $\leq 10^{-6}$ Torr). This method also allowed a semi-quantitative comparison of evaporation rates in three directions. Using a microscope with micrometer eyepiece the length of the edges was measured as a function of time. One crystal was particularly suitable because it formed a nearly regular parallelepiped: original dimensions, $x_0 = 1.3$, $y_0 = 0.68$, $z_0 = 0.4$ mm, $V_0 = 0.35$ mm³, $M_0 = 0.82$ mg with x_0, y_0 being the edges of the $(\bar{1}02)$ face. The crystal was finally reduced to: $x_f = 0.63$, $y_f = 0.5$, $z_f = 0.35$ mm, $V_f = 0.11$ mm³, $M_f = 0.25$ mg in *ca.* 20 h. Hence the average weight loss rate was 0.03 mg h^{-1} (*i.e.* 5×10^{-4} mg min^{-1}) which is *ca.* 1 400 times slower than the free evaporation rate observed by Weber and Ewing.²⁷ The relative rates of evaporation in the directions *x, y, z* were 1.0:0.3:0.08 where *x* coincides with the S–N chain direction and *z* is approximately perpendicular to the $(\bar{1}02)$ plane.

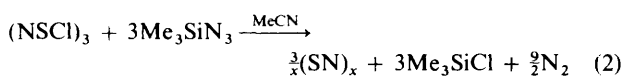
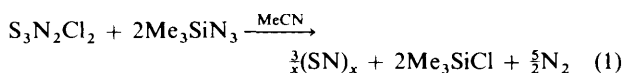
The smallest of the reduced crystals ($0.3 \times 0.2 \times 0.2$ mm) was used in the Gandolfi randomiser and the simulated powder pattern was in excellent agreement with the calculated pattern based on the PENN structure⁶ (*cf.* Table 3). Another reduced crystal was found to be identical with the PENN structure by the precession camera method. However, it was free from the usual (100) twinning inherent to $(SN)_x$ single crystals polymerised from S_2N_2 . A complete X-ray structure analysis of this crystal will be published elsewhere.²⁸

Discussion

Poly(sulphur nitride) of high chemical purity can be prepared from S_2N_2 , but the polymerisation is slow (6–8 weeks) at room temperature. The known reaction using $(NSCl)_3$ and Me_3SiN_3 provides the most rapid, safe and convenient alternative synthesis³ and so, the route has been re-examined to improve

polymer purity, and the product has been studied as a source material for coating.

Published³ reactions (1) and (2) were studied. A similar



procedure (Experimental section) was adopted for the two reactions. The first route gave an inferior product (excess sulphur and up to 7% silicon, see entries for sample 1 in Tables 1 and 2) and so it was abandoned.

(A) Preparation and Purification of the Powdered Polymer obtained from $(\text{NSCl})_3$.—A systematic study of experimental conditions has shown that gram quantities of polymer can be prepared from $(\text{NSCl})_3$ and Me_3SiN_3 (molar ratio 1:7.5) in MeCN at -18°C . Compared with previous work,³ the considerable improvements in purity and (to a lesser extent) yield were achieved principally through rigorous exclusion of moisture (at all stages of synthesis, manipulation, and purification) and exhaustive extraction of impurities with liquid SO_2 . The major impurities after extraction were silicon, carbon, and chlorine (Table 2). In samples with nearly stoichiometric S:N ratio, these elements were present typically below 1%. However, when polarographic grade acetonitrile (*i.e.* after reflux over AlCl_3 , Li_2CO_3 , KMnO_4 , *etc.*)¹⁹ was used as solvent the resulting samples contained an excess (up to 33 mol %) of sulphur which appeared to be incorporated into the structure. Consequently, for optimum purity (and yield), the acetonitrile solvent purification steps are limited to refluxing over, and distillation from, both P_4O_{10} and CaH_2 .

Evaporation of the filtrate from each reaction gave almost pure S_4N_4 and a little $(\text{MeCN}_2\text{S}_2)_2$. The latter compound is highly sensitive to moisture. Its isolation is a useful indicator that the measures to eliminate moisture are adequate. Slow hydrolysis of $(\text{MeCN}_2\text{S}_2)_2$, *e.g.* in an inadequately sealed melting point tube, produced a blue layer on the tube wall, presumably of $(\text{SN})_x$.

The $(\text{MeCN}_2\text{S}_2)_2$ isolated (*ca.* 50 mg in the solid state) represented only a small proportion of the total produced; the reaction solution was purple-black due to this dissolved dimer. The high volatility of $(\text{MeCN}_2\text{S}_2)_2$ resulted in it being largely distilled away with the solvent. The formation of this unusual species can be rationalised as follows. Nitriles RCN ($\text{R} = \text{alkyl}$) react with $(\text{NSCl})_3$ to give 1,2,3,5-dithiadiazolium chlorides $(\text{RCNSSN})\text{Cl}$ and these are easily reduced to dithiadiazoles.²⁰ Since Me_3SiN_3 dechlorinates $(\text{NSCl})_3$ to $(\text{SN})_x$, it can be expected that some reduction of $[\text{RCN}_2\text{S}_2]\text{Cl}$ to $(\text{RCN}_2\text{S}_2)_2$ might occur.

In the previous work,³ the major impurities (NH_4Cl , S_8 , $\text{S}_4\text{N}_3\text{Cl}$, *etc.*) were removed by washing with solvents including water. We found that this partially decomposed the $(\text{SN})_x$ to a much more reactive product. Other authors^{29,30} have also reported the serious effect of water on purity, stability and other properties. We found that the washing with anhydrous formic acid also decomposed the polymer. Films of $(\text{SN})_x$ obtained by high-vacuum sublimation of ppsn washed with HCOOH were unstable even under dry N_2 ; the originally bronzy films soon degraded and lost their reflectance within a few weeks.

Heterogeneous (*i.e.* admixed and adsorbed) impurities were conveniently removed from powdered $(\text{SN})_x$ by continuous extraction with pure liquid SO_2 in a closed extractor.²² Liquid SO_2 does not degrade the ppsn and it dissolves a wide range of potential impurities (mostly side products and unchanged reactants): *e.g.* S_4N_4 , $(\text{NSCl})_3$, $\text{S}_4\text{N}_3\text{Cl}$, $\text{S}_6\text{N}_4\text{Cl}_2$, $[\text{MeCN}_2$ -

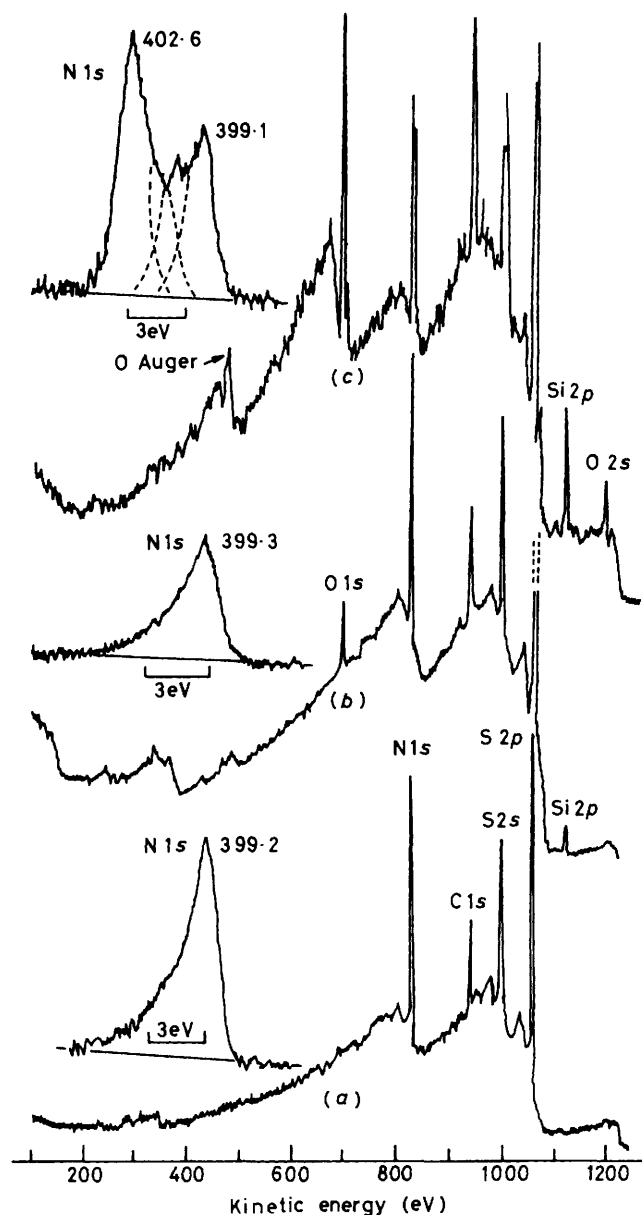
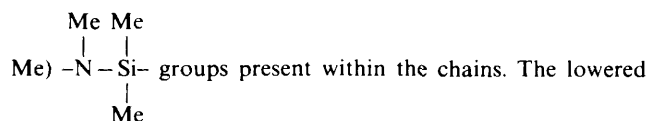


Figure 5. Wide-scan core-level p.e. spectra of vacuum-deposited $(\text{SN})_x$ films (*ca.* 1 μm thick): (a) deposited from cpsn (film exposed to moist air for *ca.* 15 min), (b) deposited from ppsn (sample 5) (exposed to dry nitrogen only), (c) deposited from ppsn (sample 5) (exposed to moist air for *ca.* 15 min). The insets show the resolved N 1s peaks with binding energies

$\text{S}_2]\text{Cl}$, $(\text{MeCN}_2\text{S}_2)_2$, and Me_3SiN_3 . Sulphur and NH_4Cl are practically insoluble (*ca.* 0.008% S_8 , 0.003% NH_4Cl , both at 25°C) but these two impurities were not found in the crude samples. Consequently a single (1–2 d) extraction with SO_2 rendered ppsn very largely free of heterogeneous impurities.

Constitutional (*i.e.* chemically bonded) impurities were held more tenaciously. Chemical analyses of SO_2 -extracted samples showed up to *ca.* 1.2% Si, 0.6% Cl, and 0.9% C. It is likely that the crude polymer contained groups such as $-\text{N}-\text{SiMe}_3$ or $-\text{S}-\text{Cl}$ as chain 'end-stops' and possibly (through migration of



threshold to detonation by compression (at *ca.* 2 kbar) and the increased reactivity after SO₂ extraction indicate that the liquid SO₂ cleaves bonds to silicon in the ppsn; loss of silicon removes protective end stops and shortens the chains.

However, some total analyses were unsatisfactorily low (much less than 100%), but there appeared to be no clear correlation with either analyses for specific elements, or procedure. Perhaps the deficit in the total was due to oxygen, for which there was no convenient method of analysis. E.s.c.a. measurements on layers, produced from the polymer by high-vacuum sublimation, gave clear indirect evidence for the presence of oxygen (Figure 5). Oxygen was also very easily introduced through chemisorption of moisture when the highly dispersed (high surface area) polymer powder was being prepared for analysis.

(B) Characterisation and Mechanism of Formation.—X-Ray powder diffraction patterns of the powdered and the crystalline polymer (Table 3) show that both have the β-(SN)_x structure reported by Mikulski *et al.*⁴ An extra line for ppsn (with $d_{hkl} = 4.45$ Å) can be assigned to diffraction by the (010) plane which is disallowed in space group *P2₁/c*; the possibility of S₄N₄ contamination was eliminated. Hoel and Dingley³¹ observed (010) and (030) spots in their electron diffraction studies, and postulated that they may be caused by small atomic displacements perpendicular to the plane of the chain.

Adsorption isotherm measurements showed that two of the SO₂-extracted polymer samples (2 and 5) have surface areas of 14 and 22 m² g⁻¹ respectively, comparable with the higher end of surface areas (0.01–10 m² g⁻¹) characteristic of non-porous adsorbents such as carbon black, SiO₂, and TiO₂, and some porous adsorbents, *e.g.* Kieselguhr (typically tens of m² g⁻¹).³² Because of the fibrous nature, an average particle size calculation is of little value (for equivalent spherical particles the corresponding diameters would be of the order of 0.12 and 0.2 μm for samples 2 and 5 respectively). However, qualitatively it confirms that the powdered (SN)_x is highly dispersed (possibly with low chain lengths) and this rationalises the greater volatility and high reactivity (*e.g.* towards atmospheric moisture) compared with the classical polymer (cpsn).

The powdered polymer sublimes (110 °C) *in vacuo* ($\leq 10^{-5}$ Torr) to give SN oligomers that polymerise to (SN)_x layers on a cooled substrate (*e.g.* glass slides at room temperature). This sublimation occasionally produced crystals, in the residue, which were large enough and suitable for crystal structure determination.²⁸ Unfortunately the conditions for the growth of such crystals were sensitively dependent upon conditions and impurities present. Perhaps thermally labile silicon–sulphur–nitrogen compounds act as chemical transport intermediates which provide the nutrient vapour for crystal growth.

Both t.g.a. and d.s.c. curves showed the great contrast in thermal properties of high-grade (SN)_x and samples containing excess sulphur. Crystalline polymer (cpsn) showed no (t.g.a. or d.s.c.) thermochemical event below 200 °C; rapid or explosive decomposition set in at 200–210 °C. Powdered samples prepared from (NSCl)₃ gave a smooth monotonic t.g.a. curve [Figure 2(a)] due to steady decomposition to S₄N₄ (and hence vaporisation of the S₄N₄ from the open crucibles) followed by further decomposition. Weight loss started at *ca.* 90 °C. Under the different conditions of d.s.c. (sealed crucibles) changes were detected only at higher temperatures (≥ 104 °C, see below). In contrast the polymer product (sample 1) prepared from S₃N₂Cl₂ showed [Figure 2(b)] two points of inflexion (at *ca.* 92 and 135 °C) and a sharp discontinuity (at *ca.* 163 °C). The rapid exothermic decomposition above 160 °C, presumably to sulphur and nitrogen, was accompanied by melting of the residue (composed mostly of S₄N₄ and S₈). The release of considerable heat associated with the rapid decomposition was

followed by a much lower rate of weight loss, presumably due to change in composition and in surface area (due to melting).

The d.s.c. data for powdered polymer (Table 4) showed that the major thermal process was irreversible exothermic conversion to S₄N₄ with $\Delta H_{\text{conversion}}$ of only $-(20 \pm 1)$ kJ per mole of four SN units. Since the mean SN distances are slightly shorter in (SN)_x [1.626(2) Å in S₄N₄,³³ 1.585(10) Å in (SN)_x³⁴] and the (less important) closest interactions between non-bonded sulphur atoms are shorter in S₄N₄ [2.590(1) Å in S₄N₄,³³ and 2.75(1) Å in (SN)_x³⁴], it is not surprising that the enthalpy of conversion is low. The facile conversion to S₄N₄ is favoured by two further energies; the entropy term ($T\Delta S$) and the high surface free energy of the powdered polymer, arising from its high surface area.

For freshly prepared polymer (sample 5) the d.s.c. decomposition to S₄N₄ started at *ca.* 104 °C [Figure 3(a)]. Six months aging of ppsn (sample 5) raised the onset temperature to *ca.* 116 °C [Figure 3(b)].

These curves [Figure 3(a) and (b)] also showed a small shoulder, for (a) at *ca.* 108 °C, for (b) at *ca.* 120 °C (more pronounced in the latter case). After curve resolution (using a DuPont 310 Analog Curve Resolver), the area under the small peak was found to be only *ca.* 4% of the total peak area. This shoulder may be due to a phase transformation or ordering in the ppsn prior to the ppsn → S₄N₄ conversion.

The double peak in Figure 3(c) is interpreted as a superposition of an exothermic ppsn → S₄N₄ conversion and endothermic melting involving S₄N₂ formed from S₄N₄ and excess sulphur (S:N ratio = 1.59:1 in sample 7) probably present in some polymeric form (it is not extracted by benzene). The mild pyrolysis of S₄N₄ (in the presence of sulphur is known³⁵ to generate S₄N₂).

For products with S:N ratio > 1:1, the chains may be built up from both (SN)_a and (SS)_b units, or they may be (SN)_x mixed with amorphous (S_yN)_z polymer where *y* is variable (average value calculable from elemental analyses). Large amounts of amorphous (S_yN)_z could well give no lines in the X-ray powder photographs and show up only weakly in i.r. spectra.

Several aspects of the reaction of (NSCl)₃ and Me₃SiN₃ show that it must be a complex heterogeneous process. The reactant (NSCl)₃ at -18 °C has a very low solubility in MeCN and the polymer product is insoluble. The ¹⁵N-labelling experiment showed that only $14.8 \pm 2.2\%$ of the Me₃SiN₃ nitrogen entered the product. Thus the synthesis of (SN)_x may proceed by both the reduction of (NSCl)₃ without azide nitrogen incorporation, and *via* S₃N₂Cl₂ (formed as an intermediate) according to equation (1) with incorporation of azide nitrogen (*i.e.* 33.3% of the total nitrogen in the ppsn). Thus $14.8 \pm 2.2\%$ incorporation of azide nitrogen in the product is consistent with *ca.* 50% participation of routes (1) and (2) in the overall reaction mechanism.

(C) Formation and Characterisation of Layers.—*Deposition of (SN)_x layers.* During coating from the vapour phase substrates became uniformly coated even on the side which rested on the flat bottom of C (Figure 4) indicating that the adsorbed SN oligomers possess a high surface mobility. For the same reason it was impossible to deposit a predetermined pattern by masking the substrates, *e.g.* by wrapping them tightly in a perforated tin foil. The growth of the layer extended almost uninhibited under the masks.

Relatively more air-stable coating from the ppsn sources was obtained on freshly cleaved (100) faces of KBr crystals, possibly because of epitaxial ordering of the (SN)_x chains. A preferred orientation parallel to the [110] directions could be seen under a polarising microscope. Under comparable conditions the (SN)_x layers were *ca.* 3 times thicker on KBr than on glass. The transmission i.r. spectrum [Figure 1(b)] of a thin film obtained

Table 7. Comparison of the conditions for the deposition of (SN)_x films and their characteristics from the standard polymer crystals (cpsn) and the powdered polymer (ppsn)

	cpsn glass	ppsn glass
Amount (mg) of source material ^a necessary for deposition of films ca. 1 μm thick	10	100
Total time (h) required for the deposition of film ca. 1 μm thick	24	72
Non-volatile residue	nil	ca. 3% (w/w)
Colour	bright gold	gold to bronze
Crystallinity (reflection electron diffractography, r.e.d.)	polycrystalline, ^b partial ordering with SN chains parallel to substrate surface, pronounced for layers ≥ 1 μm	polycrystalline, random even for layers > 1 μm
Stability: ^c		
(i) dry N ₂	stable indefinitely	stable indefinitely
(ii) moist air	good	poor, immediate formation of iridescent surface layer on exposure
S:N ratio (e.s.c.a.)	1:1	ca. 1.3:1
Electrical conductivity (Ω ⁻¹ cm ⁻¹) at r.t.	50–100	2–7

^a Weight of 1 μm thick layer of (SN)_x is 0.23 mg cm⁻². ^b R.e.d. revealed an arc pattern with the main periodicities of 3.25 Å, which is the distance between the (102) planes. ^c cf. e.s.c.a. spectra in Figure 5.

by vacuum thinning of an originally ca. 3 μm layer of polymer was indistinguishable from the spectrum of (SN)_x deposited from a cpsn source obtained likewise.

Characterisation of layers. Polymer films (from cpsn and ppsn) were characterised by analysis (Table 2), physical properties (Table 7), and their stability to air (surface quality, after exposure to air, was assessed by using an e.s.c.a. machine with a glove-box entry). A few films (from ppsn) deposited on a freshly cleaned (100) face of KBr were also studied under a polarising microscope (magnification 400).

Figure 5 shows the wide-scan photoelectron (p.e.) spectra of three specimens of (SN)_x films on glass: (a) from cpsn, (b) from ppsn (exposed to dry N₂ only), and (c) from ppsn [both (a) and (c) exposed for ca. 15 min to moist air]. The p.e. spectra showed that: (i) a pure cpsn source yields analytically pure (SN)_x films that are only very slowly attacked by moist air, (ii) the (SN)_x films from ppsn (without contact with moist atmosphere) contained excess sulphur (see Table 2), oxygen, and silicon, as the main impurities, and (iii) on exposure to air, the films from ppsn became surface contaminated with (combined) oxygen. The split on the N 1s peak (see inset) showed the presence of two or possibly three types of bond to nitrogen. The peak with binding energy (b.e.) 402.6 eV was presumably due to N–H bonds [cf. pure (SN)_x, b.e. 399.2 eV, Figure 5(a)].

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