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Polymerization and structure of poly(sulphur nitride) prepared under high pressure

H. KANAZAWA*, J. STEJNY, A. KELLER
H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

Poly(sulphur nitride) was prepared by spontaneous solid state polymerization of disulphur dinitride crystals immersed in perfluoro(methyl cyclohexane). The polymerization was carried out at hydrostatic pressures of up to 3.5 kbar in order to eliminate the lattice strain due to the mismatch in the monomer and the polymer lattice in the polymerization direction. It was observed that the pressure had no marked effect on the polymerization rate. The structure of the $(SN)_x$ samples polymerized at high hydrostatic and at atmospheric pressure was examined by electron microscopy and electron diffraction techniques. They were complemented by the measurements of $(SN)_x$ densities and electrical conductivities in the direction along and across the polymer chains. The results show that there is no significant difference in the structure and in the density of the high and the low pressure polymerized $(SN)_x$. A modest increase in the electrical conductivity parallel to the polymer chains observed in the high pressure polymerized $(SN)_x$ is explained by a pressure induced increase in the average chain length. It is concluded that the long range lattice strain originating from the monomer–polymer lattice mismatch in the polymerization direction is less important for the solid state polymerization of $(SN)_x$ than the nearest-neighbour interactions in the direction across the chain.

1. Introduction

Poly(sulphur nitride) $(SN)_x$ is a unique polymer; it is a highly anisotropic synthetic metal which undergoes a superconducting transition at temperatures close to absolute zero. As such a behaviour is rather unusual for polymers, $(SN)_x$ structure and properties have been the subject of extensive studies over the past 10 to 15 years [1–3].

Poly(sulphur nitride) is prepared by spontaneous solid state polymerization of disulphur dinitride crystals [4, 5]. In the early stages of polymerization the polymer chains grow in solid solution in the monomer crystal lattice until some intermediate conversion is reached when a phase transformation occurs. During this transformation a chain aligned, but otherwise rather disordered solid solution is transformed into a more ordered polymer β-phase [6]. Regardless of better three-dimensional order of the $(SN)_x$ chains in fully polymerized β-phase the $(SN)_x$ crystals are highly fibrous on the scale down to about 20 nm [7, 8]. The fibrils are oriented parallel to the chain axes and, together with other structural defects, they seriously interfere with the determination of inherent properties of $(SN)_x$ chains and defect-free polymer crystals [9].

Solid state polymerization studies suggest [10] that if the polymerization of perfect monomer crystals takes place in solid solution over the whole conversion range then such a polymerization should yield polymer crystals with no fibrosity. If a phase separation occurs at some intermediate conversion the resulting polymer crystals are, however, expected to be fibrous. A crucial condition for polymerization taking place in solid solution and preventing a phase separation is that the difference between the monomer and polymer lattice dimensions is sufficiently small. If this condition is fulfilled then no appreciable stress can develop in the partly polymerized crystal, the phase separation is not favoured and the polymerization can proceed in solid solution up to the full conversion.

The differences between the lattice parameters of single phase S_2N_2 crystals which were partially polymerized to about 20% conversion [11] and their initial values for pure monomer are $a = -0.56\%$, $b = -0.32\%$, $c = +0.24\%$ and $V = -0.24\%$. The largest difference is along the a axis which is the polymerization direction in the monomer crystal. After the phase transformation this direction becomes the b axis in the monoclinic cell of fully polymerized $(SN)_x$ and it coincides with the direction of its chain axis. Even in the fully polymerized $(SN)_x$ the decrease in the lattice period in the polymer chain direction as compared with the pure monomer is, however, only about 1%. This value is much less than the corresponding contraction along the chain direction observed in the solid state polymerization of diacetylene toluene sulphonate (PTS) crystals which takes place in solid solution over the whole conversion range and does not undergo a phase separation [12].

The mismatch between the length of $(SN)_x$ chain in the polymer and the corresponding length of the

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* *Present address*: Faculty of Education, University of Fukushima, Matsukawa-Machi, Fukushima-Shi, 960-12, Japan.

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monomer stack in disulphur dinitride crystals means that the monomer matrix in the partly polymerized solid solution of $(SN)_x$ is compressed in the polymerization direction. Lochner *et al.* [13, 14] using PTS as an example have shown that this mismatch and the corresponding stress can be reduced by the application of hydrostatic pressure. The longitudinal elastic moduli of polymer chains (especially in a planar zig-zag conformation as in $(SN)_x$) are much higher than those of monomer crystals, hence with increasing hydrostatic pressure the difference in the polymer and the monomer crystal lattice period in the chain direction should decrease and, eventually, become zero at some particular value of the pressure. At this point the stress on the monomer–polymer boundary in the single phase partly polymerized crystal should disappear. At even higher hydrostatic pressures the monomer lattice period may become smaller than that of the polymer chain resulting in a cross-over of the lattice period against pressure curves for the monomer and the polymer.

In order to determine the value of hydrostatic pressure needed for such a stress free single phase solid state polymerization, the compressibilities of the polymer and the monomer crystal lattice have to be known. The compressibilities of $(SN)_x$ crystal in different crystallographic directions were determined by Clarke [15] using X-ray diffraction methods for pressures up to 22 kbar. As expected, the linear compressibility in the chain direction is less than half of the compressibility values in the directions across the chains. Unfortunately, the compressibilities of disulphur dinitride crystal are not known. It can, however, be assumed that they will not differ significantly from the lateral compressibilities of $(SN)_x$ because there is little difference in the dimensions of the lattice and the nature of the bonding between disulphur dinitride and $(SN)_x$ in the directions across the chains. It was therefore assumed that the compressibility of disulphur dinitride in the polymerization direction is not smaller than the minimum value of compressibility of $(SN)_x$ found in a direction across the chains. According to Clarke [15] this compressibility minimum lies in the (2 0 1) crystallographic plane which is the plane of the chain zig-zag and it is also the plane of the closest packing of the $(SN)_x$ chains [11].

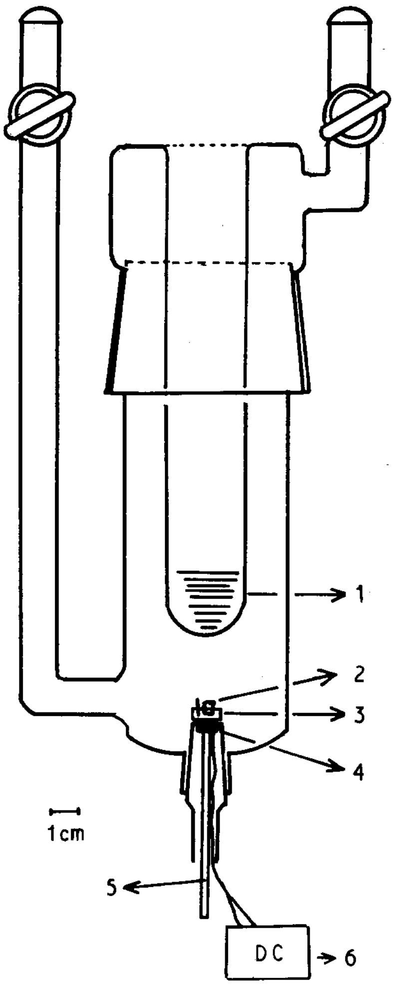

Figure 1 Cell used for the growth of S_2N_2 crystals. (1) cold finger, (2) crystals, (3) cup, (4) Peltier module, (5) copper rod as heat sink, (6) power source for the Peltier module.

Taking account of the assumptions discussed above, Clarke's data were used in this work to estimate the upper limit of the hydrostatic pressure needed for stress free solid state polymerization of disulphur dinitride. The value obtained is 4 kbar which can be achieved by conventional hydraulic apparatus. In this work the solid state polymerization of disulphur dinitride at 3 to 3.5 kbar hydrostatic pressure was carried out. The structure and properties of the resulting $(SN)_x$ polymer were examined and compared with those of the $(SN)_x$ crystals polymerized at atmospheric pressure but otherwise identical conditions.

2. Experimental procedure

2.1. Preparation of disulphur dinitride crystals

Disulphur dinitride was prepared by pyrolysis of tetrasulphur tetranitride as described previously [5, 7]. A cell shown in Fig. 1 was used to grow large crystals of S_2N_2. Purified S_2N_2 was introduced under vacuum into the cell and trapped on a cold finger (1) containing liquid nitrogen. The cold finger was warmed rapidly to room temperature (23 °C) and the S_2N_2 was allowed to sublime in vacuum into a cup (3) facing the cold finger and cooled by a Peltier element (4). The temperature of the cup was monitored by a thermocouple and maintained at 10 to 12 °C below the temperature of the finger (1). Prismatic crystals of S_2N_2 with typical dimensions of 5 to 7 mm in length (corresponding to the chain direction in the polymer crystal) and 2 to 5 mm in width were obtained after 6 to 12 h of crystal growth. Over this period of time the crystals progressively darkened from white to blue–black indicating that spontaneous polymerization takes place. However, it was found that the amount of polymer formed in the blue–black crystals was negligible because they were volatile and left practically no deposit after their evaporation in vacuum at room temperature.

2.2. Polymerization of disulphur dinitride crystals

In order to transmit hydrostatic pressure to the polymerizing disulphur dinitride crystals a suitable liquid medium was needed. It was found that perfluoro(methylcyclohexane) was chemically inert and a non-solvent for both disulphur dinitride crystals and $(SN)_x$. No difference was observed in the polymerization process or the structure of $(SN)_x$ when disulphur dinitride crystals were polymerized at atmospheric pressure while fully immersed in perfluoro(methylcyclohexane) as compared to the crystals polymerized in vacuum or dry nitrogen. Perfluoro(methylcyclohexane) was therefore used as the medium for high pressure polymerization of disulphur dinitride crystals.

The high pressure polymerization was carried out in a cell of about 20 ml internal volume filled with methanol–castor oil mixture used as the hydraulic fluid and connected to a high pressure generator capable of delivering 4.5 kbar hydrostatic pressure [16]. Disulphur dinitride crystals were sealed in a polypropylene container filled with perfluoro(methylcyclohexane) which was placed in the high pressure cell kept at 40 °C and left to polymerize at 3 to 3.5 kbar pressure for up to 26 days. Safety precautions were observed when handling disulphur dinitride crystals owing to the explosive properties of this material [17]. Disulphur dinitride crystals polymerized under the same conditions but the atmospheric pressure were used as the reference.

2.3. Crystal density

The densities of $(SN)_x$ crystals polymerized under atmospheric and high hydrostatic pressure were measured by the flotation method. A mixture of heptane and bromoform was used.

2.4. Electron microscopy

Thin fibres of $(SN)_x$ were stripped off from the sides of the $(SN)_x$ crystals using an adhesive tape. The fibres were dispersed in chloroform and deposited on copper grids for examination in a Philips E301 transmission electron microscope.

The surface of $(SN)_x$ crystals was examined in a JEOL 840 scanning electron microscope.

2.5. Electrical conductivity

Direct current (d.c.) conductivities in the directions along and across the $(SN)_x$ chain axis ($\sigma_{\parallel}$ and $\sigma_{\perp}$, respectively) were measured by a four-probe method under the guidance of Dr Gugan of this Department [9]. Gold wires were used as potential and current probes glued on to the surface of $(SN)_x$ crystals with gold paint. A typical distance between neighbouring two probes was 1 to 1.5 mm, the current used for the conductivity measurements was 10 to 100 μA.

3. Results and discussion

3.1. Polymerization

The compression of the monomer matrix in the polymerization direction caused by the mismatch between the monomer and polymer lattice should have a pronounced effect on the polymerization kinetics. A theory of this effect was developed by Baughman [18] who has shown that the lattice strain should significantly change the initiation and propagation rates. These changes would result in an autocatalytic character of the polymerization kinetics and they were invoked to explain the induction period and the autoacceleration observed in the single phase solid state polymerization of PTS crystals [19]. It was also found [13] that the autocatalytic effect in PTS polymerization disappeared at about 3 kbar hydrostatic pressure when the monomer and the polymer lattice dimensions were equal. However the induction period decreased with pressure at much faster rate than that predicted by Baughman's theory [14].

Our previous work [20] has shown that the kinetics of solid state polymerization of $(SN)_x$ at atmospheric pressure is autocatalytic, the shapes of conversion curves are sigmoidal and similar to those observed in the polymerization of PTS. It was therefore expected that the application of hydrostatic pressure to S_2N_2 would have similar effect and greatly increase the polymerization rate. It was however found that there is no significant difference in the polymerization rate (as judged by the time needed to reach golden lustre) between polymerization at atmospheric pressure and at pressures of up to 3.5 kbar. This result leads to the conclusion that the long range strain caused by the lattice mismatch in the polymerization direction is not the dominant factor determining the polymerization kinetics of $(SN)_x$. This claim is supported by the results of our previous study of polymerization kinetics of $(SN)_x$ [20] which suggests that the nearest-neighbour interactions between the growing chain and the monomer lattice are more important than the long range lattice strain. The importance of the lattice strain for the solid state polymerization kinetics of diacetylenes was questioned by Williams *et al.* [21] who found that the autocatalytic character of polymerization curves was widely different for diacetylenes with similar lattice strain.

3.2. Structure

Transmission electron micrographs of $(SN)_x$ polymerized under atmospheric and high hydrostatic pressure are shown in Fig. 2a and b. They both exhibit identical fibrous structure which is characteristic for $(SN)_x$ polymerized in solid state [7]. Fig. 3a and b show electron diffraction patterns from fibres stripped from the same samples. Both patterns were taken with the beam perpendicular to the fibre axis giving patterns which correspond to the reciprocal lattice sections containing the unique b^* axis. The patterns exhibit characteristic streakiness along the layer lines which is related to the lateral size of the fibrils. It was found that there is no significant difference in the electron diffraction patterns and the size of the streaks for the $(SN)_x$ samples polymerized at the atmospheric and the high hydrostatic pressure. Both the micrographs and the diffraction patterns show that application of hydrostatic pressure on polymerizing S_2N_2 has little effect on the structure of the resulting polymer. This is also supported by our scanning electron microscopy

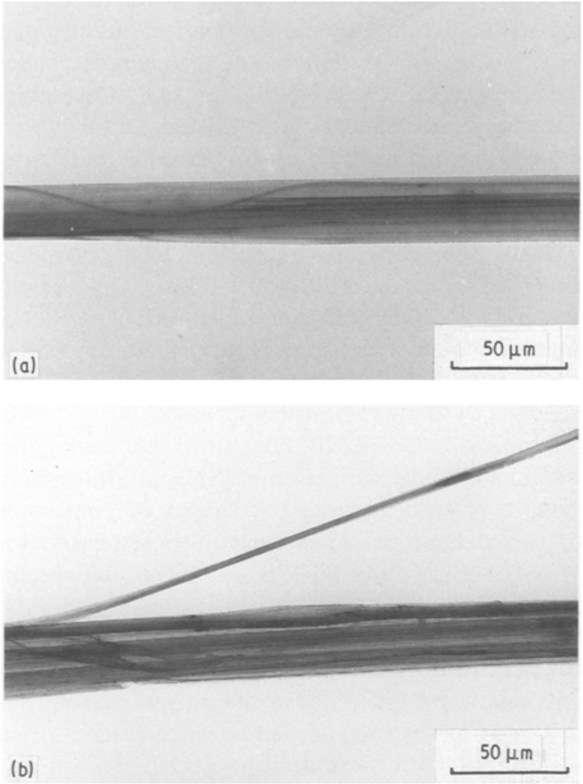

Figure 2 Transmission electron micrograph of $(SN)_x$ prepared (a) under 3.5 kbar hydrostatic pressure, (b) at atmospheric pressure.

investigation (Fig. 4) and by our results of density measurements which gave values close to the crystal lattice density ($d = 2.306$) and showed no change for the samples polymerized at high pressure.

3.3. Electrical conductivity

Fig. 5 shows the results of electrical conductivity measurements of $(SN)_x$ samples prepared under atmospheric and high pressure in the direction along and across the chain axis. The measurements were carried out over the temperature range from 4.8 to 250 K. As follows from the Fig. 5 the conductivities in the chain direction ($\sigma_{||}$) are up to 8 times higher for the high pressure polymerized $(SN)_x$ while the conductivities across the chain ($\sigma_{\perp}$) are practically the same for both samples. This increase can be explained if the effect of the lattice strain on the chain length is considered. As follows from Baughman's theory [18] the reduction of lattice mismatch in the polymerization direction by the hydrostatic pressure would generally increase the chain propagation length and especially the propagation length of those chains formed at the early stage of polymerization. The increase in the chain propagation length should result in the increase in $\sigma_{||}$ provided that the concentration of impurities and other structure defects are low and that other conditions (quality of contacts, etc.) which can influence the conductivity measurements remain the same. An increase in the chain length and in the conductivity of a substituted polydiacetylene polymerized under high hydrostatic pressure was reported by Tanaka *et al.* [22]. Our values of $\sigma_{||}$ obtained on bulk pressure polymerized $(SN)_x$ crystals are, however, still by up to an order of magnitude lower than the highest $\sigma_{||}$ values of SN_x samples which were prepared from S_2N_2 whiskers polymerized at atmospheric pressure in our laboratory [23] and elsewhere [24]. This fact shows that a superior crystal perfection and purity expected for

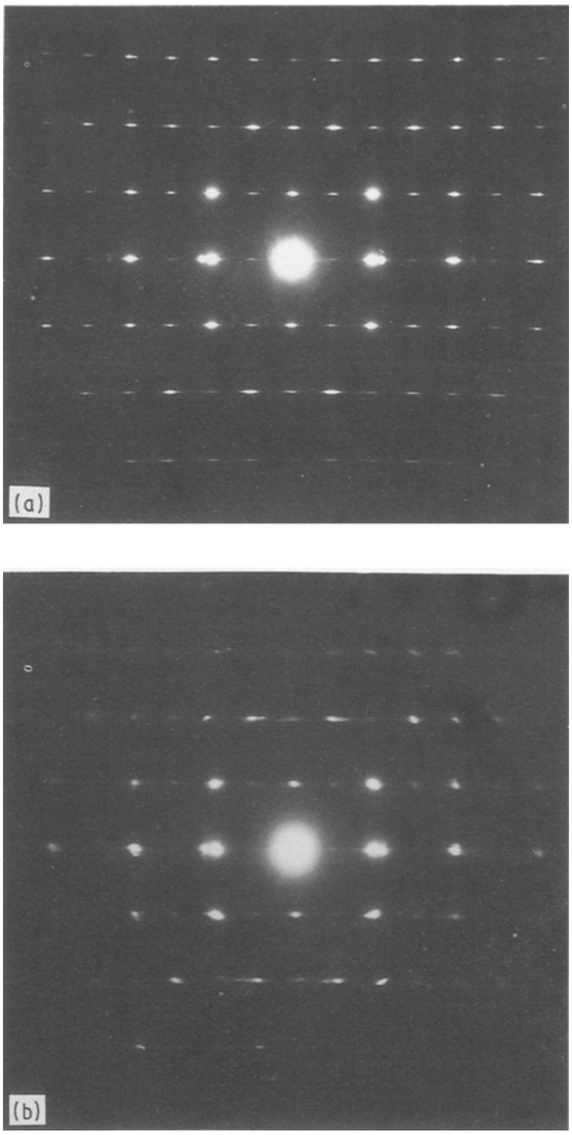

Figure 3 Electron diffraction pattern of $(SN)_x$ prepared (a) under 3.5 kbar hydrostatic pressure, (b) at atmospheric pressure.

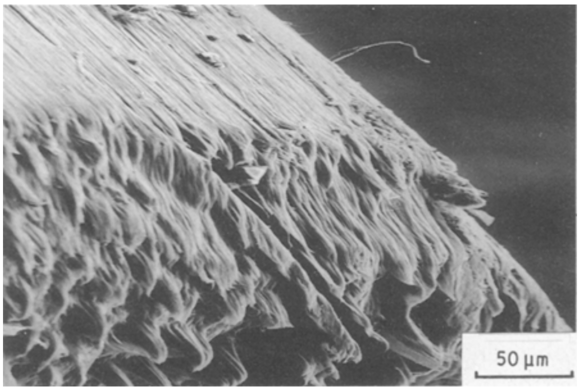

Figure 4 Scanning electron micrograph of the surface of SN_x crystal prepared under 3.5 kbar hydrostatic pressure.

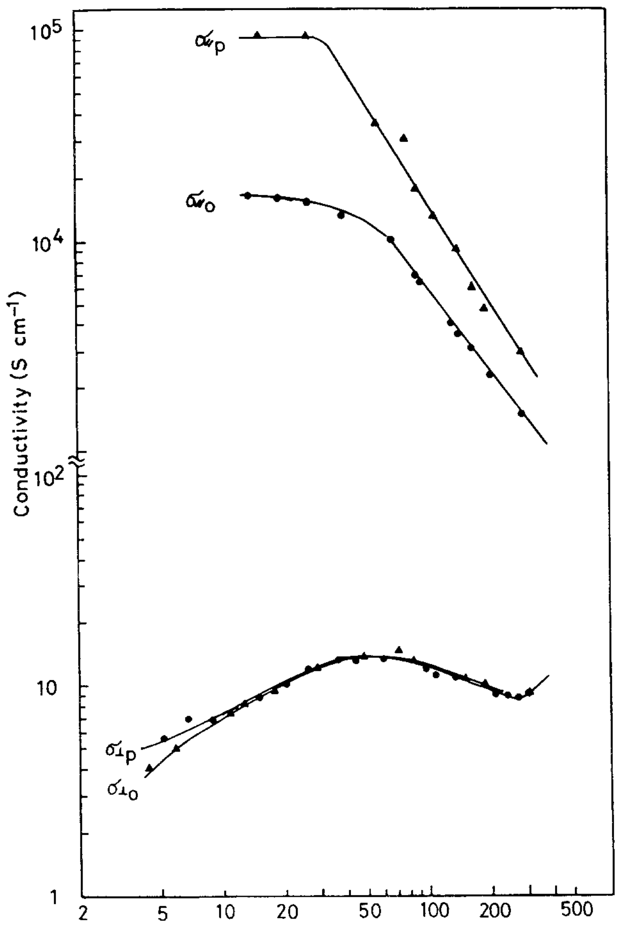

Figure 5 DC conductivity σ along (∥) and across (⊥) the chain direction of $(SN)_x$ samples prepared under 3.5 kbar hydrostatic pressure (p), and at atmospheric pressure (o).

disulphur dinitride whiskers and/or their higher surface to volume ratio are at least as important as the polymerization pressure for achieving highly conducting $(SN)_x$. The important role of the surface to volume ratio for the polymerization process of $(SN)_x$ was established in our previous work on its polymerization kinetics [20] where it was shown that the kinetics of solid state polymerization of $(SN)_x$ is drastically influenced by the surface to volume ratio of the S_2N_2 crystals. It was inferred that the nearest-neighbour interactions in the lattice are more important for the polymerization kinetics than the long range lattice strain due to the lattice mismatch in the chain direction. This conclusion is also supported by the results of our present study of high pressure polymerization of $(SN)_x$.

4. Conclusions

The main result of this work shows that there is no significant effect of hydrostatic pressure on the polymerization rate and on the structure of pressure polymerized $(SN)_x$. A modest increase in the electrical conductivity of the pressure polymerized SN_x in the direction parallel to the chains can be explained by an increase in the average chain length induced by the pressure. These results lead to the conclusion that the long range lattice strain originating from the mismatch between the monomer and the polymer lattice in the chain direction is less important for the polymerization process of SN_x than the nearest-neighbour interactions in the lateral directions. This conclusion follows also from the results of our previous study on the polymerization kinetics of SN_x.

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References

1. V. V. WALATKA Jr., M. M. LABES and J. H. PERLSTEIN, *Phys. Rev. Lett.* **31** (1973) 1139.
2. C. H. HSU and M. M. LABES, *J. Chem. Phys.* **61** (1974) 4640.
3. R. L. GREENE, G. B. STREET and L. J. SUTTER, *Phys. Rev. Lett.* **34** (1975) 577.
4. C. M. MIKULSKI, P. J. RUSSO, M. S. SARAN, A. G. MacDIARMID, A. F. GARITO and A. J. HEEGER, *J. Amer. Chem. Soc.* **97** (1975) 6358.
5. G. B. STREET and R. L. GREENE, *IBM J. Res. Dev.* **21** (1977) 99.
6. R. H. BAUGHMAN and R. R. CHANCE, *J. Polym. Sci. Polym. Phys. Ed.* **14** (1976) 2019.
7. J. STEJNY, J. DLUGOSZ and A. KELLER, *J. Mater. Sci.* **14** (1979) 1291.
8. J. STEJNY, R. W. TRINDER and J. DLUGOSZ, *ibid.* **16** (1981) 3161.
9. P. BARRETT, D. GUGAN, W. G. HERRENDEN-HARKER and R. JEWSBURY, *J. Phys. F* **11** (1981) 557.
10. J. KAISER, G. WEGNER and E. W. FISHER, *Israel J. Chem.* **10** (1972) 157.
11. M. J. COHEN, A. F. GARITO, A. J. HEEGER, A. G. MacDIARMID, C. M. MIKULSKI, M. S. SARAN and J. KLEPPINGER, *J. Amer. Chem. Soc.* **98** (1976) 3844.
12. D. BLOOR, L. KOSKI, G. S. STEVENS, F. H. PRESTON and D. J. ANDO, *J. Mater. Sci.* **10** (1975) 1678.
13. K. LOCHNER, Th. HINRICHSEN, W. HOFBERGER and H. BÄSSLER, *Phys. Status Solidi a* **50** (1978) 95.
14. K. LOCHNER, H. BÄSSLER and Th. HINRICHSEN, *Ber. Bunsenges. Phys. Chem.* **83** (1979) 899.
15. R. CLARKE, *Solid State Commun.* **25** (1978) 333.
16. G. J. HILL, PhD Thesis, University of Bristol, Bristol (1962).
17. A. J. BANNISTER, in "Inorganic Syntheses", Vol. XVII, edited by A. G. MacDiarmid (McGraw-Hill, New York, 1977) p. 197.
18. R. H. BAUGHMAN, *J. Chem. Phys.* **68** (1978) 3110.
19. R. R. CHANCE and G. N. PATEL, *J. Polym. Sci. Polym. Phys. Ed.* **16** (1978) 859.
20. H. KANAZAWA, J. STEJNY and A. KELLER, *J. Mater. Sci.* **25** (1990) 3838.
21. R. L. WILLIAMS, D. J. ANDO and D. BLOOR, *Polymer* **21** (1980) 1269.
22. Y. TANAKA, S. IIJIMA, T SHIMIZU, H. FUJIKAWA, H. MATSUDA, H. NAKANISHI, M. KATO and S. KATO, *J. Polym. Sci.* **C24** (1986) 177.
23. P. BARRETT, PhD Thesis, University of Bristol, Bristol (1981).
24. H. KAHLERT and K. SEEGER, Physics and Semiconductors, Proceedings 13th International Conference, North-Holland Publ. Amsterdam, 1976, p. 353.

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