

Deformation and defects in $(SN)_x$ kink bands

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Crystals of $(SN)_x$ were mechanically deformed and examined using transmission electron microscopy. Numerous kink bands with axes perpendicular to the chain axis were formed as part of the deformation process. The kink bands were observed to have the following characteristics: (1) high distortion beyond their edges, (2) ultimately full return of the material on either side of the kink band to the mean crystal orientation, (3) apparently random angles of kinking and (4) continuous change in orientation across the kink edge. It was noted, in describing how kink bands would form, that chain continuity poses problems that would not be present in simpler solids. A kink-band formation model is presented. In this model, particular attention is paid to chain continuity. By allowing elastic regions within the kink-band edge, it is possible to attain arbitrary kink angle.

1. Introduction

Solid state polymerized polymers provide a useful proving ground for studying the mechanical properties of polymer crystals. In contrast to the very fine, defective crystals formed by crystallization from melt or solution, solid state polymerized (SSP) materials are relatively large and perfect, with dimensions of over 1 cm obtainable and perfections high enough that individual defects can be imaged using X-ray topography. The macroscopic mechanical behaviour of SSP polyoxymethylene [1–3] and a polydiacetylene sulphonate [4] have been reported. Twin deformation, in the form of kink bands, has been observed for the same polydiacetylene sulphonate [5–7]. A stress-induced, martensitic phase transition is seen in $(SN)_x$ [8, 9]. Observations of individual defects have been reported for the polydiacetylene sulphonate [10, 12]. The present paper deals with electron microscopic observations of kink bands in $(SN)_x$ and presents a model for their generation under stress.

2. Experimental details

Crystals of $(SN)_x$, some 2 to 3 mm in all dimensions, were supplied by Dr R. H. Baughman. The

preparation of such crystals from S_2N_2 monomer, via S_4N_4 , has been described by Walatka *et al.* [13], Street and co-workers [14, 15], and Mikulski *et al.* [16]. The crystals are monoclinic, with space group $P2_1/b$ [16–19]. The chain axis, in this space group representation, is along c . The lattice cell dimensions are $a = 7.637 \text{ \AA}$, $b = 4.153 \text{ \AA}$, $c = 4.439 \text{ \AA}$, $\gamma = 109.7^\circ$.

The crystals fibrillate very easily. Material for electron microscopy was formed by pulling the crystals apart, using needle-point tweezers. The fine fibrils which result are transmissible to electrons [17, 18, 20] and the material is highly deformed in this process. Other material has been deformed by compression between glass slides. The defects seen after pulling apart and after compression are identical. All figures in this paper represent material which has been pulled apart.

A JEOL 200A transmission electron microscope, operating at 200 kV, was used in this work.

3. Results

Fig. 1 is a scanning electron (SEM), micrograph of the surface of an undeformed crystal. All other photos in this work are transmission electron micrographs. Since it has not been possible to

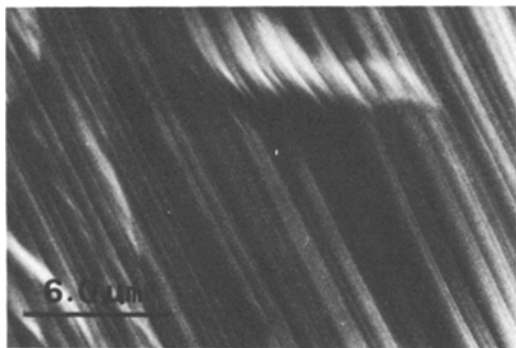


Figure 1 Scanning electron micrograph, showing “perfect” straight crystalline fibrils and one grown-in large kink.

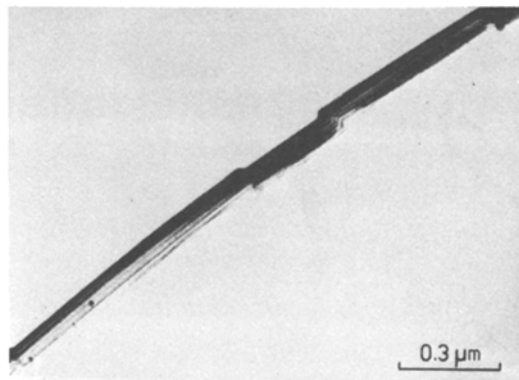


Figure 2 Bright-field transmission electron micrograph, showing four kink bands.

transmit through the undeformed material, it is necessary to use SEM to establish the nature of the virgin material. This crystal is composed of very long fibrils running in the chain direction. One very large grown-in kink band is observed; otherwise the fibrils appear to be free of gross defects. When deformed regions are observed, as in the remainder of the micrographs, a high density of relatively fine kink bands is observed.

Fig. 2 shows a bright-field electron micrograph of an $(SN)_x$ fibril exhibiting four distinct kink bands. Such kink bands are very common in this material and their characteristics are described below. In each case we show only one micrograph, but the observations are qualitatively common to the specimens. The characteristics are:

(1) The material directly on either side of a kink band is heavily distorted. This is seen in Fig.

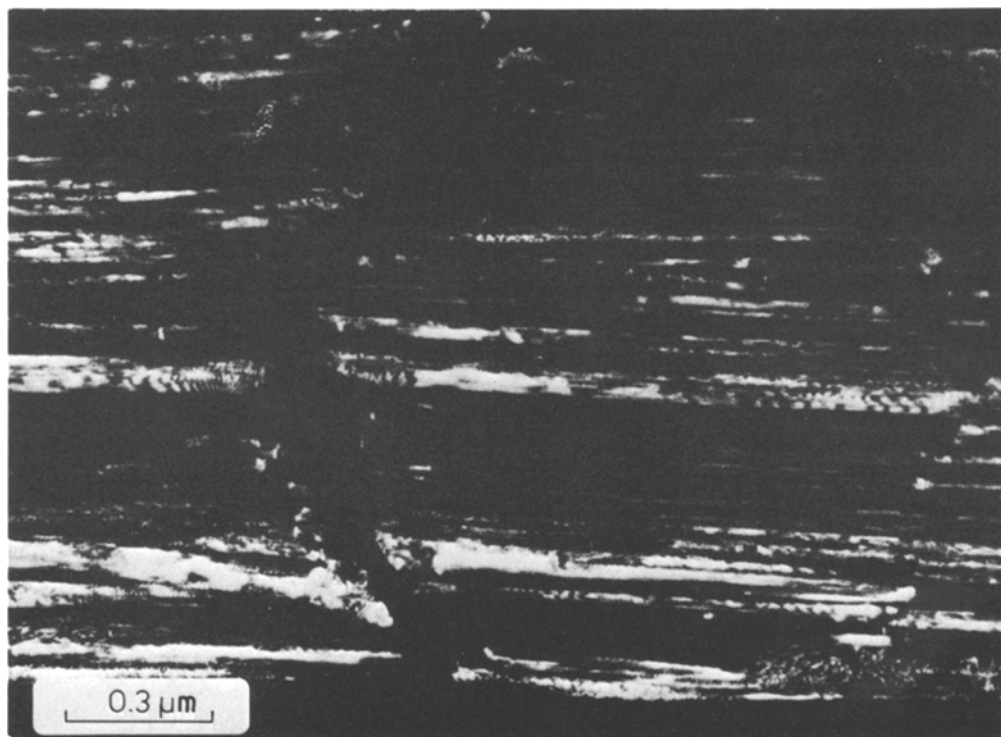


Figure 3 ($h k 0$) dark-field transmission micrograph illustrating distorted regions near a kink band.

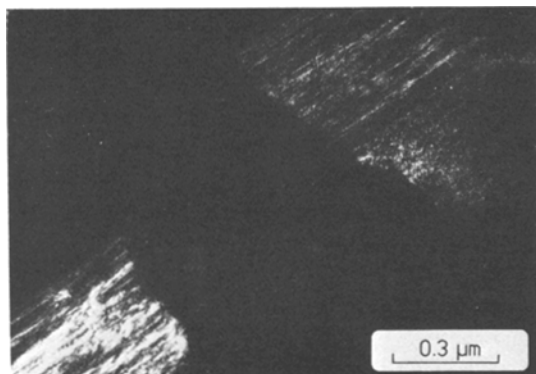


Figure 4 ($hk0$) dark-field micrograph illustrating the continuity of orientation on either side of the kink band.

3, a dark-field micrograph from an ($hk0$) reflection. The kink band here is a dark band running generally north-south. On either side of the band are seen striations (arrows) running normal to the chain direction. In general, the striae evidence localized strain fields which increase in density as the kink band is approached. The details of this deformation are described elsewhere [21].

(2) The kink bands have produced a plastic deformation. Kink bands are seen near the free ends of crystal ribbons. Relaxation of all elastic stress would occur there, but the kink bands always remain.

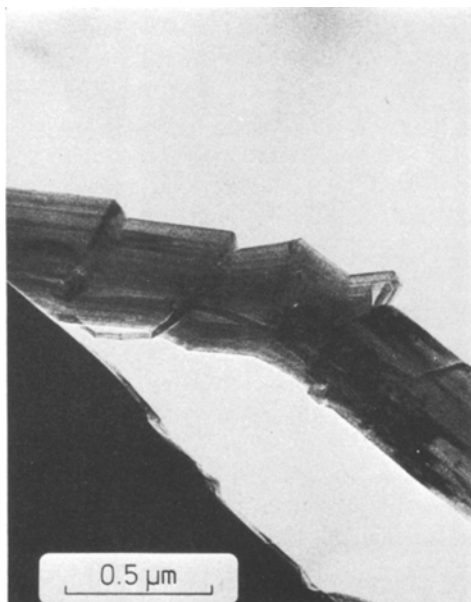


Figure 5 Bright-field electron micrograph showing several kink bands, with different angles of kink.

(3) Away from the immediate vicinity of the kink band itself, the orientation of the material on either side of a kink band is identical. This is seen in Fig. 4, again an ($hk0$) dark field micrograph. Here the regions on both sides of the band are imaged simultaneously, indicating that they have identical orientation to an accuracy of less than 0.1° . Similar behaviour is seen when the imaging reflection has a component along c .

(4) The angles of kinking are random. A very large number of kink angles has been observed and there is no evidence of strong crystallographic control. Fig. 5, a bright-field micrograph, shows one fibre exhibiting several kink angles. Fig. 6 shows one kink band: the material within the kink band has fibrillated and one observes again several kink angles among the fibrils.

(5) The change in orientation over a kink band is not discontinuous. A kink band and, correspondingly, a selected-area diffraction pattern taken from its ridge are shown in Fig. 7. Patterns representing both orientations are seen, as well as arcs joining the spots of the two orientations. The arcs show that the lattice reorientation is continuous.

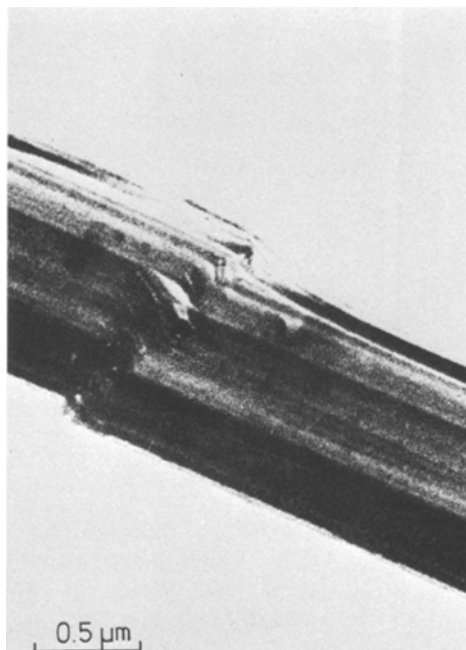


Figure 6 Bright-field electron micrograph of a single kink band, showing fibrillation and many different kink angles among the fibrils.

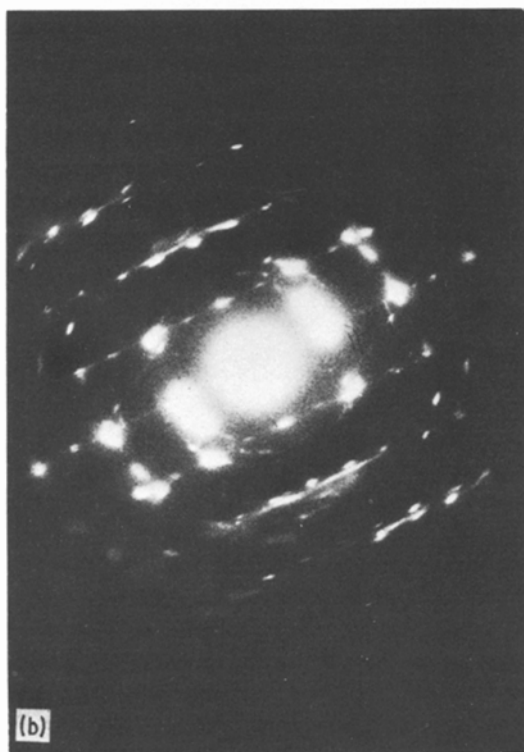
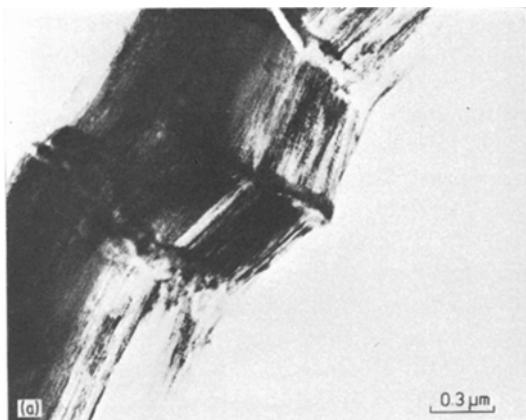


Figure 7 (a) Bright-field electron micrograph of a double kink band; (b) selected-area diffraction from the ridge of the kink.

4. Discussion

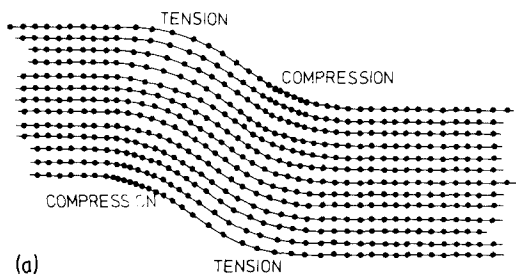
In lower molecular weight materials (e.g. hcp metals) kink bands form under compressive loading when slip is restricted to the loading direction [22]. Slip must also be restricted when polymeric materials are loaded in compression parallel to the chain axis. The motion of dislocations on slip planes at any angle to the chain axis would produce a wake of kinks in the chains through which it has glided. Thus plastic deformation

by a defect mechanism is limited to defects whose effective Burgers' vector lies in the chain direction along the compression axis. Hence the basic condition for kinking is met in a polymer single crystal just as in hcp metals. Indeed, kink bands formed under compressive loading have been reported for Nylon 610 [23], a polydiacetylene [5–7], and polyethylene [24, 25]. In the former two cases, the angles of kinking are crystallographically restricted, whereas for polyethylene they are not.

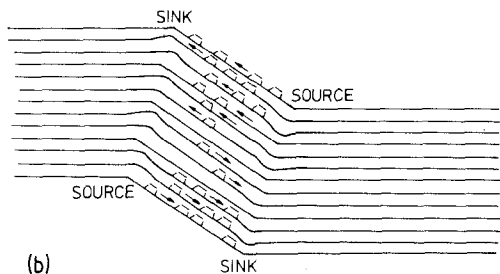
The elementary defect leading to plastic flow in a polymer crystal would be a kink in a chain. This term refers to any set of local changes in conformation which will take portions of the chain out of the general axis direction and then return the chain to its prescribed course in a small number of molecular bond rotations. (In this case, "kink" refers to a defect in a single chain and "kink band" refers the co-operative deformation of a large number of chains across two parallel planes.)

There is a problem associated with the transport of matter during the formation of such kinks. To form a single kink, a chain would need to reduce its end-to-end length by an amount equal to the contour length of the kink. This requires the motion of repeat units along the chain. For very long chains perfectly extended in the crystal, two possibilities for such translation exist. One possibility is the simultaneous motion of an entire rigid length of chain past its neighbours, from the chain end to the kink. The other possibility involves the generation of a kink at a chain end and the subsequent motion of that kink to the slip plane. The former of these two processes would have a very high energy; the latter would require that the chain transmit information and stress, from the slip plane to the chain end. It may also be possible for the chain to break and a kink to form at the new chain end. Both such chain breakage and the rigid translation of a chain past its neighbours are energetically unfavourable, provided that some other simple mode of kink formation in the chain interiors is possible. We, therefore, look for a mechanism whereby [1] chain lengths are maintained constant and [2] the chain deformation responds to a *local* field.

Fig. 8 indicates such a process, resulting in the formation of a kink band. Under the application of a compressive stress, a workpiece should respond by reducing its length parallel to the



(a)



(b)

Figure 8 (a) Elastic double bending under a compressive load. (b) Mechanism of kink formation and migration to sinks, leading to a plastic kink band.

compression direction. In our case, we suppose a compressive stress with a component parallel to the chain axis. Fig. 8a shows how beads on elastic threads would behave. An elastic kink band would form. In the tensile regions, the elastic threads could stretch; in the compressive regions, the beads would move closer together. In a polymer chain, the covalent bonds effectively prohibit the extensive stretching needed in the tensile region. For many polymeric materials, however, the energy needed to rotate around a covalent bond is relatively small, and the molecular units can locally rotate out of their usual positions and form single, double or multiple kinks. As we have already seen, one effect of chain kinking is to shorten the contour length of the chain. Thus the compressive regions, in which the chains need to become shorter, could act as sources of kinks; similarly, the tensile regions would act as sinks. At the neutral axis of the piece, no net extension or contraction takes place, and no kinks are needed. At the outer surfaces, the greatest number of kinks are needed, in order to compensate the relatively large tensile and compressive stresses.

The following process is then envisaged. The material, under longitudinal compression, begins to form a double elastic bend, as in Fig. 8a. As the outermost chains reach a critical strain level,

kinks are formed at the sources (compressive regions) and migrate to the sinks (tensile regions). The stress at the outer surfaces is thus relaxed. Additional stress will then cause chains further interior to nucleate kinks and for them to migrate. The process of kink generation and reposition will be repeated. Kinks will form in chains further and further toward the interior as the stress is raised.

It must be pointed out that twin boundaries of perfect coincidence can result under specific conditions. Recall that the kinking process should begin at the outermost planes and then work its way inward. Suppose now that each kink displaces the chain longitudinally by one repeat distance. Coincidence will be achieved then if each successive plane creates and absorbs exactly an integral number of kinks more than its predecessor. It is not geometrically necessary to have such a situation, however. Suppose that the difference in kink numbers between successive planes is not integral. The one expects to have lattice coincidence on the kink boundaries only every n planes (3 in the illustration). In order for the lattice to maintain its integrity beyond the kink band the chain elements in between must then form "elastic" bends in which lattice mismatch energies could be large. This is illustrated in Fig. 8b. It should be noted that this model is consistent with the observed continuous change of orientation about a kink-band edge. It must also be noted that the angle of kinking cannot, however, be quite arbitrary, or the kink planes could consist only of "elastic" bends, with no coincidence sites to keep the energy at an acceptably low level. Presumably histograms produced from a large volume of data on kink angles would show broad maxima when one moves too far from coincidence.

From the limited data at hand, it would appear that chain architecture is important in limiting the possible angles of kinking. The polydiacetylene reported by Bloor and co-workers [5-7] exhibits kink bands whose angles are limited to those for perfect coincidence. Zaukelies reported a similar crystallographic coincidence for compression-induced kink bands in Nylon 610 [23]. The behaviour of polyethylene kink bands [23, 25] is, however, similar to that observed in $(SN)_x$; i.e. there is no observable specificity in the kink angle. Indeed, Robertson reports a gradual change in the kink angle during the growth of a kink band [25]. In the case of Nylon 610, it is likely that the strong lateral hydrogen bonding provides a deep

energy valley, which makes non-crystallographic kinking energetically unfeasible. Such a deep energy valley is probably also present in the polydiacetylene. Here, however, the large pendant groups may contribute principally to an increase in lattice energy as they become displaced from their equilibrium sites. $(SN)_x$ has no pendant groups and no hydrogen bonding; polyethylene has only hydrogens pendant from the chain and also shows no hydrogen bond. The kink angles in these systems are, therefore, less restrained than in Nylon 610 or the polydiacetylene. From this standpoint, it would appear that chain architecture is important in limiting the kink angle.

5. Conclusions

Fine-scale kink bands are observed to have formed during the deformation of $(SN)_x$ crystals. The kink bands exhibit arbitrary angles of kinking. Chain continuity during kink band formation requires that a source and sink for the kink be available at the time of its creation. A model in which the source and sink are adjacent regions of tensile and compressive stress is given. By allowing the kink band to contain elastically strained regions, as well as localized kinks, arbitrary kink angles are predicted.

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