Preparation of a Conducting Iodinated Poly(sulphur nitride)

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Tetrathiatriazenium chloride (S_4N_3Cl), vaporised at 130 °C, when treated with sodium iodide supported on glass wool at 250 °C, followed by cooling of the exit gases to 10 °C gives a black iodinated poly(sulphur nitride) $(S_aN_bI_c)_x$ with *a ca.* 3.0, *b ca.* 2.1, and *c ca.* 0.5. A lower temperature of condensation leads to a product contaminated with iodine. The conducting polymeric product is moisture sensitive and decomposes above 40 °C *in vacuo* (*ca.* 10^{-6} Torr) to sulphur, tetrasulphur tetranitride, and iodine.

POLYMERIC sulphur nitride $(SN)_x$ is the first example of a polymer containing no metal atoms which becomes superconducting at low temperatures,[1,2] and does not undergo a Peierls transition.[2] The unusual nature of this quasi-one-dimensional metal has prompted many studies of its structure and physical properties.[2,†]

A few halogen derivatives have been described,[3-8] some of these with d.c. conductivities (at 4.2—300 K) greater than that of pure $(SN)_x$. There are two synthetic routes, equations (1) and (2) (Y = halogen atom). No

$$S_4N_4 \longrightarrow S_2N_2 \xrightarrow{3\text{—}4\text{ weeks}} (SN)_x \xrightarrow{Y_2} (SNY_x)_n \quad (1)$$

$$S_4N_4 \xrightarrow{Br_2} (SNBr_x)_n \quad (2)$$

iodinated polymer has to-date been clearly characterised. We have therefore studied vapour-phase methods of producing S_2N_2 and I_2 simultaneously at a reaction surface and we report a rapid single-stage preparation of an iodinated poly(sulphur nitride) from tetrathiatriazenium chloride (cyclo-3,5,7-triaza-1,2,4,6-tetrathienium chloride) and sodium iodide, which avoids isolation of potentially explosive tetrasulphur tetranitride and disulphur dinitride (cyclotetra-aza-λ^4-thiene and delocalised cyclodiazathiene respectively).

EXPERIMENTAL

Infrared spectra (250—4 000 cm^{-1}) of Nujol mulls prepared under nitrogen were recorded using KBr plates and a Perkin-Elmer 457 prism grating spectrophotometer. Mass spectra were obtained on an A.E.I. MS9 mass spectrometer at 70 eV with an accelerating potential of 8 keV.‡ *X*-Ray data were obtained on a Guinier–de Wolff fully focusing powder camera (Nonius) using Fe-$K_{\alpha 1}$ radiation (30 kV, 10 mA with exposures ranging from 12 to 48 h). Resistance measurements at 1.5 V were made using a pellet of material (3.1 mm diameter, 3.1 mm thick) pressed in a die with a hydraulic press at 2 GPa maximum pressure § and placed between platinum electrodes connected to an Avometer. E.S.C.A. data were obtained on an A.E.I. 200 electron spectrometer with a Mg-$K_{\alpha 1,2}$ soft *X*-ray source. The probe chamber was at 10^{-8} Torr and the binding energies quoted are coded with respect to the C_{1s} spectrum arising from the hydrocarbon contamination layer which builds up on the sample. This surface contamination probably originates from pump oil. A Haake (F2-C) refrigerated bath circulator was used to provide a thermostatted cold zone at the top of the pyrolysis tube.

Solvents and reagents were purified as follows. Methanol was treated with magnesium ribbon (1 g per 100 cm^3) and distilled on to an activated molecular sieve 3A, under a nitrogen atmosphere. The glass wool (6.09 g; fibre diameter *ca.* 3—5 μm) was vacuum dried (300 °C, 12 h) and shaken with a solution of vacuum-dried (350 °C, 48 h) sodium iodide (*ca.* 2 g) in dry methanol (35 cm^3). After evaporation of the methanol, the glass wool was vacuum dried (20 °C, 4 h) and weighed (7.35 g). The molar ratio of S_4N_3Cl : NaI was 1 : 1.75.

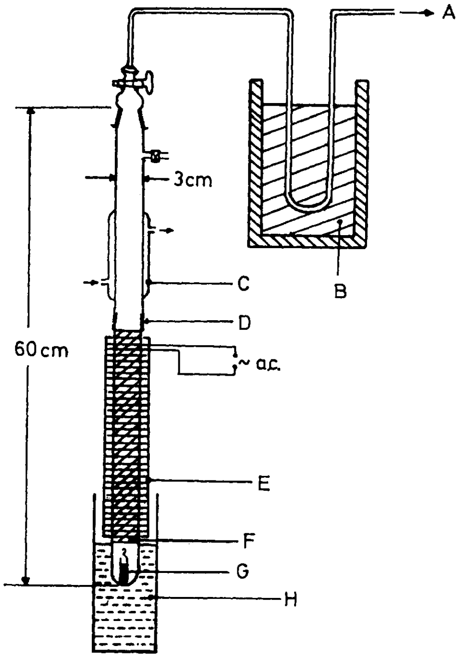

FIGURE Pyrolysis apparatus

Tetrathiatriazenium chloride was prepared from $S_3N_2Cl_2$ according to Jolly.[9] Nitrogen analysis was by the standard micro-Kjeldahl method, sulphur by the modified oxygen flask combustion,[10] and iodine by oxygen flask combustion followed by iodometric titration.[11]

Preparation of Iodinated Poly(sulphur nitride).—The apparatus consisted (Figure) of a glass pyrolysis tube (60 × 3 cm outside diameter) connected *via* a tap, ball and

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‡ Throughout this paper: 1 Torr = (101 325/760) Pa; 1 eV ≈ 1.60×10^{-19} J.

† Between 1973 and 1978, Chemical Abstracts reported *ca.* 150 papers which deal with the structure and physical properties of poly(sulphur nitride).

§ Care must be taken when compressing the material in pellet formation since S–N compounds are liable to explode under pressure.

socket joint, and liquid-nitrogen trap (B) to a vacuum line fitted with a mercury diffusion pump (A). Tetrathiatriazenium chloride (G) (1.0 g, 0.004 8 mol) was contained in a pre-weighed glass bucket at the bottom of the pyrolysis tube. The plug of glass wool–sodium iodide (F) (height 20 cm) was packed loosely in the tube covered by the heating mantle (E). This heater consisted of a glass former (24 × 3 cm outside diameter) wound with loops of nichrome wire from Wadite Wire Co. Ltd., Salford (117 loops, 2 mm spacing, wire resistance 26.25 Ω m^{-1}) cemented concentrically inside a glass tube (24 × 4.5 cm outside diameter). This design provides an excellent heat profile (± 1 °C over ± 4 cm at the centre of the mantle) and a temperature of 250 ± 5 °C over the whole tube with an applied potential of *ca.* 145 V. In run 1 the top of the pyrolysis tube was surrounded by a hinged polystyrene box containing solid carbon dioxide coolant (−77 °C). In run 2 a glass cooling jacket (14 × 6 cm outside diameter) was added to provide a lower cooling zone (C) (circulating alcohol at 10 °C). D is a B24 O-ring joint.

The system was gradually (over 15 min) pumped to $<5 \times 10^{-3}$ Torr pressure using rotary vacuum and mercury diffusion pumps. The electric mantle was heated to 250 °C and then the oil-bath (H) gently heated to a maximum of 130 °C. Pumping was continued for 3—4 h or until all the tetrathiatriazenium chloride had vaporised.

TABLE 1

Analytical data obtained for fractions of the polymeric material

Origin of sample	Analysis (%) N	S	I	Total	Empirical formula
Run 1: Rapid cooling of product at −77 °C	12.1	36.1	47.3	95.5	$S_{3.00}N_{2.30}I$
Run 2: Two zones of cooling					
(*a*) 10 °C fraction	15.9	49.9	34.0	99.8	$S_{3.00}N_{2.19}I_{0.51}$
(two scrapings)	15.25	49.9	35.0	100.15	$S_{3.00}N_{2.10}I_{0.53}$
Average	15.6	49.9	34.5	100.0	$S_{3.00}N_{2.15}I_{0.52}$
(*b*) −77 °C	11.0	34.45	55.1	100.55	$S_{3.00}N_{2.19}I_{1.20}$
fraction (two scrapings)	11.1	33.1	56.3	100.5	$S_{3.00}N_{2.31}I_{1.29}$

During the reaction a compact layer of black flaky material condensed in the cold zone. The product was removed in a dry inert atmosphere to avoid surface hydrolysis. Yield: 0.90—1.04 g. Analysis (Table 1) gave 49.9% S; 15.59% N, and 34.5% I, which corresponds to $S_{3.00}N_{2.15}I_{0.53}$. Table 1 shows the analytical consistency, and Tables 2—4 the i.r., mass spectra, and *X*-ray data. The d.c. resistance of a plug (3.1 mm diameter × 3.1 mm) at room temperature between platinum electrodes was found to be *ca.* 10 Ω. Table 5 shows the preliminary results of an E.S.C.A. run on a sample of polymer.

DISCUSSION

In attempts to find new synthetic routes to S_4N_4 and $(SN)_x$ we have studied [12] solution reductions of sulphur–nitrogen–chlorine compounds. Infrared spectra and thin-layer chromatography (t.l.c.) of the products indicated that all reactions produced sulphur, tetrasulphur tetranitride, and S_4N_2. In two cases, (a) S_4N_3Cl–aqueous $H_2PO_2^-$ and (b) S_3N_2Cl–I^-, i.r. spectra showed the probable presence of iodinated poly(sulphur nitride). The latter reaction appeared to be a combination of (3) [12] and (4) below; these are already known as separate reations. In both reactions (a) and (b), it appeared that moisture was essential for the formation of the black polymeric material, as found by Smith *et al.*,[13] because under anhydrous conditions the reactions gave predominantly S_4N_4; the solutions were deep red and solid residues contained no black material. Unfortunately, in the solution reaction (b) the presence of water resulted in some hydrolysis and caused S_4N_4 and iodinated polymer to be precipitated in a finely divided and potentially explosive state. **CAUTION:** A sample (*ca.* 0.5 g) of dried black solid, isolated after an attempt to remove the iodine product (from an S_3N_2Cl–I^- solution reduction) using aqueous thiosulphate ion, suddenly became hot and exploded, 5 min after encapsulation in a sample bottle. Similar explosion hazards have not been found in manipulating the product of the vapour-phase reactions (described in this paper) but adequate safety precautions should be taken, especially when heating or compressing the material. Therefore to

$$S_4N_3Cl + \text{reducing agent} \longrightarrow S_4N_4 \qquad (3)$$

$$S_4N_4 + I_2 \longrightarrow (SNI_x)_n \qquad (4)$$

TABLE 2

Infrared absorptions (cm^{-1}) of $(SN)_x$, S_4N_4, and black iodinated poly(sulphur nitride)

$(SN)_x$	S_4N_4	'$S_{3.00}N_{2.15}I_{0.53}$'
		3 200—3 100w
1 400m		1 390m
1 225s		
		1 190vw,br
		1 110m, br
1 047w		1 030vw, br
1 015ms		
	925s	923ms
		850—750w, br
	726s	705ms, br
	701vs	
685mw		
657mw		
		610m, br
600m		
	555s	563ms
		460br
	347s	348ms

TABLE 3

Mass spectral analysis of black iodinated poly(sulphur nitride) at 70 eV and 280 °C

m/e	Species	Relative intensity (%)
46	SN^+	100
48	SO^+	12
64	S_2^+, SO_2^+	35
78	S_2N^+	24
92	$S_2N_2^+$	83
110	S_3N^+	7
124	$S_3N_2^+$	5
127	I^+	22
128	HI^+, S_4^+	10
138	$S_3N_3^+$	57
140	$S_3N_3H_2^+$	11
156	$S_4N_2^+$	4
184	$S_4N_4^+$	8
254	I_2^+	62

TABLE 4

X-Ray diffraction data (*d* spacing/Å with relative intensity in parentheses) of black iodinated poly(sulphur nitride) before and after heating *in vacuo*, also of sulphur, iodine, $(SN)_x$, and S_4N_4 [Si calibration ASTM (5-0565)]

				'$S_{3.00}N_{2.15}I_{0.53}$'	
Sulphur	Iodine	$(SN)_x$	Tetrasulphur tetranitride	Before heat treatment	After heat treatment
			6.345(60)		6.341(30)
			6.077(45)		6.076(25)
					5.781(20)
5.128(40)					
		5.061(35)			
				4.782(f)	
			4.765(100)		4.752(100)
			4.645(85)		4.636(95)
				4.575(f)	
			4.415(70)		4.403(45)
			4.361(20)	4.361(f)	4.349(40)
					4.067(30)
				3.921(f)	3.935(25)
		3.894(10)			3.895(20)
				3.869(f)	3.862(10)
			3.731(40)		3.728(50)
	3.708(66)				
	3.635(62)				
			3.602(30)		3.603(15)
					3.572(15)
3.567(100)					
			3.499(35)		3.500(25)
					3.455(75)
			3.408(30)		3.400(45)
					3.346(60)
		3.333(35)			
		3.301(30)			
				3.282(f)	
		3.253(40) (d)			
				3.237(f)	
3.217(100)					3.217(70)
			3.170(30)	3.163(f)	3.167(40)
			3.136(70)	3.135(f)	3.125(65)
3.121(70)					
	3.103(100)				
			3.096(35)		3.094(45)
				3.063(f)	3.063(15)
			3.034(25)		3.032(20)
3.017(80)				3.012(f)	3.003(15)
2.925(80)					
2.902(60)			2.901(70)	No more resolved	2.901(30)
					2.856(<50)
			2.824(75)		2.820(<50)
			2.798(70)		2.795(<50)
			2.778(85)		2.772(<50)
			2.751(25)		2.745(<50)
					2.697(<50)
			2.672(25)		2.670(<50)
			2.624(40)		2.628(<50)
			2.607(35)		2.605(<50)
	2.534(14)				
2.495(60)					
	2.456(23)				
					2.432(<50)
2.385(40)					
			2.378(50)		2.376(15—20)
			2.343(20)		
2.316(45)			2.318(15)		2.319(15—20)
					2.294(15—20)
			2.245(45)		2.246(15—20)
			2.231(30)		2.231(15—20)
		2.224(100)			
			2.185(20)		2.180(15—20)
					2.154(15—20)
		2.143(70)	2.143(75) (d)		
		2.125(60)			2.121(15—20)

f = Faint, d = diffuse.

minimise hydrolysis, and contamination by solvent, an iodide reduction similar to (b) was carried out in the vapour phase using S_4N_3Cl; this is a less hazardous starting material than S_4N_4 [and less air sensitive than S_3N_2Cl used in reaction (b)].

TABLE 5

E.S.C.A. data for a sample of iodinated poly(sulphur nitride) condensed onto a glass plate and for some standard compounds: binding energies (eV) with relative intensities (%) in parentheses

	Iodine						Nitrogen			Sulphur	
	3*d* (anionic) Spin states		3*d* (neutral) Spin states		3*d* (cationic) Spin states		1*s* (neutral)	1*s* (cationic)		2*p* (doublets)	
	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$					
Iodinated poly(sulphur nitride)	619.5	631.0	621.2	632.8			398.8	400.3	401.8	164.0	166.1
$S_{3.00}N_{2.15}I_{0.53}$	(41)	(28)	(14)	(10)			(55)	(21.5)	(10)	(73)	(21.5)
$[IPh_2][PF_6]$					623.7	635.2					
$[IPh_2]I$	619.7	631.4	621.0	632.2	623.2	635.1					
$[NH_4]I$	619.7	631.3						401.9			

The black polymeric product had a compact and brittle constitution and could be scraped off the pyrolysis tube wall as rigid flakes. It had a semi-metallic lustre which tarnished only slightly over several months when kept in a sealed sample bottle. The polymer was moisture sensitive and when left exposed to air (3—4 d) it hydrolysed fairly rapidly to give a greyish powder with release of iodine. Examination of the surface-hydrolysed product under the microscope (×175 and ×500) showed that the material had a dull pitted surface and was non-crystalline. The consistency in analytical data for separate scrapings of the same fraction indicated that the 10 °C fraction was largely homogeneous. The amount of iodine in the product depended on the temperature of condensation; at the lower temperature (−77 °C) the polymer was heavily contaminated with iodine. Attempts to remove this excess of iodine by extraction with CS_2 at room temperature were found to lead to hydrolysis of the product. Infrared absorptions (Table 2) revealed that some hydrolysis [absorptions at *ca.* 1 390 and 3 200 cm^{-1} are due to ν(N–H)] and some decomposition to tetrasulphur tetranitride had occurred. Other peaks were within the typical range of S–N absorptions (600—1 500 cm^{-1})[14] but differed from those of S_4N_4[15] and $(SN)_x$.[16,*]

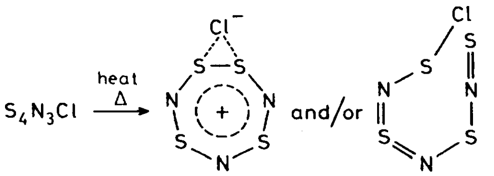
The mass spectrum, Table 3, is typical of the general breakdown of a sulphur–nitrogen ring or chain and is similar to that for $(SN)_x$ and S_4N_4.[17] The absence of any sulphur–nitrogen–iodine peaks, such as SNI^+ (*m/e* 173) and $S_2N_2I^+$ (*m/e* 219), indicates either that these species are too short lived to be recorded, or that the polymer itself breaks down under the probe conditions and what we are observing is the mass spectrum of the decomposition products, sulphur, tetrasulphur tetranitride, and iodine. Mass spectra of old samples revealed the progress of hydrolysis since the relative intensities of peaks at *m/e* 48, 64, and 128 due to SO^+, SO_2^+, and HI, respectively, were greatly increased when the sample was run several days after preparation.

Confirmation of the low degree of crystallinity in the polymer is afforded by the *X*-ray powder diagrams. Diffraction lines were only faintly visible even after 48 h exposure to *X*-rays. The *X*-ray powder data, Table 4, did not show any crystalline iodine in the polymer. Iodine was probably present in the polymer as anions and/or terminal S–I. Hydrolysis of the S–I bonds would explain the formation of free iodine. Sulphur does not appear to be an impurity in the original polymer but there is evidence for its presence in the residue after heat treatment. The diffraction lines of the polymer were substantially different from $(SN)_x$. This evidence supports the view that we have an iodinated poly(sulphur nitride) which decomposes on heating *in vacuo* (40 °C, 10^{-6} Torr) to give iodine (sublimed) and a brown residue containing S_4N_4 and S_8, equation (5).

A pressed plug of the polymer with platinum contacts showed low d.c. resistance (indicating a delocalised polymeric structure). Anomalously high resistance measurements were noted with silver and phosphor bronze electrode materials. This was probably due to the formation of a higher resistance metal iodide at the polymer–electrode interface. A possible mechanism for

$$(S_aN_bI_c)_x \longrightarrow S_4N_4 + S_8 + I_2 \qquad (5)$$

the gaseous reaction could be the initial formation of $S_4N_3^+Cl^-$ ion pairs † and/or an open chain S_4N_3Cl [equation (6)] ‡ which then reacted by halogen exchange



(6)

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* The absorptions cited in ref. 16 were confirmed using $(SN)_x$ made by catalytically cracking S_4N_4 in similar pyrolysis apparatus to that described above.

† Such a triangular relationship of a halide ion to a disulphide grouping is known to be stable in, for example, phenyldithiolium halides. See A. Hordvik, *Quart. Reports Sulphur Chem.*, 1970, **5**, 33.

‡ B. E. Svenningsen and R. G. Hazell (personal communication) have shown that the l.u.m.o. (lowest unoccupied molecular orbital) in $S_4N_3^+$ is antibonding with respect to the bond from the disulphide S to N but bonding with respect to S–S, hence a likely bond scission to form the open-chain iodide would be the S–N bond as shown.

with the sodium iodide on glass wool. Some loss of terminal SN would account for analyses [in between $(S_4N_3I)_x$ and $(S_3N_2I)_x$]. It is likely that the interaction of the iodine with the sulphur–nitrogen species occurs in the hot zone (rather than in the condensation zone), because Street *et al.*[3] have observed that iodine does not react with either $(SN)_x$ or S_4N_4 below 125 °C.

The initial results of an E.S.C.A. study on the iodinated poly(sulphur nitride) are shown in Table 5. Data for the binding energies (eV) of the I_{3d} molecular state, when compared with standard compounds, give some indication as to the possible nature of the charge on the iodine in the polymer. The data suggest that two types of iodine exist in the iodinated poly(sulphur nitride), anionic and neutral. Detailed examination of the E.S.C.A. results is now in progress.

Conclusion.—Work is envisaged to further characterise this new material, especially using E.S.C.A. techniques, but the present results suggest that this iodinated polymer may be similar to brominated $(SN)_x$, and polymeric brominated S_4N_4, both of which have varying bromine compositions.[6,18,19]

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