JOURNAL OF MATERIALS SCIENCE 25 (1990) 3838–3842

Kinetics of solid state polymerization of poly(sulphur nitride)

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

Kinetics of the solid state polymerization of disulphur dinitride into poly(sulphur nitride) was investigated using Fourier transform infrared spectroscopy in the temperature range 22 to 40° C. It was found that the polymerization is autocatalytic. The polymerization rate is strongly dependent on temperature and the overall activation energy of the polymerization in this temperature range was found to be 41 kcal mol^{-1}. The polymerization is also strongly dependent on the crystal size, at 23° C the polymerization of needle-like crystals of about 5 μm in width was complete in about 6 h but crystals of several millimetres in size reached conversion of only 40% in 6 days. It is concluded that the polymerization is much faster at the crystal surface than in its interior. Hence, it is suggested that the polymerization begins at the crystal surface and progresses towards the interior of the monomer crystal. The polymerization mechanism is discussed in terms of Baughman's theory of single-phase solid state polymerization; it is suggested that the autocatalytic character of S_2N_2 polymerization is better described by the effect of the nearest neighbour interactions than by the effect of long range lattice strain.

1. Introduction

Poly(sulphur nitride) $(SN)_x$ is singular amongst polymeric materials: it is a good conductor of electric current in general and a superconductor below 0.3 K in particular. It is not therefore surprising that this unique compound has been the focus of extensive studies in the past [1–3] to which the present work is a further addition. Generally, it is prepared by spontaneous solid state polymerization of crystallized disulphur dinitride S_2N_2 at room temperature [4, 5]. In most of the preparations the criterion for the completion of the polymerization was the appearance of a lustrous golden colour. A period of several days to several weeks was reported to be needed to reach full conversion [2, 4–6].

Although crystal structure transformations in polymerizing S_2N_2 were investigated in detail [6–8] there is little information on the kinetics of the polymerization. The intractability of the polymer and the reactivity and associated explosion hazard of the monomer (disulphur dinitride crystals are reported to explode if subjected to mechanical shock or rapid heating [9]) makes the choice of the experimental techniques rather limited. Infrared spectroscopy method involving no handling of the monomer was considered the most suitable. The IR spectra of S_2N_2 and $(SN)_x$ [10–12] exhibit a number of bands specific for the monomer and the polymer state hence the conversion can be easily determined from the absorbance of a particular band.

In this work the polymerization rate was determined by FT–IR in the temperature range 22 to 40° C. The apparent overall activation energy was estimated from the Arrhenius plot. In addition, the effect of the size of S_2N_2 crystals on the polymerization kinetics was established and a likely polymerization mechanism is suggested.

2. Experimental details

2.1. Preparation of disulphur dinitride

Disulphur dinitride was obtained by pyrolysis of tetrasulphur tetranitride S_4N_4 vapour on a silver wire at about 290° C under vacuum of 10^{-4} to 10^{-5} torr [5]. The S_2N_2 was trapped in an U-tube immersed in liquid nitrogen and purified by fractional sublimination. The purity was checked by IR spectroscopy.

Tetrasulphur tetranitride was prepared as described earlier [13] and purified by recrystallization from dioxane or benzene.

2.2. Polymerization of disulphur dinitride

Polymerization rates of crystalline films of disulphur dinitride were measured by FT–IR technique using a specially constructed thermostated cell placed in the sample well of Nicolet 7199 FT–IR instrument. The cell was evacuated and vapour of S_2N_2 was introduced and condensed on its KBr window which was cooled with liquid nitrogen. After a continuous film of S_2N_2 was formed, the cell was filled with dry nitrogen in order to prevent any subsequent transfer of S_2N_2 and the IR spectrum was recorded to check the purity and the amount of monomer. Much attention was paid to avoid contamination with water throughout the whole procedure. The spectra taken in some experiments

---

* *Present address*: Faculty of Education, University of Fukushima, Sugumichi, Matsukawa-machi, Fukushima-shi, 960-12, Japan.

have shown that very small amounts of impurities can decompose the monomer and produce some sulphur nitride derivatives.

After checking the purity of the monomer the cell was heated up and reached the required polymerization temperature within several minutes. The change in the IR spectra of the polymerizing monomer was monitored at a constant temperature over a period of time. Twenty seconds were needed to record each spectrum and four different polymerization temperatures were used (22, 30, 35 and 40° C).

The polymerization rates of large crystals of S_2N_2 were estimated gravimetrically as follows: an agglomerate of prismatic crystals with dimensions 1 to 3 mm in length and 0.2 to 1 mm in width was grown slowly from the vapour and was allowed to polymerize under nitrogen atmosphere at 23° C for 6 days. The unreacted monomer has been extracted by benzene and chloroform, the remaining polymer was thoroughly dried and the conversion was determined from its weight.

3. Results and discussion

3.1. Polymerization of the crystalline film of S_2N_2

After checking the amount and purity of S_2N_2 deposited at the KBr window at liquid nitrogen temperature by sampling the IR spectrum, the cell was heated up and reached the specified polymerization temperature within several minutes. No bands associated with the polymer were detected in the IR spectrum taken after reaching the polymerization temperatures of 22, 30 and 35°C and only negligible polymer peaks were found in the spectrum at 40° C. Hence, the polymerization time zero was assumed for this stage.

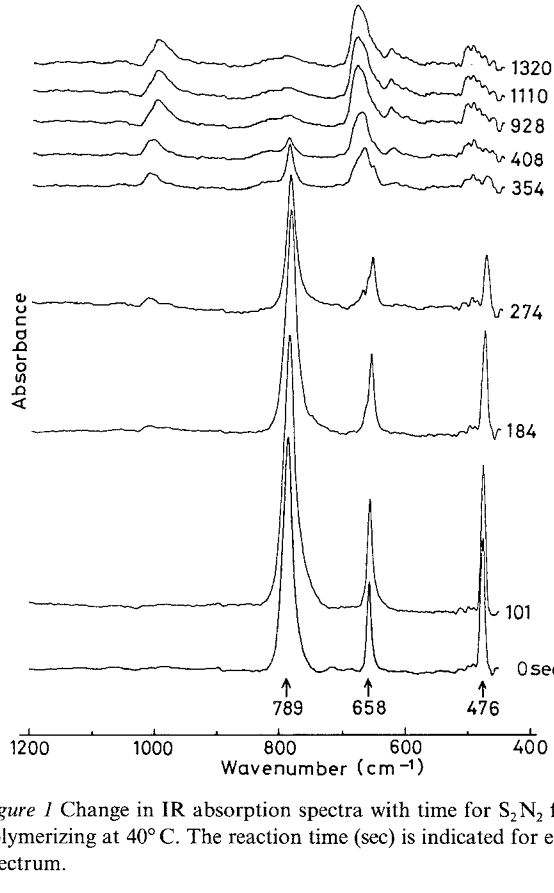

Figure 1 Change in IR absorption spectra with time for S_2N_2 film polymerizing at 40° C. The reaction time (sec) is indicated for each spectrum.

Figure 1 shows the spectra of S_2N_2 polymerized at 40° C. The spectrum of the unreacted S_2N_2 shows three sharp absorption bands at 476, 658 and 789 cm^{-1} which correspond to peaks observed by Warn and Chapman [10] at 474, 663 and 795 cm^{-1} which they assign to the vibration modes of B_{1u}, B_{2u} and B_{3u} respectively. As shown in Fig. 1, the absorbances of these peaks decrease rapidly with time with simultaneous appearance and growth of new peaks at around 1000, 670, 625 and 500 cm^{-1} which are associated with the resulting polymer. Macklin *et al.* [12] observed strong absorption peaks at 1001, 689, 629 and 500 cm^{-1} in the IR spectrum of $(SN)_x$ which coincide with peaks assigned to the polymer in our work. It was observed that the peaks at around 1000 cm^{-1} and around 670 cm^{-1} shift from 1012 to 1000 cm^{-1} and from 670 to 675 cm^{-1}, respectively, as the polymerization proceeds. The former peak corresponds to that found by Macklin *et al.* [12] at 1001 cm^{-1} and assigned to the ν_1A symmetric stretching of the S–N bond oriented across the polymer chain direction, the latter may correspond to the peak at 689 cm^{-1} with a shoulder at 662 cm^{-1} assigned to the ν_2A symmetric stretching of the S–N bond parallel to the chain [12]. The shift may be caused by the increase in the polymer molecular weight, by the anisotropy of the polymer chains or by the intermolecular interactions.

Because of its sharpness the monomer peak at 789 cm^{-1} was chosen as the most suitable for monitoring the polymerization. The values of polymer conversion at a given time were calculated from the ratio of the peak absorbance at that time to the peak absorbance at the time zero.

Fig. 2 shows the polymerization conversion curves for four different polymerization temperatures. The curves have a sigmoidal shape with a significant induction period inferring an autocatalytical character of the polymerization. At 22° C the induction period is about 40 min while it is only 1 or 2 min for the polymerization at 40° C. The apparent linearity of the curve at 22° C may be caused by an inadvertent temperature drift from 22 to 25° C at about half way through the polymerization time.

Maximum reaction rates were read from each curve in Fig. 2 and Arrhenius plots were obtained as shown in Fig. 3. The apparent overall activation energy (E_a) for the polymerization was 41 kcal mol^{-1}. This value is larger than activation energies in other solid state polymerizations: the activation energy reported for thermally initiated solid solutions of diacetylene toluene sulfonate (PTS) polymerization is 22 kcal mol^{-1}, the corresponding values for radiation and photo-initiated polymerization of PTS are even lower [14].

3.2. Electron microscopy of polymerized films of $(SN)_x$

Lustrous golden film of $(SN)_x$ was observed on the KBr window of the IR cell after the polymerization was complete. The film was stripped off and examined in a scanning electron microscope. Figs. 4a and b show micrographs of the polymer film obtained at 35° C in the experiment whose conversion curve

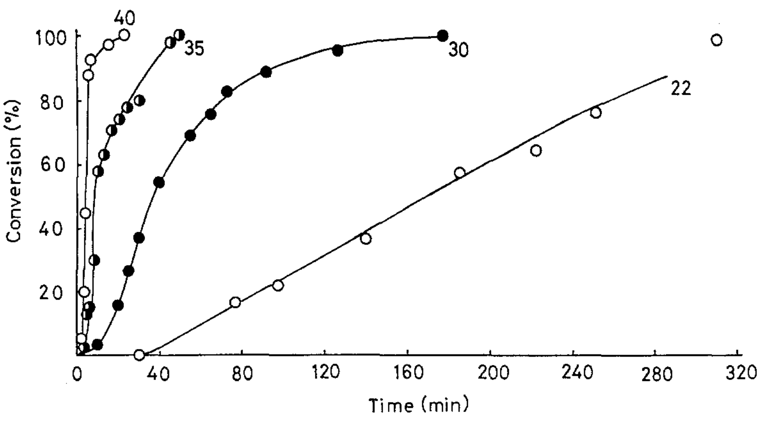

Figure 2 Conversion–time curves for S_2N_2 films polymerizing at 22, 30, 35 and 40° C.

is shown in Fig. 2. The micrographs indicate that the film consists of needle-like or prismatic crystals which are made of fibrous bundles of polymer. Typical dimensions of prisms are about 50 μm in length and about 5 μm in width, the prisms appear to be made of fibrous bundles of 0.5 to 0.7 μm in width.

Electron diffraction patterns of the polymer taken in a transmission electron microscope were found to correspond to the crystal structure reported previously [15].

3.3. Polymerization of large crystals of S_2N_2

It is known that the polymerization of large crystals of S_2N_2 does not reach completion in several days. Usually, the crystals are left at room temperature for several weeks in an inert atmosphere to complete the polymerization. This is in agreement with our results of conversion measurement obtained on large crystals by gravimetry when we got only 40% conversion after 6 days polymerization at 23° C. However, it contrasts with our FT-IR measurements of polymerization kinetics obtained on thin films (Fig. 2) when 40% conversion was reached in about $2\frac{1}{2}$ h. It also disagrees with the ESR measurements of concentration of radicals in polymerizing S_2N_2 crystalline film [6] which show that the radicals decay in about 12 h indicating the completion of the polymerization. The discrepancy between slow polymerization rates observed in large crystals and fast polymerization rates in microcrystalline films of S_2N_2 suggests that the surface to volume ratio plays an important role in polymerization kinetics of S_2N_2. This conclusion is supported by the observation of Mikulski *et al.* [4] who noticed that the polymerization of S_2N_2 crystals appears to commence on their surface.

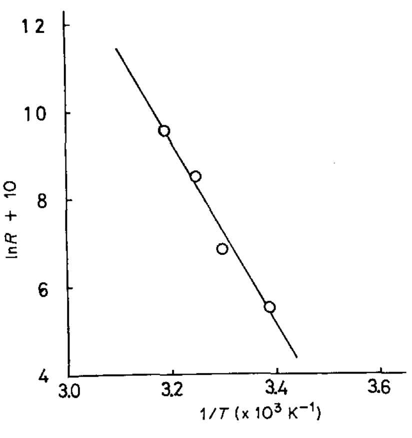

Figure 3 Arrhenius plot of the maximum polymerization rates.

3.4. Polymerization mechanism

It is accepted that the polymerization of S_2N_2 crystals takes place in solid solutions up to some intermediate conversion followed by phase transformation from a chain aligned but otherwise disordered polymerized dimer phase into more ordered polymer β-phase [8]. The crucial conditions for polymerization in solid solution is that there is little difference between the size of the monomer and the polymer crystal lattice so there is no appreciable stress developed in the partly polymerized crystal. In the single phase crystal of S_2N_2 polymerized to about 20% conversion the change in the *a*, *b*, *c* parameters of the lattice and in its volume is -0.56, -0.32, $+0.24$ and -0.24%, respectively, as compared with the initial values for pure unpolymerized S_2N_2 [6, 8]. The largest difference is along the *a* axis which is the polymerization direction and becomes the *b* axis of a monoclinic unit cell in the fully polymerized $(SN)_x$. However, even in the fully polymerized $(SN)_x$ the period along the chain direction is smaller by only about 1% than the corresponding period in the monomer lattice. This value is much smaller than the contraction along the chain direction of about 5% observed in the solid state polymerization of PTS [16]. The polymerization of PTS proceeds in single phase solid solution over the whole conversion range [14] regardless of considerable lattice strain developed at an intermediate conversion.

The sigmoidal shape of the conversion curves shown in Fig. 2. strongly resembles the shape of the autocatalytic conversion curves observed in the single phase polymerization of PTS [16]. Baughman [17] proposed a theory of single phase solid state polymerization and applied it successfully to the polymerization kinetics of PTS. He has shown that the autocatalytic character of PTS can be explained by the effect of lattice strain on the initiation and propagation rates. However, according to Baughman, even in the dimensionally invariant single phase polymerization, the change in the nearest neighbour interaction energy occurring in the polymerizing crystal will have a profound effect on the polymerization kinetics. This will result in a variety of shapes of the conversion curves ranging from autoinhibiting to autocatalytic depending on the value of the interaction energy change.

The theory of single phase solid state polymerization

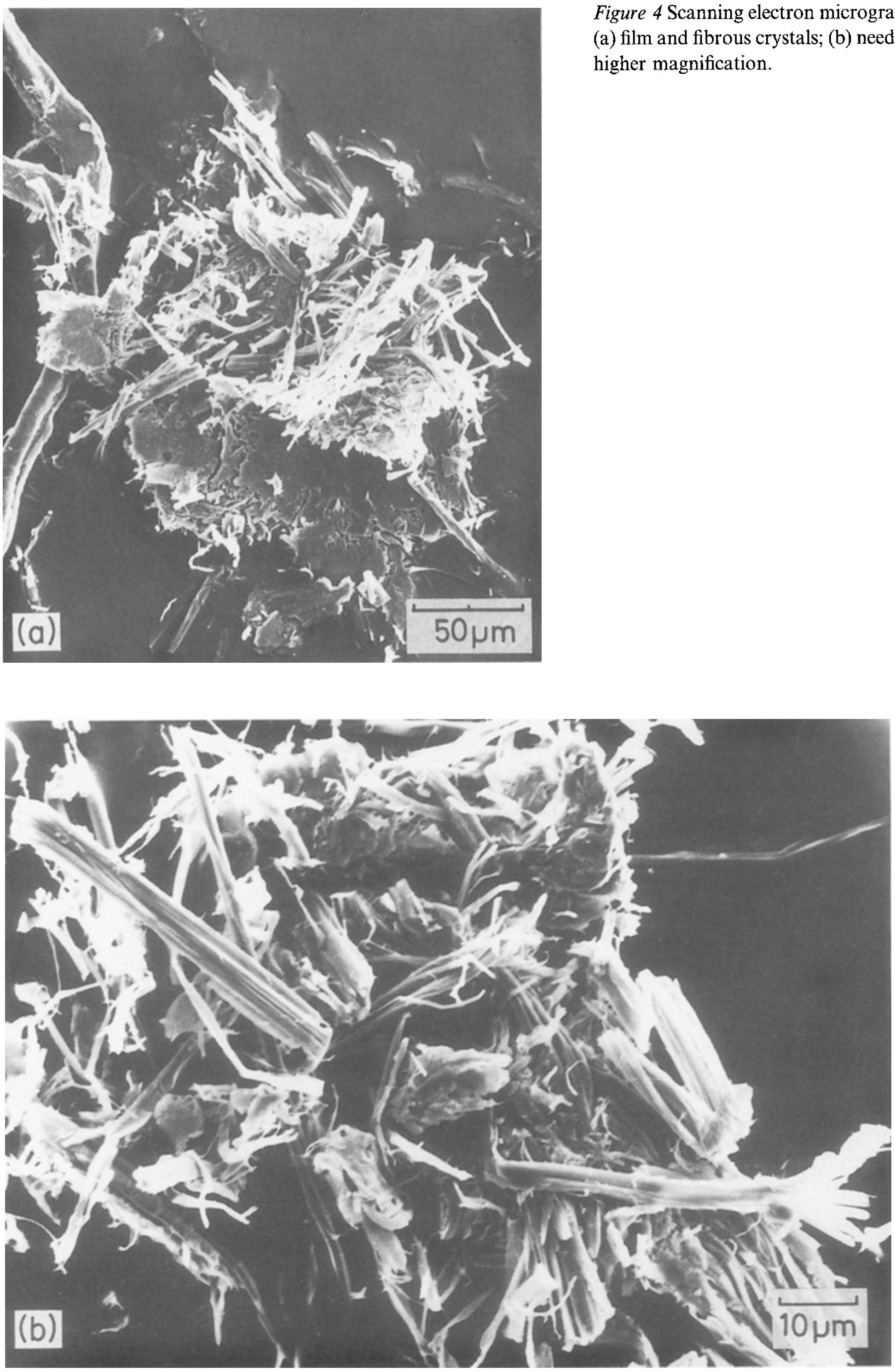

Figure 4 Scanning electron micrographs of $(SN)_x$ obtained at 35° C: (a) film and fibrous crystals; (b) needle-like and prismatic crystals at higher magnification.

should be applicable in principle to the polymerization kinetics of $(SN)_x$ experimentally studied in this work. As the monomer–polymer lattice mismatch in general and in the polymer chain direction in particular is relatively small for $(SN)_x$ it seems likely that the effect of the lattice strain on the polymerization kinetics of S_2N_2 will be smaller than its effect on the kinetics of the PTS polymerization. This assumption is supported by our preliminary results of polymerization of S_2N_2 under hydrostatic pressure when it was observed that the polymerization rate was not significantly affected by pressures of up to 4 kbar [18].

X-ray diffraction studies of polymerizing S_2N_2 crystals show that there is considerable disorder in partly polymerized S_2N_2 as compared with the pure monomer or pure polymer phase [6, 8]. The effect of lattice defects and their energies introduced to the polymerizing monomer lattice by $(SN)_x$ chains could be invoked to explain the observed polymerization kinetics in accordance with Baughman nearest neighbour mechanism. However Baughman theory considers the effect of nearest neighbour interactions inside an infinite crystal lattice and does not explicitly account for the effect of the crystal surface. It is obvious that the number of nearest neighbour interactions and their energies will be different on the surface of the polymerizing crystal as compared to its interior. The effect of the nearest neighbour interactions on the polymerization rate will be most pronounced on those crystal faces which are parallel to the polymerization direction. It can be therefore expected that the polymerization rate will be significantly different for the monomer stacks located on the surface of such crystal faces as compared with the stacks in the interior of the crystal.

The results of this work together with other available evidence discussed above point to the following picture emerging for the thermally initiated solid state polymerization of S_2N_2. The polymerization starts in solid solution but it is considerably faster on the $0kl$ indexed faces of monomer crystals than in their interior. This leads to a polymer concentration gradient in the polymerizing crystal directed towards its exterior. The autocatalytic shape of the conversion curves found in this work can be better explained by Baughman's nearest neighbour interaction theory than by his theory of long range lattice strain effect [17]. Apart from the strong influence of the surface on the polymerization rate, the polymerization is further complicated by the polymer recrystallization and a phase separation in the later stage of the polymerization. It seems likely that the polymer concentration gradient established in monomer crystals at an early stage of the polymerization will later result in a formation of an interface between the solid solution and the recrystallized polymer. Such an interface will move towards the interior as the polymerization progresses and it was first visualized by Baughman [8] in his proposal of a mechanism leading to an improvement in the structure perfection of $(SN)_x$ crystals.

4. Conclusions

It was shown that the polymerization kinetics of poly(sulphur nitride) could be followed in thin films by infrared spectroscopy by which the autocatalytic nature of the polymerization reaction could be established and the overall activation energy of polymerization determined. Further, it emerged that in bulk monomer crystals the polymerization reaction was non uniform spreading from the surface inwards. Some inferences could be drawn about the polymerization mechanism in the light of existing propositions combining the features of autocatalysis and surface initiation.

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. Am. Chem. Soc.* **97** (1975) 6358.
5. G. B. STREET and R. L. GREENE, *IBM J. Res. Dev.* **21** (1977) 99.
6. M. J. COHEN, A. F. GARITO, A. J. HEEGER, A. G. MACDIARMID, C. M. MIKULSKI, M. S. SARAN and J. KLEPPINGER, *J. Am. Chem. Soc.* **98** (1976) 3844.
7. R. H. BAUGHMAN, R. R. CHANCE and M. J. COHEN, *J. Chem. Phys.* **64** (1976) 1869.
8. R. H. BAUGHMAN and R. R. CHANCE, *J. Polym. Sci. Polym. Phys. Ed.* **14** (1976) 2019.
9. A. J. BANISTER, in "Inorganic Syntheses", Vol. XVII, edited by A. G. MacDiarmid (McGraw-Hill, New York, 1977) p. 197.
10. J. R. W. WARN and D. CHAPMAN, *Spectrochimica Acta* **22** (1966) 1371.
11. A. A. BRIGHT, M. J. COHEN, A. F. GARITO, A. J. HEEGER, C. M. MIKULSKI, P. J. RUSSO and A. G. MACDIARMID, *Phys. Rev. Lett.* **34** (1975) 206.
12. J. W. MACKLIN, G. B. STREET and W. D. GILL, *J. Chem. Phys.* **70** (1979) 2425.
13. M. VILLENA-BLANCO and W. L. JOLLY, in "Inorganic Synthesis", Vol. IX, edited by S. Young-Tyree Jr. (McGraw-Hill, New York, 1967) p. 98.
14. R. R. CHANCE and G. N. PATEL, *J. Polym. Sci. Polym. Phys. Ed.* **16** (1978) 859.
15. J. STEJNY, J. DLUGOSZ and A. KELLER, *J. Mater. Sci.* **14** (1979) 1291.
16. D. BLOOR, L. KOSKI, G. S. STEVENS, F. H. PRESTON and D. J. ANDO, *ibid.* **10** (1975) 1678.
17. R. H. BAUGHMAN, *J. Chem. Phys.* **68** (1978) 3110.
18. H. KANAZAWA, J. STEJNY and A. KELLER, preliminary results.

Received 13 June
and accepted 29 June 1989