JOURNAL OF MATERIALS SCIENCE 6 (1971) 479–483

Molecular Mechanism of the Deformation of High Polymers

Part 1 *Introduction and Results on the Shear of Polyamid 11*

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In the course of shearing deformation of double textured samples of nylon-11 the following facts emerged: the deformation of both superlattice and subcell can be accounted for by the same sliding displacement along consecutive hydrogen bonded planes; the deformation of the whole sample is the mean of the deformation of the two types of structural units. This gives support to, and additional information about, a classical model: in its whole area, the sample is made of parallel arrays of crystalline and amorphous layers.

On the other hand, it is not possible to define the superlattice in terms of low index subcell planes, in fact the superlattice planes change continuously on shearing, in accordance with the shearing of the sample as a whole. This may well invite reconsideration of the whole lamellar, two phase picture upon which the presently accepted interpretation of the low angle reflections rests [2].

Concerning the structure of the subcell, the present investigation brings direct proof of slip along hydrogen bonded planes and suggests various methods for the study of the polymorphism of polymeric material and a more complete description of polymer crystals.

1. Introduction

On the basis of currently accepted ideas on the morphology of bulk polymer samples, it would be expected that:

(*a*) a well-defined orientation of the superlattice with respect to the subcell would be observed.

(*b*) at least at relatively low temperatures, simple relationships must exist between the changes of the size and the shape of a sample on annealing, drawing, etc. and the changes of its low angle scattering diagram.

(*c*) however, concerning this last point, it must be emphasised that the following suggestion has been made: "In addition to the structural units responsible for the small angle X-ray scattering (SAS) diagram, one may suppose the existence of another phase" [1]. If such an assumption is made, no conclusions can be obtained by comparison of macroscopic and SAS data.

As shown by work in progress in our laboratory, polyamides are most suited for examination of these points. In this first paper data on nylon-11 are sufficient to point out the main directions of the present investigation [2].

2. Orientation of the Superlattice with respect to the Subcell

In polyethylene [3] and in polyamides [4], crystallised from solution, the long period obtained from SAS corresponds to the thickness of lamellae. The fold surface of the lamellae have a definite orientation with respect to the subcell. For example, observations [4] on nylons – 6/6 – 6/10 – 6/12 (and others) show that the indices of the fold surface are (001).

In bulk polyethylene samples [5] prepared by drawing, rolling and annealing (301) and (201) indices have been proposed. However, in truly single textured samples [6], displaying a two point asymmetric diagram, the angle between the axis of this diagram and the chain axis is significantly larger than 45°. New measurements [2] on these samples give the value of 50 ± 1° for this angle, a value which does not correspond to any simple indexing.

To obtain confirmation of this last result, polyamides which have a much larger identity period are particularly well suited.

Nylon-11 samples with a double orientation (taken as example in the present paper) were obtained by rolling or by rolling and annealing. The orientation of the subcell with respect to X, Y, Z (taken respectively along the normal to the rolling plane, the rolling direction and the normal to the rolling direction lying in the rolling plane) is shown in fig. 1.

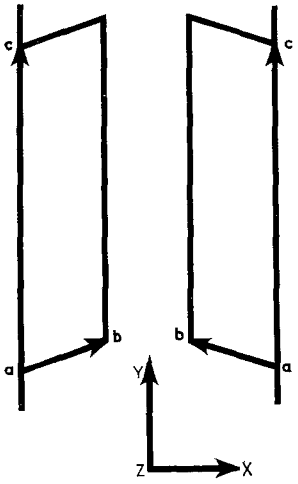

Figure 1 Polyamid 11. Orientation of the subcell versus macroscopic directions of the specimen.
a (9.6 ± 0.6) Å α(72 ± 2)°
b (4.2 ± 0.2) Å β 90°
c (15.0 ± 0.2) Å γ (63.5 ± 1)°
Macroscopic directions; Y rolling direction ZY rolling plane; X normal to the rolling plane.

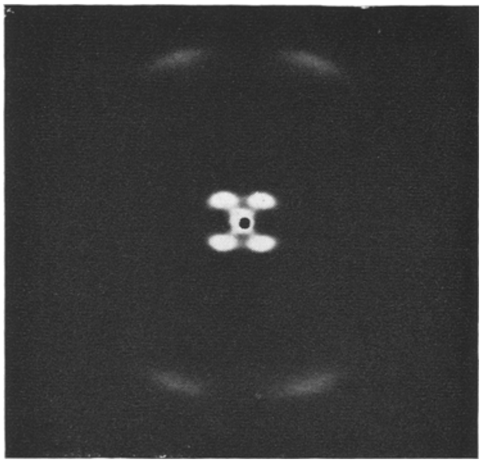

Figure 2 WAS and SAS diagrams of rolled nylon-11.

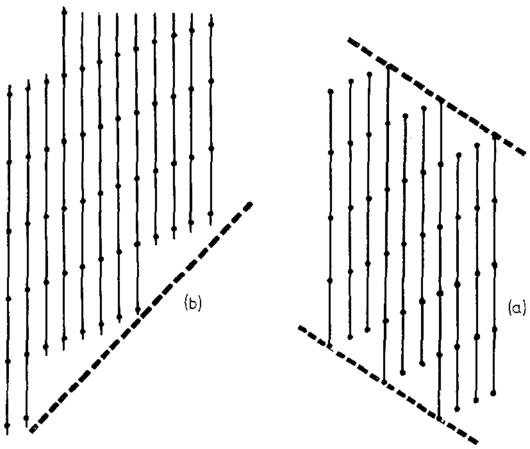

Figure 3 Schematic drawing of fold surfaces in lamellae.

The low angle diagram is a symmetrical four point diagram. The maxima lie in the XY plane at 45° to the Y direction. This does not correspond to any simple low index plane with respect to the subcell. This conclusion remains valid within the whole assignment range permitted by the spread of the SAS and (001) wide angle X-ray (WAS) reflection in fig. 2.

A schematic drawing with the fold surfaces normal to the direction of the SAS maxima in the four point pattern is shown in fig. 3. We see that there is no simple low index plane in the subcell which corresponds to such lamellar surfaces.

Another currently accepted hypothesis to explain orientation of the SAS maxima is based on the different spatial requirements of a chain in a crystalline and in an amorphous area. But in different nylons, different values of the angle are obtained. Therefore, this hypothesis requires careful examination.

3. Correlation Between Changes in Size and Shape of the Sample and the Change of the SAS Diagram

If a high polymeric sample is supposed to be made of linear arrays of repeating units, constituted by a crystalline layer and an amorphous layer, then the asymmetric two point, or symmetric four point SAS diagram may be explained.

Furthermore, it is usual in the case of samples obtained by drawing or rolling (with eventual annealing and subsequent redrawing) to make the assumption that the axis of the linear arrays and the axis of drawing are parallel, or almost so [8].

If ϕ is the angle between the axis of the arrays and the normal to the limiting faces of the crystalline and amorphous layers, if d is the thickness of the repeating units, and if the macroscopic dimension in a direction parallel to the axis of the stack is l, it would be expected that l is proportional to $d/\cos\phi$.

In some cases, this assumption holds with good [8c] or even remarkable accuracy [7]. But in other cases, despite the fact that ϕ varies reproducibly and reversibly with l [1], the proportionality between l and $d/\cos\phi$ is only qualitative and not quantitative.

As another example, consider fig. 4, which shows the size and shape of high pressure polyethylene sample of truly single texture [2b, 2c] (obtained as explained in [6]) before and after annealing at 70°C. The same figure also shows the maxima of the SAS patterns. In the present case, the above prediction is violated not only quantitatively, but also qualitatively.

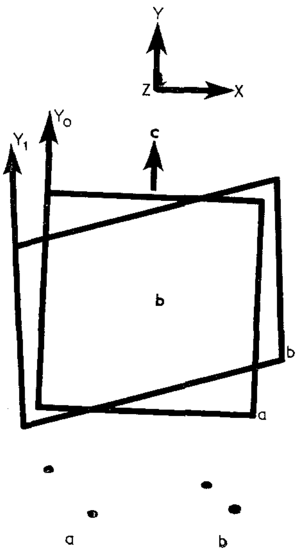

Figure 4 Low density polyethylene. Representation of the cross section of the XY plane and correspondent small angle scattering patterns (a) after rolling (b) after rolling and annealing at 70° C.

Some simple suggestions seem, at first sight, to show a way out of these difficulties:

(*a*) Is the currently accepted assumption about the orientation of the stacks of amorphous and crystalline layers valid?

(*b*) Interlamellar and intralamellar slip can induce rotation of the axis of these stacks.

(*c*) Relative gliding of stacks of lamellae is a possible mode of deformation of the sample.

It may be shown [2b, 2c] that, even if these remarks are taken into account, the quoted discrepancies persist.

Other suggestions are the following:

(i) The axis of the SAS diagram is not perpendicular to the plane of the platelets and the positions of the observed maxima depend on the shape factor of the array [9].

(ii) The number of lamellae in a stack changes by melting and recrystallisation of the crystals [10].

(iii) SAS patterns reflect the organisation of parts of the sample, but another hypothetical amorphous phase is responsible for the major part of the deformation of the sample [1].

(iv) Some lamellae are pulled out of the stack as a result of strains due to the presence of tie chains connecting the lamellae in a stack [2b, 2c].

The first one of these suggestions does not hold; in fact in the best samples second and third orders of the SAS reflections are observed.

The second is unlikely, in view of the low value of the annealing temperature and of the continuous variation of the macroscopic and submicroscopic parameters of the sample as a function of the annealing temperature. The fourth one, which we believe to be essentially correct [2] is to be discussed in another paper. In what follows we shall concentrate on the third assumption and shall demonstrate why it can be discarded.

4. Changes of WAS and SAS X-ray Diagram on Shearing of Nylon-11

By shearing (shearing plane normal to X, direction of shearing Y) it is possible to deform a parallelepiped with a rectangular base in the XY plane into a parallelepiped in which the base parallel to the XY plane is a skew parallelogram with an angle ρ. The sample (dimensions: 2 × 10 × 2 mm along the X, Y and Z directions respectively) is clamped between steel plates which are moved by a complex mechanism in order to obtain the deformation just quoted. Fig. 5 shows the SAS and part of the WAS diagram of such a deformed sample.

Table I gives:

(a) the value of the angle α (see also fig.6) between the axis connecting the (001) spots and the chain axis.

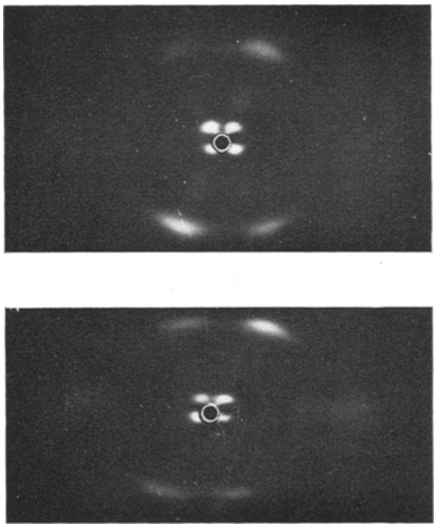

Figure 5 WAS and SAS diagrams of a rolled sample of nylon-11 before and after shearing.

TABLE I

Sample number	Angle (in degrees)						
	β_1	β_2	α_1	α_2	ρ	ρ_{SAS}	ρ_{WAS}
0	45	45	23	23	90	90	90
3	41	50	16	31	79	81	81
4	42	55	15	36	75	75	74
1	36	56.5	(8.5)	41	68	69	70

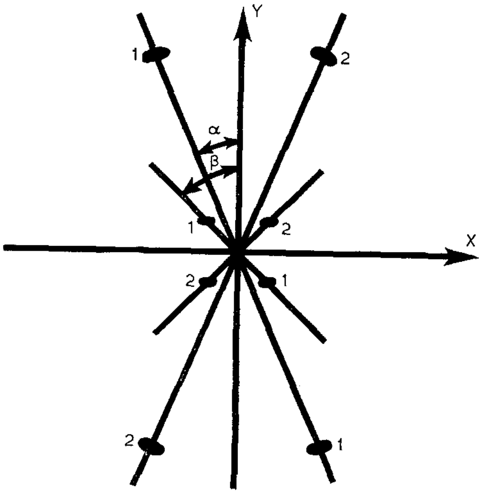

Figure 6 Schematic drawing of the X-rays scattering diagram of nylon-11.

(*b*) the value of the angle β between the axis connecting the SAS diffraction maxima and the chain axis as a function of the macroscopic angle ρ.

Fig. 7 is a graph of the values of tan β_1 (or tan β_2) versus tan α_1 (or tan α_2).

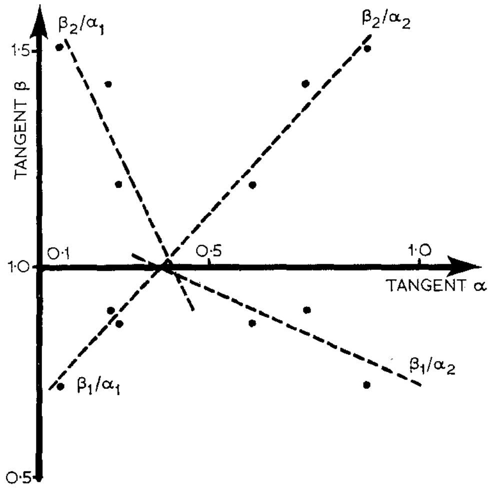

Figure 7 Plot of tan β versus tan α.

As shown by fig. 8, if the superlattice and the unitcell are deformed by shearing and both by the same amount, the values of tan β – tan α are constant.

However, we have two values of β and two values of α. The question is the following: "Is the subcell of the lamellae which gives the reflection 1 of the SAS diagram the one which gives the reflection 1 in the WAS diagram, or the one which gives the reflection 2, or vice versa?" The plot of both tan β_1 and tan β_2 values firstly versus tan α_1 and secondly versus tan α_2 denoted as β_1/α_1, β_1/α_2 etc. leads to a test of the hypothesis of identity of the amount of deformation of the subcell and the superlattice and to an answer to the question "what is the orientation of the unitcell in each of the linear arrays of crystals?"

Let us first consider the variation of tan β_1 versus tan α_1. The difference (tan β_1 – tan α_1) does not vary with the magnitude of the shear (in the limit of accuracy of the present measurements).

This observation leads to the following conclusion: If the reflections 1 of the SAS diagram correspond to the limiting faces of the crystals, the subcells which gives the reflections 1 in the WAS diagram (fig. 6), the deformation may be thought of as due to slip along the plane of hydrogen bonded chains. This slip taking place on each consecutive hydrogen bonded plane (or on blocks of a few hydrogen bonded planes) and always in the same direction, will shear both the subcell and the superlattice, and both by the same amount.* Fig. 8 shows how this hypothesis leads to the observed constancy of $\tan\beta_1 - \tan\alpha_1$. The experimental facts are compatible with the accepted model of a sample made up of stacks of crystalline and amorphous platelets and give additional information of the mode of deformation by shearing of such a structural unit. For the purposes of describing the geometry of the deformation, the existence of the amorphous material may be ignored; it needs only be invoked to explain the non zero intensity of the SAS reflections. Fig. 7 shows also a similar constancy for $\tan\beta_2 - \tan\alpha_2$ (slope of β_2/α_2 line is unity) but values of $\tan\beta_1 - \tan\alpha_2$ and of $\tan\beta_2 - \tan\alpha_1$ vary with the magnitude of the shear.

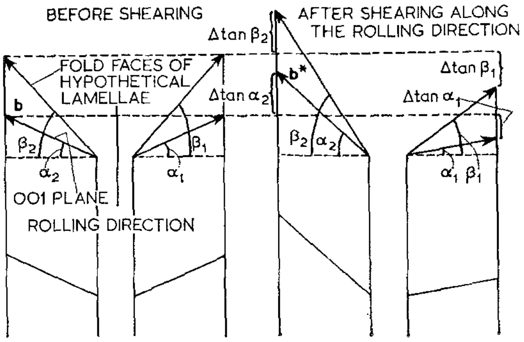

Figure 8 Schematic representation of the mechanism of shearing in nylon-11.

This figure shows the orientation of the subcell and of the superlattice of nylon-11, if the assumption of a shearing of both by the same amount is made.

In the drawing, the assumption is made that the 1 spots of the WAS diagram corresponds to the 1 spots of the SAS diagram. The conclusion is the constancy of $\tan\beta_1 - \tan\alpha_1$ and of $\tan\beta_2 - \tan\alpha_2$.

Experimental values (fig. 7) are in agreement with these predictions. Another assumption is for example that the 1 subcell corresponds to the 1-superlattice, but the corresponding data of fig. 7 are not on a parallel line to the bisector of the figure axis.

The sample is made of two types of structural units (which are in the undeformed sample in mirror reflection). To the first ones correspond the 1 reflections of fig. 6, and to the others the 12 reflections.

This last remark is closely related to that made in a recent paper on truly single textured samples of high pressure polyethylene [6]. The magnitude of the shear is not the same for the two types of structural units.

It is also noted that the area defined by the four points in the SAS diagram (the points are moving along a layer line) varies with the extent of shearing. This is another way of pointing out that the four point diagram is not due to the existence of a two dimensional array of crystals. (If this assumption is made, the area of the cell of such a two dimensional array varies, but in fact the area of the XY face of the sample is constant.) The obliquity of the line connecting two corresponding reflections is due to the internal organisation of linear arrays, the axis of which is along the rolling direction.

Let us now compare the mean shear for the lattice and superlattice with the shear as estimated from the deformation of the whole sample. Values of

$$\rho_{\mathrm{SAS}} = \mathrm{cotan}^{-1}\,1/2(\tan\beta_1{}^0 - \tan\beta_1 + \tan\beta_2 - \tan\beta_2{}^0)$$

and

$$\rho_{\mathrm{WAS}} = \mathrm{cotan}^{-1}\,1/2(\tan\alpha_1{}^0 - \tan\alpha_1 + \tan\alpha_2 - \tan\alpha_2{}^0)$$

are used to describe the shearing deformation from X-ray observations and the calculated values are in the table I. They are equal to the values of ρ obtained from macroscopic measurements.

The present investigation does not give any support to the idea of an extra compliant phase which may undergo large deformation. The deformation of the whole sample is thought to be due to the deformation of the stacks of amorphous and crystalline platelets.

Shearing processes, deformation with low extension ratio at a comparatively low temperature (discussed at the beginning of the preceding paragraph) are supposed to be deformation processes during which the number of lamellae in a stack is constant.

As quoted earlier, other deformation processes involving pulling out crystals from the stacks are to be discussed in another paper.

5. Intercrystalline Slip

As is well known, changes with respect to the subcell of the orientation of the limiting faces of

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*The displacements of consecutive hydrogen bonded sheets for the successive samples in table I increase approximately in arithmetic progression, with an increment of close to 0.4 Å. This length corresponds to about $\frac{1}{6}$ of a chain zig-zag. It follows that if slip takes place on each consecutive hydrogen bonded plane the methylene group subcell itself will be sheared. In order to preserve this subcell undeformed, slip would have to occur between consecutive blocks of six sheets. It happens that this would be consistent with the block structure in fig. 3b postulated to account for the superlattice plane of the initial structure.

crystals may be accounted for by intracrystalline slip. But other processes may be responsible for such changes. It is shown here, in a particular case, that the intracrystalline glide can effectively account for the whole change of crystal habit.

We are aware that the use of Bragg's law is not completely justified; but good correlation between experimental results is obtained. It is therefore not necessary to make calculations taking into account crystal imperfections and the small size of crystals.

Studies on shearing processes in various polyamides in conjunction with measurement of the WAS intensity is a new way of studying the polymorphism of high polymeric materials, and may perhaps lead to suggestions concerning specific problems (for instance indexing of the plane of the folds as shown by the discussion of figs. 7 and 8). Work along these directions is just starting in our laboratory.

As preliminary results, we note that:
(*a*) intracrystalline plastic slip is not so easy in the − direction (see fig. 9) as in the + direction. (No symmetry considerations are in conflict with this conclusion.)

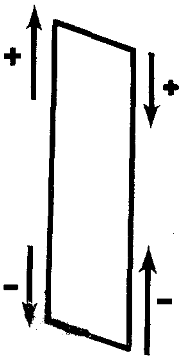

Figure 9 Preferred direction of plastic slip.

(*b*) Despite intracrystalline slip, the observed relative orientation of the limiting faces of the crystals and of the subcell makes it difficult to define the fold surface, even in the case of the deformed samples.

In this respect, it is to be stressed that the drawing (a) of fig. 3 has been ruled out in the preceding section. At the present time, no useful comments can be made on the large width of the steps present in the limiting faces of the hypothetical lamellae.

Acknowledgement

The authors are very grateful to Professor Keller for his stimulating discussions, and to Professor Guinier and A. Pilatte for their interest. They are indebted to M. Abrassart, F. Lhote and R. Limbourg for technical assistance. The support of a portion of this research by the Fonds National de la Recherche Scientifique is also acknowledged.

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Received 30 November 1970 and accepted 15 March 1971.