A New Phase of $(SN)_x$

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Summary A new phase of $(SN)_x$, with the same chain geometry as the monoclinic form but having orthorhombic symmetry and very different interchain interactions, can be produced by a martensitic-like phase transformation.

WE have discovered that mechanical shear transforms the known monoclinic phase of polymeric sulphur nitride (phase I)[1,2] to a new phase of orthorhombic symmetry (phase II). The chain geometry is essentially unaltered by the transformation. However, there are important differences in interchain interactions for the two phases. Numerous investigations have convincingly shown the importance of these interchain interactions in determining the properties of phase I $(SN)_x$.[3]

The phase I → II transformation results from mechanical shear on planes parallel to the chain axis direction. This mechanical shear can be produced most simply by grinding the phase I polymer in a mortar and pestle, although the phase I → II crystal transformation can be optimized by more careful selection of deformation conditions. We have investigated the structure of the sheared phase I fibres using single crystal Weissenberg, oscillation, and precession diffraction techniques. These sheared fibres are found to consist of phase I and phase II components, which are stable with respect to interconversion at temperatures as high as 175 °C. The unit cell parameters determined for the phase I component of the sheared polymer are $a_I = 4{\cdot}040(2)$, $b_I = 4{\cdot}429(8)$, $c_I = 7{\cdot}849(3)$ Å, and $\beta_I = 109{\cdot}3(1)°$. These values differ somewhat from the most accurate published values for phase I: $a_I = 4{\cdot}153(6)$, $b_I = 4{\cdot}439(5)$, $c_I = 7{\cdot}637(12)$ Å, and $\beta_I = 109{\cdot}7(1)°$.[2] We believe the differences are a consequence of stacking faults introduced by mechanical stress. The existence of such stacking faults are suggested by the electron density distribution of *as*-polymerized $(SN)_x$.[2,4]

The diffraction spectra for phase II are consistent with an orthorhombic unit cell with the following dimensions: $a_{II} = 6{\cdot}251(3)$, $b_{II} = 4{\cdot}429(8)$, $c_{II} = 4{\cdot}807(4)$ Å, with the probable space group $P2_12_12_1$ from observed systematic absences. Therefore, the chain repeat dimension (b) and the chain symmetry (2_1) are the same before and after the shear transformation.

From the zero-level Weissenberg diffraction data about the chain axis direction, we have determined the orientational relationship between the phase I and phase II unit cells. The results are shown in the Figure. Also shown in the Figure is the structure for phase II derived from molecular packing calculations.[5] Approximating the chain geometry to be exactly the same for both phases, only two parameters are required for the determination of the structure of phase II *via* the selection of packing modes which minimize van der Waals overlap. We choose for these parameters: (i) the angle between the plane of the backbone and the (100) plane of phase II, and (ii) the chain direction displacement between translationally inequivalent chains. We find that the latter parameter is essentially the same (within 0·16 Å) for both phases and that the backbone plane is within about 18° of being parallel to the (100) plane.

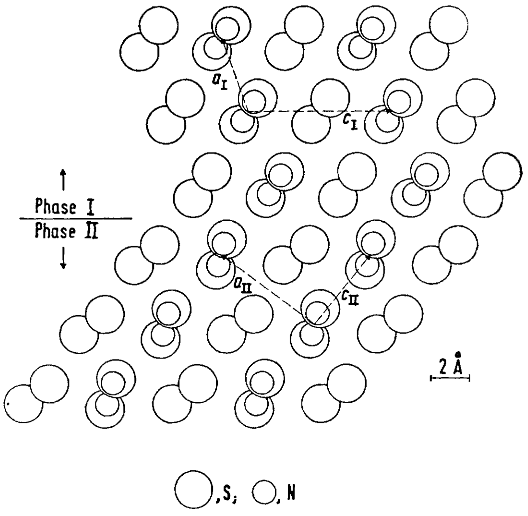

FIGURE. Chain axis projection of phase I crystal which has been sheared (bottom half) on the (100) plane in the c_I axis direction to produce the calculated phase II structure. For one-half of the chains the nitrogen atoms lie behind the larger sulphur atoms and are therefore not shown.

Since the (100) plane in phase II is nearly parallel to the backbone plane of phase I, we conclude that relatively small molecular rotations are required for the transformation. Over fairly narrow parameter ranges, we find zero van der Waals overlap, a result which supports our space group assignment. These results suggest that the phase II structure can be produced from the phase I structure by a shear displacement of about $c_I/2$ with respect to neighbouring (100) planes. We believe that the shear-induced phase transformation can be described as a martensitic transformation. Martensitic phase changes generally require (i) a specific orientational relationship between parent and daughter phases, (ii) the absence of long-range molecular displacements, and (iii) the existence of an interphase plane (habit plane) which is essentially undistorted during the transformation.[6] All these requirements are satisfied for the shear transformation in $(SN)_x$. The habit plane appears to be close to the (100) plane, since the lattice shear occurs on this plane and the relevant dimensional changes within this plane are quite small.

We feel that property measurements on phase II will lead to a more general understanding of the properties of both phases of $(SN)_x$ as well as to important tests of the various theoretical descriptions[7] of this system.

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