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Preparation and structure of poly(sulphur nitride) whiskers

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A method of preparation of poly(sulphur nitride) whiskers with diameters down to 400 nm and lengths up to 2 mm is described. Through the addition of specific impurities (borneol or camphene) to the highly pure disulphur dinitride starting material, two morphologically different whisker-types were produced. Scanning and transmission electron microscopy revealed fibrous texture in both types of whisker. The fibrils are of irregular shape and are composed of microtwins. A vapour–liquid–solid mechanism is proposed for the growth of disulphur dinitride whiskers. Also the possibility of using a correlated polychromatic percolation as a model for the subsequent polymerization of the whiskers is discussed.

1. Introduction

Poly(sulphur nitride) $(SN)_x$ is a highly anistropic synthetic metal. The physical properties of this material are rather unusual for a polymer, therefore, its preparation, structure and properties have been the subject of many recent investigations [1].

Poly(sulphur nitride) is usually synthesized by a solid-state polymerization of disulphur dinitride (S_2N_2) crystals. The crystals develop a fibrous texture during polymerization, with polymer chains parallel to the fibre axes. The width of the fibres was reported to be in the region of 2.5 to 20 nm [2–5]. The shape of disulphur dinitride crystals is preserved during polymerization so the habit of the polymer crystal is determined by that of its precursor.

The crystals of disulphur dinitride used for the synthesis of poly(sulphur nitride) are commonly obtained by sublimation of S_2N_2 vapour onto a cooled surface. Depending on the method used, the crystals grow either in the form of bulk, approximately equidimensional, crystals of up to several mm in size or in the form of needles up to 1 cm in length and 0.01 to 0.5 mm in thickness. The structure of $(SN)_x$ prepared from the bulk crystals was investigated by electron diffraction and electron microscopy techniques [2, 3, 6, 7]; however, the preparation of sufficiently transparent samples for transmission electron microscopy and electron diffraction inevitably involved the application of an external force. This could result in sample damage and the appearance of additional structural features not inherent in the nascent $(SN)_x$ [8, 9].

In this work the crystals of S_2N_2 were prepared and polymerized in the form of thin whiskers and the structure of the polymer was investigated directly without subjecting most of the samples to mechanical damage. Further, it may be expected that the crystal perfection of S_2N_2 whiskers will be superior to that of bulk crystals. Furthermore, the small lateral dimensions and the more perfect monomer phase of whiskers could restrict the fibrillation of the polymerizing crystal and thus give rise to higher quality $(SN)_x$.

2. Experimental details

Extensive studies on crystal growth have indicated that low supersaturation and the presence of specific impurities promote the growth of crystals in the whisker form. However, the number of systematic investigations concerned with the effect of specific impurities on the habit of vapour grown crystals is rather limited. Hallett and Mason [10] observed that the presence of a minute amount of camphor vapour is sufficient to suppress the established dependence of ice crystal habit on temperature and supercooling and to promote the growth

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of needles over a wide range of conditions. Similar modification of ice crystal morphology was also achieved with alcohols, ketones and silicone oil [11, 12]. The habit changing property of alcohols is not limited to ice; alkali halides crystallize from their water solutions as whiskers if traces of polyvinyl alcohol or phenol are present [13].

2.1. Preparation of poly(sulphur nitride) whiskers

The growth of disulphur dinitride crystals in needle form from the vapour at low supersaturations has been reported by many authors [1, 3, 14]. The needles were obtained with thickness down to about 10 μm and length up to 1 cm. In this work the combined effect of deliberately added impurities coupled with a low supersaturation was tried and poly(sulphur nitride) whiskers with lengths up to 2 mm and average thicknesses of several micrometres were obtained.

The synthesis of disulphur dinitride was carried out according to the method described by Street and Greene [1] and used in our previous work [3]. The starting material for the synthesis, tetrasulphur tetranitride, was purified *in vacuo* by fractional sublimation in a temperature gradient tube and the melting of the purified S_4N_4 was examined with a Perkin Elmer DSC 1b differential scanning calorimeter. The thermograms obtained at two different heating rates are shown in Fig. 1. At the faster heating rate an endothermic melting peak is observed which is followed immediately by an intense exotherm indicating the decomposition of S_4N_4[*]. At the slower heating rates only the decomposition exotherm starting at a lower temperature was observed. The metling point of tetrasulphur tetranitride determined from the onset of the endotherm peak is 200 ± 1° C which is at least 10° C higher than the value previously reported [1]. This difference can be explained by the strong dependence of decomposition temperature on the heating rate. At the slow heating rate the exothermic decomposition of S_4N_4 starts before its true melting-point temperature is reached and the heat evolved on decomposition is sufficient to melt the crystal before its melting-point temperature is indicated by the instrument.

The growth and polymerization of disulphur dinitride whiskers was carried out in a simple U-tube attached via a vacuum line to S_2N_2 and impurity containers. About 0.2 g of disulphur dinitride was first sublimed *in vacuo* and trapped at liquid nitrogen temperature in the upper part of one of the U-tube branches. A measured volume of impurity vapour was then introduced and trapped in the other branch of the U-tube. The tube was then sealed-off from the vacuum line, transferred into a temperature gradient bath filled with partially molten p-xylene [3] and left undisturbed for 48 h. During this time disulphur dinitride slowly sublimed from the top of the U-tube to the bottom where most of the crystals were grown. The tube was then filled with pure dry nitrogen to prevent any further mass transport of S_2N_2 and left for three weeks at room temperature to complete the polymerization.

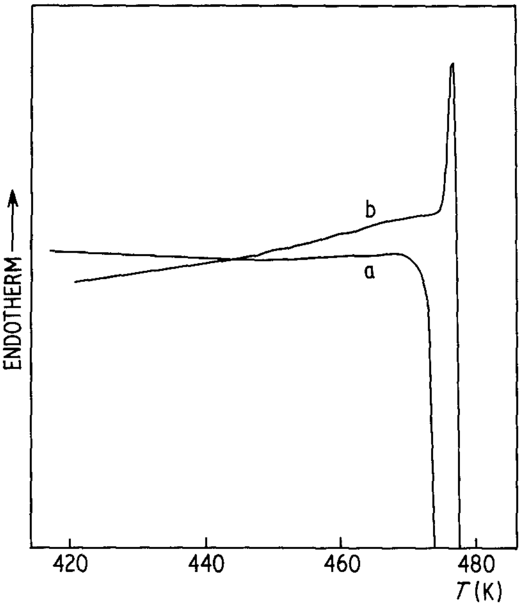

Figure 1 Differential scanning calorimetry thermogram of tetrasulphur tetranitride: (a) heating rate 16 K min^{-1} and (b) heating rate 32 K min^{-1}.

To promote the growth of disulphur dinitride whiskers three different substances were tried: camphor, borneol and camphene. All three are volatile terpenes containing keto, hydroxyl and vinylidene groups, respectively. They were obtained from BDH Chemicals Ltd and used as supplied.

The conditions and results of crystal growth of S_2N_2 in the presence of these impurities are summarized in Table I. It was found that borneol and camphene promoted the growth of disulphur

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[*] Tetrasulphur tetranitride can explode violently if subjected to shock or heated rapidly over 130° C [21].

TABLE I Preparation of poly(sulphur nitride) crystals in the presence of impurities

Impurity	Total amount of impurity (g)	Weight fraction of impurity	Morphology of the $(SN)_x$ crystals obtained
Camphor	5×10^{-5}	2×10^{-4}	Bulk crystals and some needles
Borneol	1×10^{-5}	5×10^{-5}	Whiskers with a uniform cross-section along their lengths. Average thickness about 5 μm.
Camphene	6×10^{-4}	3×10^{-3}	Whiskers consisting of tightly-packed bunches of fibrils split at their ends

dinitride crystals at low supercoolings in the form of thin ($< 10\,\mu$m) whiskers. They were of different lengths up to 2 mm and formed a densely packed layer adhering weakly to the glass surface of the U-tube. In contrast to these whiskers the $(SN)_x$ crystals obtained in the presence of camphor were similar to those grown at low supercoolings alone [3] and, therefore, were not used in the present study.

2.2. Sample preparation for electron microscopy

In order to minimize the possibility of artefacts related to the mechanical sample damage, the following procedure for sample preparation was employed. After the polymerization was completed the U-tube was cut into small segments and the $(SN)_x$ layer containing the whiskers was carefully stripped off the glass surface. Gold paint was used to attach the stripped layer to the stub for scanning electron microscopy. In transmission electron microscopy, the whiskers were examined while clamped in between two grids with no carbon film support present.

A scanning electron microscope Stereoscan Mk 2 made by Cambridge Instruments Ltd and a Philips EM 301 transmission electron microscope were employed throughout this work.

3. Results

3.1. Optical microscopy

The optical micrographs of $(SN)_x$ whiskers as-grown and polymerized on the glass surface in the presence of borneol or camphene vapour are shown in Fig. 2a and b. Vertical illumination and crossed polars were used to enhance the contrast and structural details. The comparison of whiskers shown in Fig. 2a and b revealed a distinct difference in their morphology. The whiskers grown in the presence of borneol (Whiskers I) were in the form of straight or slightly twisted rods or ribbons with no fibrosity observed by optical microscopy. However, the whiskers obtained in the presence of camphene (Whiskers II) were less perfect, they were frequently bent or kinked and striated parallel to their axes. Their ends were often split into thin fibrils.

3.2. Scanning electron microscopy

The different morphology of Whiskers I and II was clearly shown by scanning electron microscopy. Fig. 3a, b, c and d, shows the scanning electron micrographs of Whiskers I. The low magnification micrograph in Fig. 3a shows the whiskers as straight or slightly twisted rods with faceted ends. The average thickness of the whiskers is about 5 μm. The high magnification micrograph of the end of a large whisker taken in the direction parallel to its axis (Fig. 3b) shows that its surface is not smooth but broken into irregular clusters separated by cracks of about 50 to 100 nm in width. Striations on the same scale are observed on the sides of the whisker suggesting that the cracks are not localized at the top surface only but propagate deep into the whisker interior (Fig. 3c). However, it is likely that the observed surface structure of the large whiskers is the result not only of cracking but also of the re-evaporation of the momomer from the partly polymerized whisker. This suggestion is based on the fact that the fraction of the whisker top surface occupied by the "cracks" (Fig. 3b) is much larger than the 2% which represents the difference between the area of the monomer and that of the polymer crystal lattices in the plane perpendicular to the polymer chains.

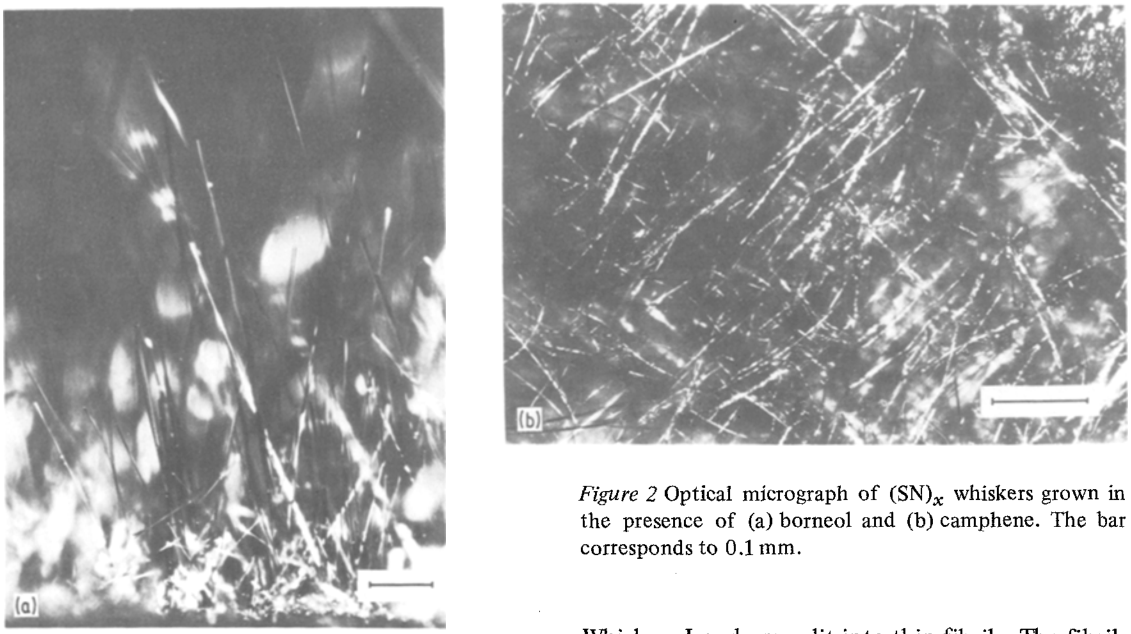

Figure 2 Optical micrograph of $(SN)_x$ whiskers grown in the presence of (a) borneol and (b) camphene. The bar corresponds to 0.1 mm.

Cracks and striations are characteristic features of large whiskers. The thinner the whisker the less frequent the cracks. Fig. 3d shows a micrograph of the end surface of a thin whisker exhibiting no visible cracks or striations.

The prominent fibrosity of Whiskers II compared with Whiskers I is clearly demonstrated in Fig. 4. Close to the substrate the whiskers consist of tightly-packed filamentary bundles which split into separate fibrils towards the whiskers' end. The minimum thickness of the individual fibrils is difficult to determine as it is comparable to the resolution of the scanning electron microscope used in this work.

3.3. Transmission electron microscopy

The minimum diameter of Whiskers I is about 400 nm. They are opaque in the electron beam and therefore not generally suitable for transmission electron microscopy. However, the presence of internal structure can be inferred from the micrograph of a partially-broken whisker shown in Fig. 5. The shape of the fragments indicates that the whiskers have a ribbon-like texture rather than one consisting of rod-like fibrils. This suggestion is also supported by scanning electron microscopy (Fig. 3b) which shows that the surface of the whisker ends is broken into highly irregular, branched units.

The whiskers grown in the presence of camphene (Whiskers II) are more fibrous than Whiskers I and are split into thin fibrils. The fibrils are sufficiently transparent in the electron beam to be suitable for transmission electron microscopy. Fig. 6a and b shows bright- and dark-field micrographs of such fibrils. The minimum thickness of individual fibrils is around 20 nm which is comparable with the periodicity derived from the electron diffraction of $(SN)_x$ specimens split off from bulk crystals [3]. The dark field micrograph shows striations parallel to the fibril and polymer chain axis with a minimum width of about 3 nm. Similar striations were also found in the transmission electron micrographs of fibrils and sections prepared from bulk $(SN)_x$ crystals [3]. This indicates that on this scale the structure of whiskers and that of bulk crystals is not basically different.

The electron diffraction pattern of a fibril branched from a Whisker II is shown in Fig. 7. The pattern corresponds to the $(h\ k\ 0)$ reciprocal lattice plane. In addition to the spots indexed on the $(hk0)$ net the pattern also contains prominent $\bar{1}\,0\,2$ reflections which indicate the twinning on the $(\bar{1}\,0\,1)$ plane [3]. The $(0\,2\,0)$ spots are extensively streaked in the direction perpendicular to the chain and the fibre axis which is consistent with the directly observed fibrosity.

4. Discussion

4.1. Vapour–liquid–solid mechanism of growth of disulphur dinitride whiskers

It is generally accepted that the fibrous texture of poly(sulphur nitride) develops during the poly-

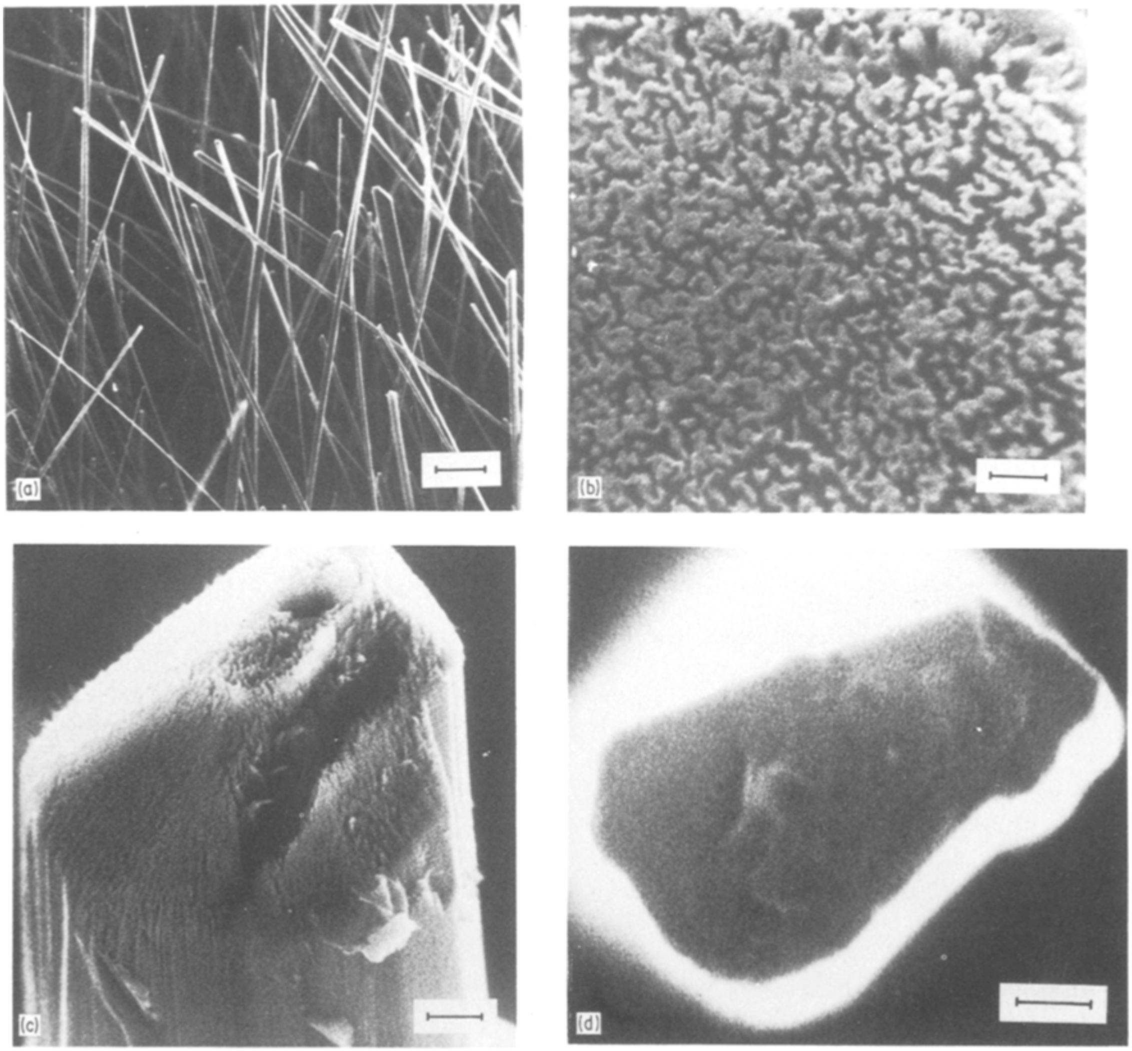

Figure 3 Scanning electron micrograph of whiskers grown in the presence of borneol. The bar corresponds to (a) 50 μm; (b) 0.5 μm; (c) 2 μm; and (d) 0.5 μm.

merization of disulphur dinitride crystals. This follows from the observation that polymerization is a much slower process than the growth of monomer crystals at the temperatures and supersaturations commonly used. The fact that the growth of disulphur dinitride whiskers is promoted by the presence of borneol or camphene vapour favours the vapour–liquid–solid (VLS) mechanism of their growth. According to this mechanism [15, 16] growth proceeds via a liquid-like layer of impurity located on the whisker tip which represents an ideally rough surface for the crystal growth. The activation energy of crystal growth by the VLS mechanism is much lower than that involved in the growth directly from the vapour [17]. The whisker therefore grows rapidly in the direction of its axis even at low supersaturations when a screw dislocation would otherwise have been necessary as a source of steps [18, 19]. Indeed, the majority of whiskers of different substances grown by this mechanism were found to be dislocation free [15, 16].

Wagner [15] has summarized the requirements necessary for impurities to promote whisker growth. Basically a suitable component should: (1) form a liquid solution with the crystalline material to be grown at the deposition temperature; (2) wet the substrate; (3) not be included at high concentration in the growing crystal; and (4) be chemically inert with the crystal substance.

It is expected that borneol and camphene can fulfill all these requirements for it is known that

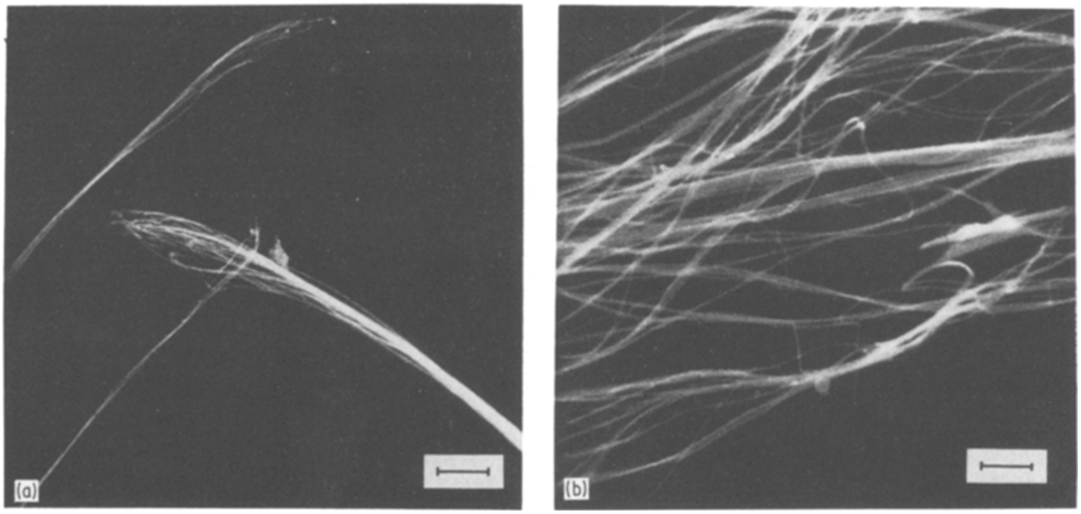

Figure 4 Scanning electron micrograph of whiskers grown in the presence of camphene. The bar corresponds to (a) 20 μm and (b) 1 μm.

disulphur dinitride is soluble in many organic solvents including alcohols, ketones, ethers, chlorinated hydrocarbons and aromatics [20]. Further, the molecules of borneol and camphene are large and, therefore, they are not expected to be included in the S_2N_2 lattice. It is likely that borneol may not be chemically inert with S_2N_2 considering that a reaction of disulphur dinitride with methanol has been reported and an adduct compound $S_2N_2 \cdot CH_3OH$ confirmed by spectral analysis [21]. Nevertheless, the reaction of S_2N_2 with alcohols is reversible and may not interfere with the whisker growth in spite of the fact that the last condition is formally violated. On the other hand the presence of the possible adduct could facilitate the formation of liquid-like layer on the whisker tip as borneol alone is solid at the growth temperature (m.p. 208.6° C).

4.2. Development of disorder during polymerization

Generally, the whiskers are known to be more perfect than the bulk crystals. It has been shown that the former have fewer defects and dislocations; this results in their superior mechanical properties [22]. There is no reason to doubt that the nascent disulphur dinitride whiskers are similar in this respect and that it is the subsequent polymerization process which is responsible for the disorder observed in poly(sulphur nitride) whiskers.

In attempting to explain the development of disorder and fibrosity during polymerization of disulphur dinitride crystals, two mechanisms have been considered [3, 23]: (1) It is suggested that there is a phase separation at some critical conversion due to the mismatch between the monomer and the polymer crystal lattices. (2) It is recalled that the ring-opening polymerization of disulphur dinitride is not a unique process [24]. It results in two different orientations of polymer chains which are in a twin relation [23, 24] and such a micro-twinning can account for the observed striations.

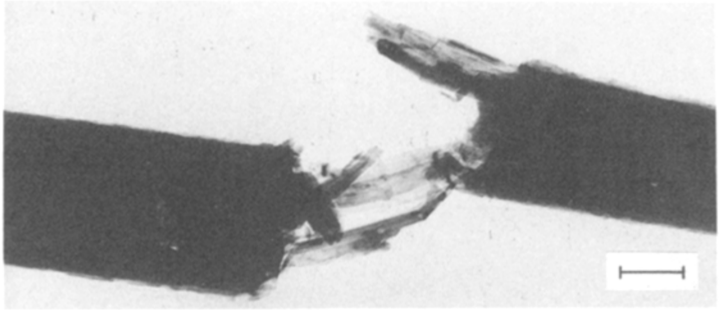

Figure 5 Transmission electron micrograph of a partially broken whisker grown in the presence of borneol. The bar corresponds to 0.2 μm.

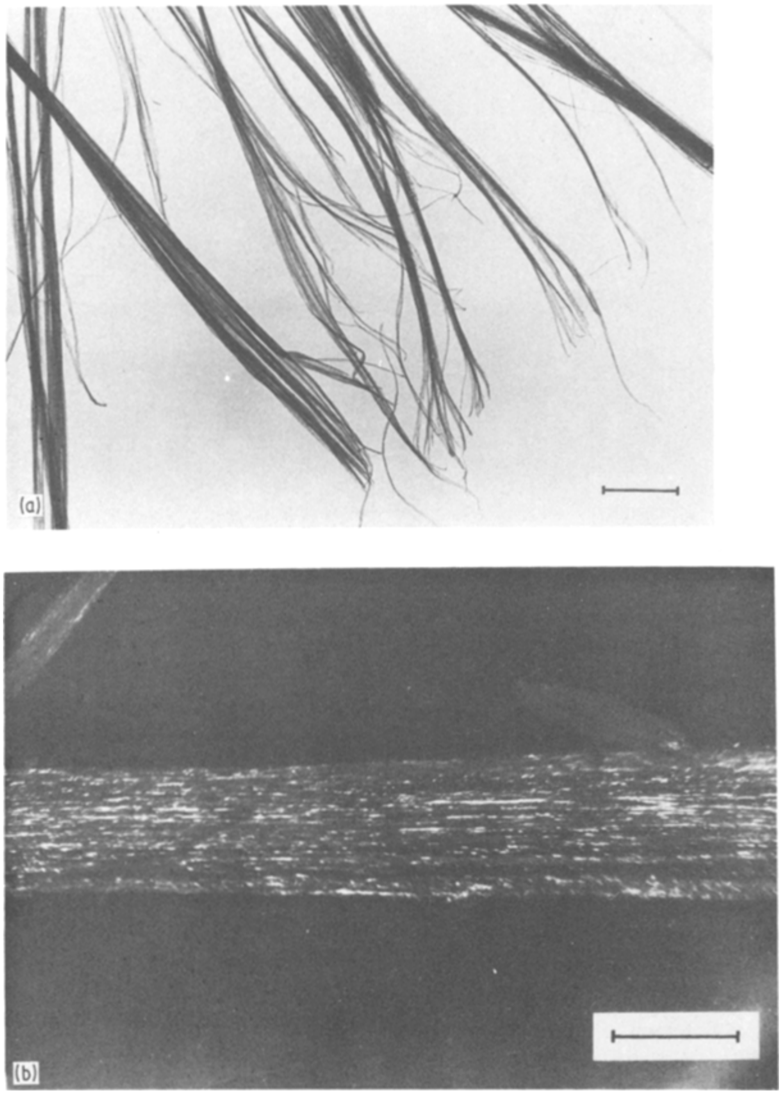

Figure 6 (a) Bright-field and (b) dark-field electron micrographs of whiskers grown in the presence of camphene. The bar corresponds to 0.5 μm.

4.3. Percolation as a model for solid state polymerization

In general, a solid-state polymerization of a perfect monomer crystal is initiated randomly throughout the crystal lattice and propagates rapidly in a crystallographically-related chain direction. If the initiation rate is much slower than the propagation rate and if the presence of a polymer chain does not influence the polymerization process of the adjacent monomer, the partly polymerized crystal will consist of oriented polymer chains randomly distributed in the monomer crystal lattice. At a low conversion there is a high probability that the polymer chains are isolated and separated from one another by the monomer. With increasing conversion the probability of another chain appearing as the nearest neighbour of a given chain becomes significant and clusters of polymer chains in the shape of fibrils are formed. This process is an analogy to a site percolation problem [25]. If only the lateral size and arrangement of the fibrils are considered, the problem can be reduced to the site percolation on a two-dimensional lattice. This general problem was extensively studied and its properties (size distribution of the clusters, their shapes, critical point, etc.) were characterized [25–27]. The development of the polymer fibrils in the partially polymerized monomer matrix can be described by this model. However, the model can not explain the fibrosity of fully polymerized $(SN)_x$ because the model predicts that with increasing conversion the fibrils should coalesce

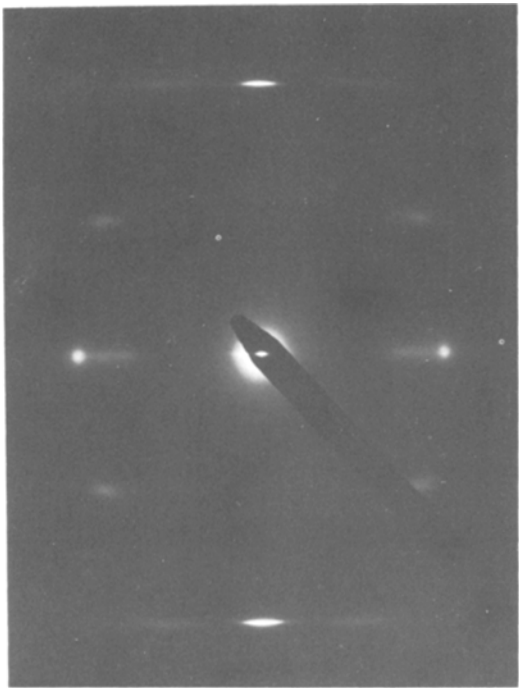

Figure 7 Electron diffraction pattern of a fibril branched from a whisker grown in the presence of camphene.

into larger ones, thus forming eventually a single polymer crystal. A possible example of the behaviour corresponding to the percolation model is the polymerization of some diacetylenes where the polymerization proceeds in solid solution over the whole conversion range [28].

4.4. Phase separation in polymerizing disulphur dinitride

The X-ray investigations by Cohen *et al.* [29] of partially polymerized disulphur dinitride led Baughman and Chance [23] to the conclusion that, at least up to some intermediate degree of conversion, the polymerization of disulphur dinitride takes place in solid solution. The possibility of a phase separation at some later stage of polymerization can not, however, be excluded on the evidence of Cohen's [29] investigation alone.

If the phase separation occurs as the result of a mismatch between the monomer and polymer crystal lattices the following mechanism can be suggested. Before the phase separation takes place the stress at the monomer–polymer boundary will increase with the lateral size of the polymer fibrils. When some critical stress is reached phase separation will occur and the fibrosity corresponding to that existing at these critical conditions will be preserved in the fully polymerized crystal. Such a development of a fibrous texture as the result of phase separation during solid-state polymerization of diacetylenes was observed by Kaiser *et al.* [30].

The separation of the polymer fibril from the monomer matrix after some critical stress has been reached will limit its maximum possible size. This will result in a fairly uniform size distribution of the fibrils compared with the broad distribution of cluster sizes in the percolation problem. The separation of the fibrils will also depend on the shape of their cross-sections, the fibrils with the same cross-sectional area but less ramified shape will separate first. This will reduce the surface-to-volume ratio of the fibrils below that characteristic for the random clusters. It is also possible that in the process of phase separation the branches of the polymer cluster (or the intruding monomer) will be broken off resulting again in a smoother surface of the polymer fibrils.

Studies of solid-state polymerization of diacetylenes have shown that the polymerization slows down or stops completely after the phase separation has occurred [28]. This observation indicates that the presence of the polymer chain in the monomer phase increases the polymerizability of the surrounding monomer. The simple percolation problem (which is based on equal probability of finding the polymer at any lattice point independently of the state of its neighbours) is not applicable in this case. An interacting (or correlated) percolation model similar to that for ferromagnets or lattice gas models for fluids [25] will have to be used. As the result of the different polymerizing probabilities at particular lattice points (depending on their positions in partly polymerized monomer) the polymerization process will consist of a nucleation stage followed by lateral growth of the polymer fibrils. The nucleation stage will be related to the polymerization induction period. A quantitative model for single-phase solid-state polymerization was proposed by Baughman [31] and autocatalytic conversion curves for a strain-dependent chain initiation and propagation were predicted. The non-randomness of the polymerization will also influence the shape of the fibrils, their cross-sections will become more compact and less likely to contain occluded monomer.

4.5. Microtwinning

The application of a simple percolation model is further complicated by the non-uniqueness of the polymerization reaction. The symmetry of the ring-opening reaction results in two different but equally probable orientations of the poly(sulphur nitride) chain [24]. The two chain orientations are in a twin relation and can not be superposed by translation or rotation along the chain axis. Each lattice point occupied by the polymer chain can therefore exist in two different states and the polymerization process can be modelled by a polychromatic percolation [25]. If the two orientations of the polymer chain occur randomly so that a chain in a given orientation does not influence the polymerization mode of the neighbouring monomer, the individual polymer fibrils will contain the chains in both orientations. According to the percolation model the chains in the same orientation will form clusters within the polymer fibrils so that most of the fibrils will be composed of microtwins. The other extreme corresponds to the situation when the polymerization mode of the monomer stack adjacent to the polymer is uniquely determined by the orientation of the neighbouring chain. In this case, most of the polymer fibrils will have a uniform chain orientation and there will be little twinning within individual fibrils provided that the concentration of nucleating chains is low. However, the relative orientation of the crystal lattice in the neighbouring fibrils will still be expected to be either nearly identical or close to that of the twins depending on the polymerization mode of the nucleating chain.

Because of these complications, the application of the percolation model to the structure of $(SN)_x$ is limited to a qualitative description only. The electron diffraction pattern (Fig. 7) and the dark-field electron micrograph (Fig. 6b) show the presence of microtwins within the individual fibrils. This observation together with the surface and internal structure found in Whiskers I indicates that the microtwinning takes place on a smaller scale than the formation of the fibrils during the phase separation. This would not favour the second of the two polychromatic pecolation mechanisms considered above, however, a quantitative analysis of the appropriate percolation model would be necessary to compare its behaviour with the development of the poly(sulphur nitride) structure during polymerization.

5. Summary

(1) A method for preparation of poly(sulphur nitride) in the whisker form by solid-state polymerization of disulphur dinitride whiskers has been established. The disulphur dinitride whiskers were grown from the vapour at low supercoolings in the presence of borneol or camphene as the whisker growth promoting impurities. The vapour–liquid–solid mechanism of whisker growth is considered to operate under these conditions.

(2) The morphology and structure of the whiskers were examined by optical, scanning and transmission electron microscopy. A difference in the morphology of whiskers grown in the presence of borneol as opposed to camphene was observed. The whiskers were found to consist of irregularly-shaped fibrils composed of microtwins. It was suggested that the development of the internal structure in poly(sulphur nitride) whiskers during polymerization can be modelled by a two-dimensional correlated polychromatic percolation.

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References

1. G. B. STREET and R. L. GREENE, *IBM J. Res. Dev.* 21 (1977) 99.
2. W. D. GILL, W. BLUDAN, R. H. GEISS, P. M. GRANT, R. L. GREENE, J. J. MAYERLE and G. B. STREET, *Phys. Rev. Lett.* 38 (1977) 1305.
3. J. STEJNY, J. DLUGOSZ and A. KELLER, *J. Mater. Sci.* 14 (1979) 1291.
4. R. L. CIVIAK, C. ELBAUM, L. F. NICHOLS, H. I. KAO and M. M. LABES, *Phys. Rev. B* 14 (1976) 5413.
5. P. BARRETT, W. G. HERRENDEN-HARKER, M. G. PRIESTLEY and E. Z. da SILVA, *J. Phys. F: Met. Phys.* (1981) in press.
6. M. BOUDELLE, PhD thesis, Claude Bernard University, Lyon, France (1974).
7. R. H. HOEL and D. J. DINGLEY, unpublished work (1981).
8. J. PETERMANN and J. M. SCHULTZ, *J. Mater. Sci.* 14 (1979) 891.
9. R. J. YOUNG and R. H. BAUGHMAN, *ibid.* 13 (1978) 55.
10. J. HALLETT and B. J. MASON, *Nature* 181 (1958) 467.
11. V. J. SCHAEFER, *Science* 104 (1946) 457.
12. *Idem, Chem. Rev.* 44 (1949) 291.
13. I. TARJAN and M. MATRAI, "Laboratory Manual on Crystal Growth" (Akademiai Kiado, Budapest, 1972).

14. H. KAHLERT and B. KUNDU, *Mater. Res. Bull.* **11** (1976) 967.
15. R. S. WAGNER, in "Whisker Technology", edited by A. P. Levitt (Wiley-Interscience, New York, 1970) pp. 47–119.
16. E. I. GIVARGIZOV, in "Current Topics in Materials Science", Vol. 1, edited by E. Kaldis (North-Holland, Amsterdam, 1978) pp. 79–145.
17. R. A. LAUDISE, "The Growth of Single Crystals" (Prentice-Hall, Englewood Cliffs, NJ, 1970) p. 317.
18. G. W. SEARS, *Acta Met.* **1** (1953) 457.
19. *Idem, ibid.* **3** (1955) 361, 367.
20. M. GOEHRING and D. VOIGT, *Z. Anorg. Allgem. Chem.* **285** (1956) 181.
21. M. GOEHRING, *Quart. Rev.* **10** (1956) 437.
22. A. P. LEVITT, "Whisker Technology" (Wiley-Interscience, New York, 1970) pp. 1–12.
23. R. H. BAUGHMAN and R. R. CHANCE, *J. Polymer. Sci. Polymer Phys. Ed.* **14** (1976) 2019.
24. R. H. BAUGHMAN, R. R. CHANCE and M. J. COHEN, *J. Chem. Phys.* **64** (1976) 1869.
25. D. STAUFFER, *Phys. Reports* **54** (1979) 1.
26. P. DEAN, *Proc. Camb. Phil. Soc.* **59** (1963) 397.
27. P. DEAN and N. F. BIRD, *Nat. Phys. Lab. Report Ma 61*, Teddington, England (1966).
28. G. WEGNER, E. W. FISCHER and A. MUNOZ-ESCALONA, *Macromol. Chem. Suppl.* **1** (1975) 521.
29. M. J. COHEN, A. G. GARITO, A. J. HEEGER, A. G. MacDIARMID, C. M. MIKULSKI and M. S. SARAN, *J. Amer. Chem. Soc.* **98** (1976) 3844.
30. J. KAISER, G. WEGNER and E. W. FISCHER, *Israel J. Chem.* **10** (1972) 157.
31. R. H. BAUGHMAN, *J. Chem. Phys.* **68** (1978) 3110.

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