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Electron microscope diffraction characterization of the fibrous structure of poly(sulphur nitride) crystals

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The work reported here concerns the fibrous microstructure of macroscopic poly(sulphur nitride) crystals of current topicality in view of their metallic and superconducting properties. Following the outline of the synthesis by solid state polymerization, together with the achievement of the desired crystal habits appropriate for this study, methods for making the crystals accessible for transmission electron microscopy and diffraction are described. The principal features of the diffraction patterns were in accord with the crystal structure reported previously but additional ones were also observed which amongst others corresponded to a doubling of the unit cell and to twinnings, including a so far unreported twin mode on $(\bar{1}\,0\,1)$. The reflections were highly streaked along the layer lines and, significantly, the streaks were observed as a set of regularly spaced spots flanking the main reflections. This indicates the existence of a periodicity perpendicular to the chains beyond that of the atomic lattice. The spacing corresponds to ~200 Å as obtained from the closest spot separation which, in turn, indicates a representative "fibre" diameter of this magnitude. The latter broadly corresponds to the 250 Å obtained as an upper limit of the "wire" diameter deduced from conductivity measurements by Civiak *et al.* The transmission image confirmed the existence of a longitudinal periodicity but this was of variable magnitude with a minimum of 25 Å. The latter is at least consistent with a fibre diameter of 30 Å previously observed on bromine-treated samples. Consistency with the diffraction pattern requires an integral relation between the range of periodicities seen, of which the 25 Å should be the basic and the ~200 Å a representative maximum unit. The origin of the fibrous structure in terms of the solid state polymerization is discussed with two possible mechanisms in view: (1) phase separation during simultaneous polymerization and crystallization, and (2) twinning occurring during polymerization from solid solution. However, neither of these would account for the periodicities observed without invoking additional factors raised in the discussion.

1. Introduction

Poly(sulphur nitride) is an inorganic polymer with unusual physical properties and is known as the first example of a superconducting polymer. In contrast to most polymers the poly(sulphur nitride) crystals consist of extended polymer chains aligned in parallel. The chain orientation is uniform over the whole macroscopic crystal and determines the high anisotropy of its properites.

Poly(sulphur nitride) is prepared by solid state polymerization of disulphur dinitride crystals. The crystals develop a fibrous texture during polymerization, although the original shape and size of crystals is preserved. It is likely that not only the chain orientation but also the presence of this fibrous texture will strongly influence most of the macroscopic properties of poly(sulphur nitride) crystals. A detailed knowledge of structure is, therefore, essential for a meaningful study of their properties.

The main purpose of this paper is to report the results of investigation of poly(sulphur nitride) structure by electron microscopy and electron diffraction techniques with particular attention being paid to the possibility of a fibrous fine texture and to the assessment of the minimum size of fibrils such as are present. It will be attempted further to relate such fine structure to the crystallography of poly(sulphur nitride) and beyond this to the underlying polymerization mechanism. The preparative preliminaries necessary for obtaining the crystals under study are also briefly surveyed.

2. Experimental details

2.1. Synthesis and preparation of poly(sulphur nitride) crystals

Poly(sulphur nitride) was prepared by solid state polymerization of disulphur dinitride crystals. The polymerization is spontaneous at room temperature and takes about 3 weeks to complete. The synthesis of disulphur dinitride was carried out according to the method described by Street and Greene [1]. The crystals of disulphur dinitride were grown from the vapour in a cell shown in Fig. 1.

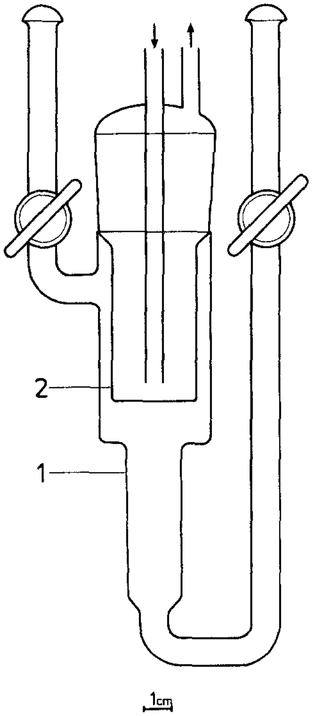


Figure 1 Cell used for the growth and polymerization of disulphur dinitride crystals. (1) evaporation surface (2) cold finger.

TABLE I Crystallization conditions and the average size of vapour grown and polymerized disulphur dinitride crystals [12]

Evaporation temperature T_{ev}(° C)	Crystallization temperature T_c (° C)	Supercooling ΔT(° C)	Average crystal size (mm)
18	9	9	1–1.5
21	15	6	2
30	26	4	3–4
30	28	2	4–5 some 7 × 5 × 2
30	29	1	no nucleation observed in 2 days

Disulphur dinitride was first sublimed in vacuum and trapped at liquid nitrogen temperature in the lower part of the cell. The cell was then sealed off the vacuum line. The temperature of the cold finger and of the outer surface of the cell were individually controlled where the resulting temperature difference allowed disulphur dinitride to sublime and crystallize on the flat part of the cold finger surface. Different temperature and supercooling were used (Table I) in order to control the size of the crystals. The crystals were allowed to grow for about 3 to 4 days under the conditions indicated in Table I and when the growth was complete the cell was brought to room temperature and filled with dry nitrogen to prevent any additional transfer of disulphur dinitride. The cell was then left undisturbed for at least 2 weeks so that the polymerization of disulphur dinitride should proceed to completion. A typical poly(sulphur nitride) crystal is shown in Fig. 2.

If a temperature gradient was maintained along an evacuated tube containing some disulphur

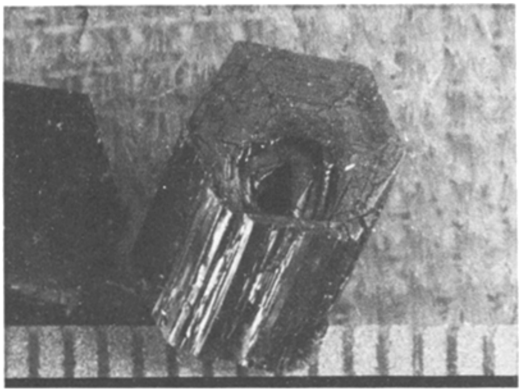


Figure 2 Typical poly(sulphur nitride) crystals. 1 division = 0.5 mm.

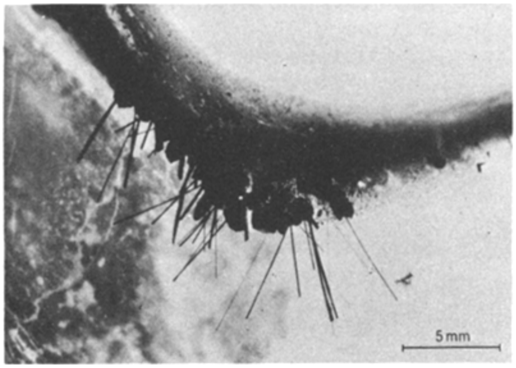


Figure 3 Needle-like poly(sulphur nitride) crystals. Polymer chains are parallel to needle axes.

dinitride a change in the crystal habit was observed and needle-like poly(sulphur nitride) crystals accompanied by some more or less equidimensional crystals were grown. A simple U tube with disulphur dinitride trapped in the upper part of the tube was used for growing the needles by this method. The gradient was obtained by transferring the U tube from a liquid nitrogen bath into a Dewar vessel filled with ice-water mixture [1] or, better, with partially molten *p*-xylene. In the latter case, a well defined vertical temperature gradient was maintained in the Dewar by the frozen (and denser) *p*-xylene at the bottom and the warmer liquid at the top. When the U tube was immersed in this bath disulphur dinitride sublimed from the top of the U tube to the bottom and needles of up to 6 mm in length and 0.01 to 0.5 mm in thickness were grown (Fig. 3). However, the needle-like crystals, while used for electrical conductivity measurements, were not the subject of the present electron microscopic study; in the course of the latter only the equidimensional crystals grown at the crystallization conditions indicated in Table I were utilized.

2.2. Sample preparation for electron microscopy

Thin fibres of poly(sulphur nitride) suitable for electron microscopy were obtained by stripping a layer from the surface of a macroscopic crystal. An adhesive tape was used for the stripping by means of which layers could be detached from different macroscopic crystal faces. In this work two crystallographically different faces were made accessible for electron microscopic examination in this way. The stripped off layers were removed from the tape by dissolving the adhesive with chloroform. The layers themselves were prone to fibrilation. As the axis of the fibres and the polymer chains were found to coincide [1], this technique provided samples suitable for electron microscopic examination in the direction perpendicular to the chain axis.

An attempt to cut sections across the chains using an ultramicrotome was not fully successful. Electron diffraction patterns have shown that the chain axes were not perpendicular to the section surface probably due to shearing in the course of sectioning; even so, the sections were thin enough to be sufficiently transparent in a transmission electron microscope.

A Philips E301 microscope was used for obtaining electron micrographs and electron diffraction patterns throughout this work.

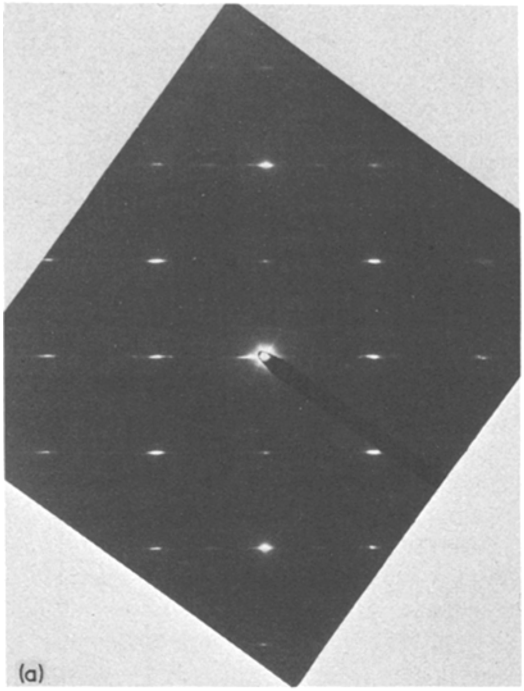
3. Results and discussion

Previous studies of the crystal structure of poly(sulphur nitride) by electron diffraction [2, 3] and X-ray [4] techniques established that the crystal lattice is monoclinic, space group $P2_1/c$, with polymer chains parallel to the unique *b*-axis. The crystal lattice parameters are: $a = 4.153$, $b = 4.439$, $c = 7.637$. $\beta = 109.7°$ [4]. The unit cell contains two polymer chains with two SN groups per chain. The polymer chain is a planar zig-zag with alternating *cis* and *trans* bonds.

Fig. 4a and b show electron diffraction patterns from single fibres stripped from two different prism faces of a poly(sulphur nitride) crystal. The patterns taken with the beam perpendicular to the fibre axis consist of rectangular nets as expected from the lattice symmetry. The *b*-axis, which is the chain direction, is common to both and the pronounced streakiness perpendicular to this direction (to be commented on further below) is consistent with the fibrosity of the crystals normal to the chain direction.

In general, the layer and row line spacings (Table II) index satisfactorily using the accepted parameters of the poly(sulphur nitride) crystal lattice [4] and the diffraction patterns shown in Fig. 4a and 4b correspond to $(h\,k\,0)$ and $(0\,k\,l)$ reciprocal lattice section planes, respectively. The fact that samples obtained from two crystallographically different faces gave the patterns corresponding to two different reciprocal lattice planes thus provides a method to preselect the crystal section to be examined in relation to the morphology of the macroscopic crystal.

Some of the reflections present, however, are not expected on the basis of this selection. They



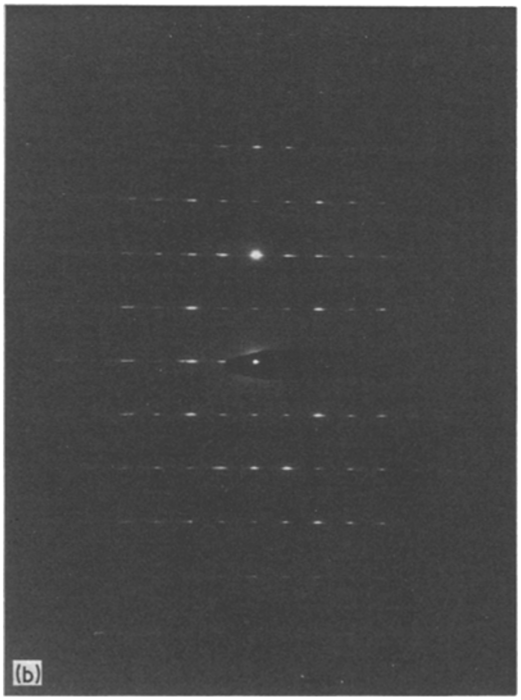


Figure 4 Selected-area electron diffraction patterns of a poly(sulphur nitride) fibre. The beam is perpendicular to the fibre axis and the fibre axis is vertical. The samples were stripped off two different faces of poly(sulphur nitride) prism and the patterns correspond to (a) ($h\,k\,0$) and (b) ($0\,k\,l$) reciprocal lattice planes.

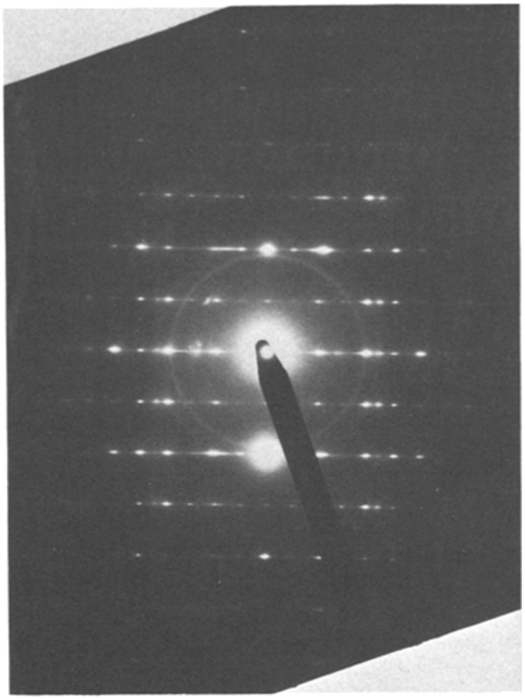


Figure 5 Selected-area electron diffraction pattern of a poly(sulphur nitride) fibre rotated around its axis by 38° from the ($h\,k\,0$) reference position.

fall into three classes. The first class comprises reflections which correspond to existing reciprocal lattice points in the appropriate reciprocal lattice plane but which should be forbidden by the selection rules arising from the space group. The appearance of such reflections, can, however, be explained by double diffraction readily verified by taking an appropriate intense spot as the primary beam (e.g. (1 0 2) in Fig. 5).

The second class comprises the weak innermost row lines in Fig. 4a with the spacing twice that of (1 0 0). This requires that the unit cell is twice as long along the a^* direction than implied by the indexing adopted. Similar problems in indexing of the diffraction pattern of the α-form of poly(sulphur nitride) were, in fact, encountered previously by Boudeulle [3] who proposed a unit cell twice as long in the a^* direction than the presently accepted value.

The third category of reflections which do not index simply by our scheme are those corresponding to existing reciprocal lattice points of the accepted structure and to reflections of finite predicted intensities but do not lie in the reciprocal lattice planes to which the rest of the reflections

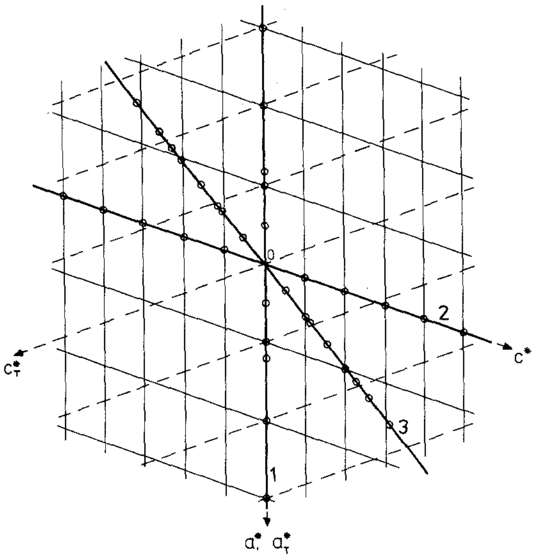


Figure 6 Projection of the reciprocal lattice of poly (sulphur nitride) along the *b*-axis. The dashed lines correspond to the reciprocal lattice twinned on (1 0 0) plane. The positions of the traces of the reciprocal lattice planes corresponding to the electron diffraction patterns shown in Figs. 4a, b and 5 are indicated by heavy lines (nos. 1, 2, 3 respectively); the positions of the reflections are shown by circles.

apparent in Figs. 4a and 5 otherwise conforms. We can account for this by the existence of twins within the area contributing to the diffraction having common *b*-axes with the parent crystal. We identified two such twin modes. The first one has (1 0 0) as the twin plane, a mode of twinning already found by Boudeulle [3]. The presence of such twinning in our samples is apparent from reflections in Fig. 5 as indicated by Table II. The nature of this twinning follows from the $h0l$ reciprocal net representation in Fig. 6 from which it will also be seen how the reflections in question can appear in the appropriate diffraction pattern. The spread of the reciprocal lattice points along the ($h0l$) reciprocal lattice plane, responsibile for the streaks already referred to, will provide the chance for reflections which otherwise may not be in the exact reflecting position to appear. However, the frequent appearance of the ($\bar{1}02$) reflections together with (1 0 0) in the diffraction patterns from a single fibre cannot be explained on the basis of this twinning mode. We suggest a second type of twinning, not yet proposed, namely twinning on ($\bar{1}01$) plane. Such twinning is represented by Fig. 7 from which it will also be

TABLE II Interplanar spacings and crystal planes indices derived from the electron diffraction patterns shown in Figs. 4a, b, 5 and 6. The spacings are calibrated with gold and they are compared with those calculated from the crystal lattice parameters given by Cohen *et al.* [4]

Electron diffraction pattern shown in	Layer lines spacings (Å)		Indices	Row lines spacings (Å)		Indices
	found	calculated		found	calculated	
Fig. 4a	4.44	4.44	$h1l$	7.80	–	doubling of the unit cell
	2.22	2.22	$h2l$	3.91	3.91	$1k0$
				3.25	3.25	$\bar{1}k2$ twinned on ($\bar{1}01$)
Fig. 4b	4.44	4.44	$h1l$	7.13	7.19	$0k1$
	2.22	2.22	$h2l$	3.64	3.59	$0k2$
	1.48	1.48	$h3l$	2.41	2.40	$0k3$
				1.84	1.80	$0k4$
Fig. 5	4.44	4.44	$h1l$	8.74	–	
	2.22	2.22	$h2l$	4.48	–	
	1.48	1.48	$h2l$	4.15	–	
				2.99	3.03	$1k1$
				2.29	2.29	$1k2$
				2.06	2.03	$\bar{2}k2$ twinned on (1 0 0)
				1.80	1.79	$1k3$
				1.49		
	Reflection spacings (Å)					Indices
	found	calculated				
Fig. 6	4.25					
	3.25	3.25				$\bar{1}02$
	2.88	2.93				$1\bar{1}0$
	2.79	2.79				$0\bar{1}2$
	1.55	1.59				$1\bar{2}2$

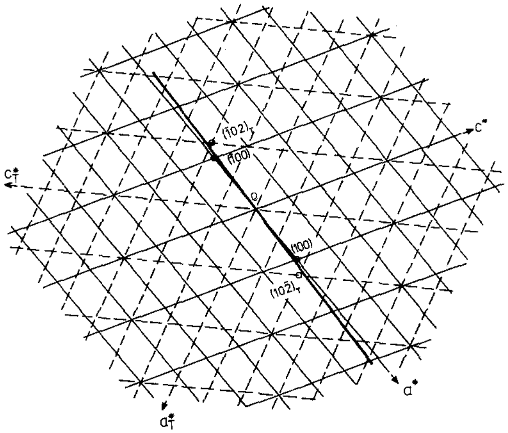


Figure 7 Projection of the reciprocal lattice of poly (sulphur nitride) along the *b*-axis. The dashed lines correspond to the reciprocal lattice net twinned on $(\bar{1}01)$ plane. The position of the trace of the reciprocal lattice plane responsible for simultaneous appearance of (1 0 0) and $(\bar{1}\,0\,2)'$ reflections is indicated by the heavy line. Subscript T refers to the twinned lattice.

apparent how the reflections in question can be accounted for.

In order to explore the reciprocal lattice also in sections other than provided by the stripping method with the beam in normal incidence to the plane of stripping the samples were rotated in the microscope. Two principal types of rotation were employed: (i) around the *b* (chain axis) readily recognizable as the long dimension of the ribbon-shaped fibrils, and (ii) around a direction perpendicular to *b*. Both (i) and (ii) had one feature in common: the reflections were all streaked along lines perpendicular to *b* itself (in case i) or to its projection on the plane normal to the beam direction (in case ii) which demonstrates that each reciprocal lattice point is spread about equally thus forming discs lying along the reciprocal lattice planes perpendicular to *b*.

(i) This rotation explores reciprocal lattice planes with *b* as a common axis, i.e. situations between those represented by Fig. 4a and b. The $(hk0)$ reciprocal lattice plane was chosen as reference and designated as zero rotation (Fig. 6). Of the several diffraction patterns obtained, Fig. 5 shows that for 38° rotation. The spacings are given in Table II and the corresponding reciprocal lattice construction in the projection on the $(h0l)$ reciprocal lattice plane is shown in Fig. 6. As seen, the reflections can be indexed taking into consideration the double diffraction, doubling of the unit cell and the twinning modes already discussed.

Figure 8 Selected-area electron diffraction pattern of a poly (sulphur nitride) fibre rotated by 45° along a direction perpendicular to its axis.

(ii) For small rotations (up to a few degrees) there was no significant change in the appearance of the diffraction pattern compared to the unrotated one. The only difference was a small increase in the reciprocal periodicity along *b*. This is consistent with the fact that each reciprocal lattice point remains in reflecting position by virtue of the extension of the reciprocal lattice "points" along planes perpendicular to *b*. The small increase of the periodicity along *b* is accountable by the tilt of the plane of reflection with respect to the *b* axis and corresponds to the increase of the distance between the intersections of the reflection plane with the reciprocal lattice discs. At larger angles of rotation, however, a discontinuous change in the appearance of the diffraction pattern occurred. This is clearly due to a new reciprocal lattice net plane coming in the reflecting position. Fig. 8 is an example of electron diffraction pattern corresponding to such a general plane inclined by 45° towards the *b*-axis. Its interpretation and orientation follows readily from Fig. 9 and is explained in the caption.

It has been already mentioned that the extensive streaking observed in all directions perpendicular to the chain axis is consistent with the fibrosity of

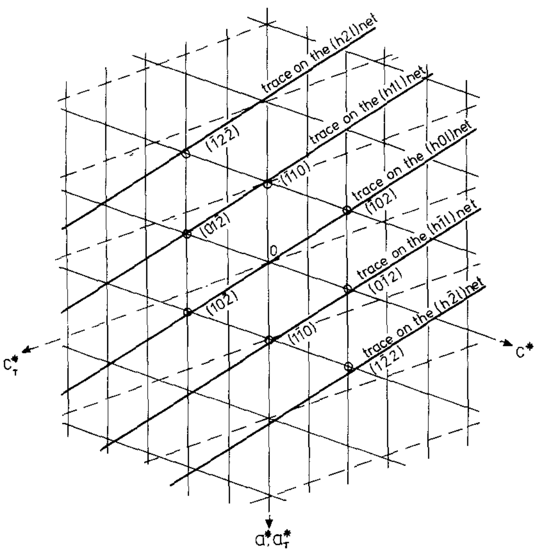


Figure 9 Projection of the reciprocal lattice of poly (sulphur nitride) along the *b*-axis. The intersections of $h\,0\,l$, $h\,1\,l$ and $h\,2\,l$ reciprocal lattice nets with the plane corresponding to the electron diffraction pattern shown in Fig. 8 are indicated by heavy lines, the positions of the reflections are shown by circles. Subscript T refers to the twinned lattice.

the crystals normal the chain direction. However, the streaks themselves reveal some unexpected novel features to which we shall give attention in what follows.

Close examination of the streaked reflections has shown that the intensity profile of the streaks is not smooth but contains a series of dots (Fig. 10). This fact suggests the existence of a regular periodic structure with a discrete period in the direction perpendicular to the chain axis. The dots are about equally spaced and the distance between the neighbours corresponds to a periodicity of about 200 Å.

A bright-field electron micrograph of a poly(sulphur nitride) fibre is shown in Fig. 11. Regular striations parallel to the fibre and polymer chain axes are observed with a minimum periodicity of 24 to 25 Å. Similar striations are also present in a dark-field electron micrograph of a section cut across the fibre axis (Fig. 12). The minimum periodicity is again about 25 Å but the striations are much shorter than those found in the fibre micrograph. As mentioned before, on the basis of electron diffraction patterns we know that the polymer chains together with the fibrils are inclined to the section surface and the length of the fibrils in the section is, therefore, limited.

As follows from the bright- and dark-field electron micrographs shown in Figs. 11 and 12, the minimum periodicity of the striations is about 25 Å. This value does not agree with the fibrillar diameter of 50 to 70 Å found by Gill *et al.* [5]. However, in poly(sulphur nitride) samples treated by bromine the same authors report the values of 20 to 30 Å for the diameter of the fibrils which agree well with our value found in untreated poly(sulphur nitride). They also claim that the inter-fibrillar regions are more readily penetrated by bromine than the interior of the fibrils. It seems plausible, therefore, that the fibrils in the brominated and

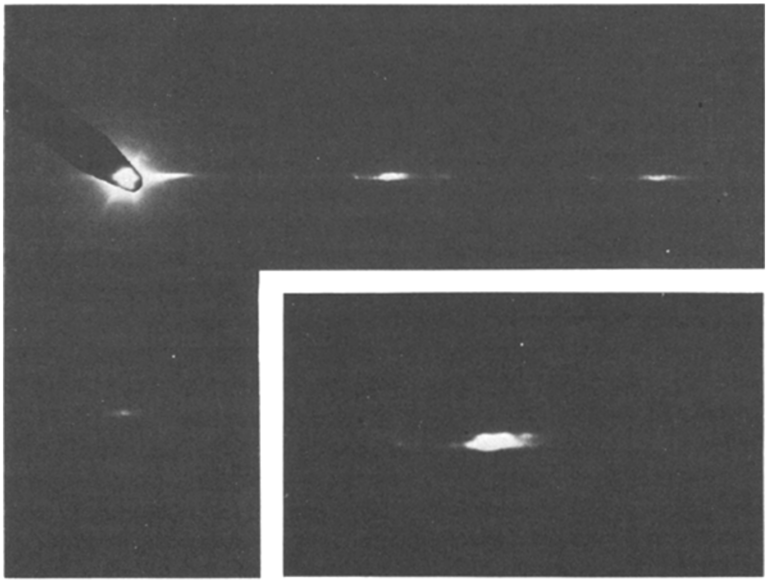


Figure 10 Enlarged sections of the electron diffraction pattern (as shown in Fig. 4a) demonstrating the fine structure of a streaked reflection, with an inset showing an enhanced enlargement.

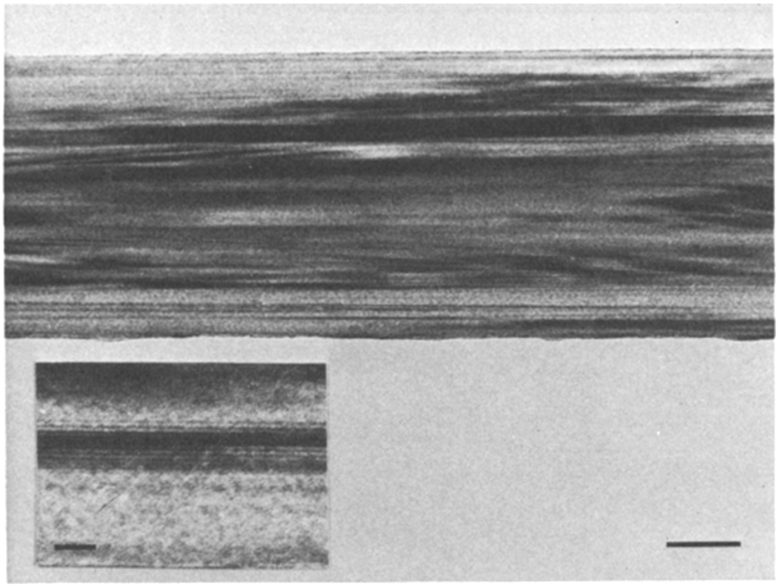


Figure 11 Bright-field electron micrograph of a poly (sulphur nitride) fibre. The bar corresponds to 1000 Å. The fine striations are shown in the inset; the bar corresponds to 200 Å.

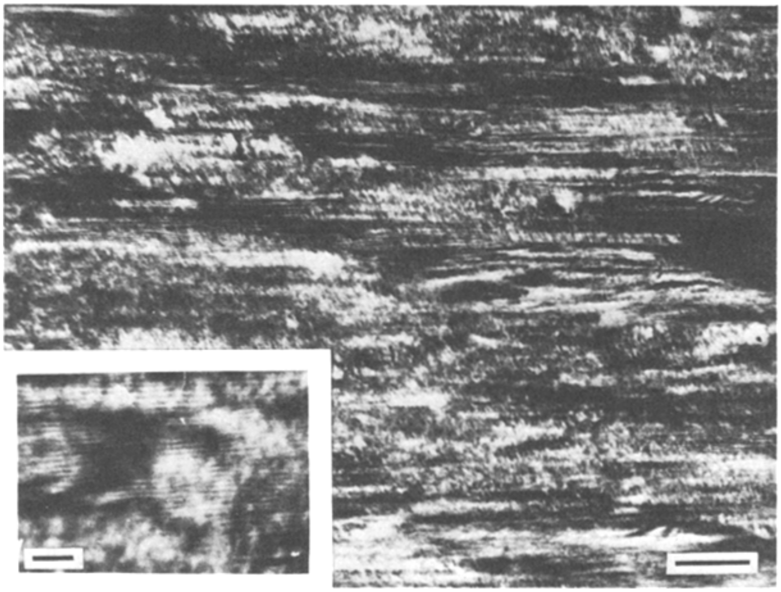


Figure 12 Dark-field electron micrograph of a poly (sulphur nitride) section cut across the chain axes. The bar corresponds to 1000 Å. The fine striations are shown in the inset; the bar corresponds to 200 Å.

the pristine poly(sulphur nitride) are of similar size, as our results indicate.

The disagreement between the striation periodicity of about 25 Å and the spacing of 200 Å derived from the distance between the neighbouring dots in the streaked reflections can be explained by the presence of several periodic structures within the area contributing to the diffraction pattern. These different periodicities have to satisfy the following two conditions: (a) they all have to be parallel both to each other and to the fibril, hence chain direction. The existence of periodic striations on different scales satisfying this condition is, in fact, readily verifiable in the electron micrographs (b) the different periodicities cannot be of arbitrary size otherwise the corresponding reflections would be irregularly spaced and, in fact, would merge along the streak. The existence of equidistant dots requires a periodicity of maximum spacing corresponding to the closest dot separation (which is about 200 Å) and that other periodicities, if such are present, (as in fact revealed by the electron micrographs down to 25 Å) should be integral fractions of the largest one. Or the other way round, there exists a range of periodicities with spacings which are integer multiples of a basic minimum. In this case each periodicity will give its own set of orders along the lines perpendicular to *b* and centred around the reciprocal lattice points of the crystal lattice proper. The higher orders of the larger spacings will coincide with the lower orders of the smaller ones giving rise to the equidistant dot separation observed.

The fact that there is fibrillar substructure in itself is not new but its ability to form a regular periodicity transverse to the chains is. As just seen, the smallest periodic unit as revealed by electron microscopic striations is about 25 Å, and larger units need to be multiples of this. However, there must be a limiting upper periodicity of about 200 Å to give rise to the closest satellite spots observed. The existence of a discrete unit of this size may well be of significance and it is of interest that Civiak *et al.* [6] deduced from the fluctuation-induced conductivity above the superconductivity transition, a transverse coherence length of the above order. In fact, they set an upper limit to the "wire diameter" of 250 Å. The same authors [7] also estimate the minimum value of the diameter as higher than 17 Å. The correspondence between figures derived from such entirely different effects is remarkable.

We shall next consider the possible origin of the periodicities indicated by the diffraction patterns and micrographs. We know that our samples are twinned, in fact we identified two different crystallographic twins with *b* (chain direction) as common axis. We have no direct evidence on the scale of these twinnings but if it were on the scale of the striations it would account for our observations. The possibility that twinning could produce such an effect arises from consideration of the polymerization mechanism [8, 9] and has, in fact, been invoked previously [5] as a possible source of the commonly recognized fibrosity in poly(sulphur nitride). However, the twinning is not the only way how fibrous texture can be developed during solid state polymerization and the polymerization mechanism of disulphur dinitride and its effect on the resulting polymer structure has to be considered to understand the origin of the fibrosity. Two possible mechanisms have been proposed: (a) simultaneous polymerization and crystallization [1], (b) polymerization in solid solution [8].

(a) Generally, the polymerization via the former mechanism [1, 10] probably starts at the crystal defects and propagates rapidly in the chain direction. The polymer chain serves as a nucleus for the polymerization of the surrounding monomer. Owing to the mismatch between monomer and polymer lattice dimensions, a phase separation occurs and further polymerization proceeds through a disordered layer at the phase boundaries. A fibrous texture is formed as the result of the phase separation. To account for our observations, however, such phase separations would have to occur periodically.

(b) In contrast to mechansim (a), there is no phase separation during polymerization in solid solution. The monomer crystal lattice transforms into the polymer crystal lattice as a continuous function of conversion. A single crystal of monomer yields a single crystal of polymer and no fibrosity on a cleaved surface is observed [10]. A condition necessary for this type of solid state polymerization is the similarity of dimensions of polymer and monomer crystal lattice.

The X-ray investigation of the crystal structure of poly(sulphur nitride) and disulphur dinitride by Cohen *et al.* [4] shows that there is no significant difference in the lattice periods along the chain direction and also in the unit cell volumes of these two related compounds. Moreover, the unit cell parameters of the partially polymerized disulphur dinitride have the values intermediate between those for the dimer and the polymer [4]. On this evidence, Baughman and Chance [8] concluded that, at least up to an intermediate degree of conversion, the polymerization of disulphur dinitride takes place in solid solution. The fibrous texture is explained by the fact that the polymerization of disulphur dinitride via the ring opening is not unique in a sense that there are two different ways in which the disulphur dinitride rings can join up [8, 9]. The resulting polymer structures are in twin relation and such twinning could then be responsible for the fibrosity [5]. However, the thickness values of such fibres would have a random distribution and would not take up discrete values as required by our observation of periodic structures. For this to arise the two kinds of ring opening themselves could not be random but would need to occur co-operatively. The randomness or otherwise of the two kinds of ring openings has been touched upon by Baughman and Chance [8] who favour random statistics from different evidence. Nevertheless, their correspondence to randomness is not exact and leaves scope for alternatives.

At present we consider that the experimental evidence available so far does not allow one to decide which of the two mechanisms, i.e. (a) or (b), is responsible for the origin of the fibrous texture observed in poly(sulphur nitride). The absence of phase separation in partially polymerized disulphur dinitride [4] and the presence of twins support the solid solution mechanism with microtwinning [5] responsible for the fibrous texture without in itself accounting for its periodic arrangement. However, the X-ray investigation of partially polymerized disulphur dinitride [4] did not explore the whole conversion range, hence the possibility of a phase separation at some later stage of polymerization cannot be excluded. Such a phase separation after the polymerization in solid solution has reached some critical conversion, was observed on other systems [11] and resulted in a fibrosity of the polymer. It is also possible that in poly(sulphur nitride), both the microtwinning and the phase separation take place and are responsible for the final structure of the polymer each on its own scale. In either event, additional factors would need to be invoked (periodic precipitation in (a) and co-operative ring opening in (b)) to account for the periodic fibril arrangement together with the existence of a basic unit and a maximum limiting size indicated by our experiments, as neither of these would follow from the phase separation or the solid state solution mechanism alone.

4. Conclusions

(1) A method was established to obtain electron diffraction patterns corresponding to different sections through the reciprocal lattice of macroscopic poly(sulphur nitride) single crystals. The results thus obtained reveal a new mode of twinning in addition to providing support to the previously reported twinning mode and unit cell doubling within the accepted crystal structures.

(2) Further evidence reveals the existence of a regular fibrous texture parallel to the polymer chains. This fibrous texture gives rise to a regular superstructure with a representative periodicity of about 200 Å as revealed by satellites in the electron diffraction patterns with finer periodicities down to a minimum of 25 Å as displayed by the electron micrographs an integral relationship between these spacings being implied.

(3) While it is not possible to decide which of the two possible mechanisms phase separation or microtwinning – is responsible for the development of the fibrous texture during polymerization, the regularity of the texture observed requires the invoking of additional co-operative effects by either mechanism.

Acknowledgement

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