

Orientation of the lamellar crystals in polyamide 12

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Three types of oriented samples of polyamide 12 have been investigated by electron microscopy, and small- and wide-angle X-ray diffraction: (a) sedimented mats of single crystals obtained by filtration from dilute solution; (b) melt crystallized samples oriented by unidirectional rolling and; (c) samples obtained by extrusion just below their melting temperature ($T_m = 170^\circ\text{C}$). The limiting faces of lamellar crystals in sedimented mats are parallel to the (001) planes. Rolled samples contain two populations of deformed lamellar crystals in a mirror relationship with respect to the rolling plane; their limiting planes are not parallel to any one of the crystallographic planes that have low Miller indices. It is only by thermal annealing in contact with formic acid, under well-defined experimental conditions, that the lamellar basal planes parallel to the (001) planes can be restored. A new crystalline phase with a triclinic unit cell is found in samples obtained by planar extrusion at 160°C , and lamellar crystals with monoclinic and triclinic unit cells coexist in these extruded samples. The two edges of the faces parallel to the rolling plane of these doubly oriented samples have an almost single texture, both at the level of the lattice and at the level of the basal planes of the lamellar crystals. Lamellar crystals with a triclinic unit cell have limiting planes parallel to the (001) planes.

(Keywords: doubly oriented polyamide 12; unidirectional rolling; single crystals; single-texture sample; monoclinic and triclinic unit cells)

INTRODUCTION

It is largely accepted that single crystals grown from dilute solution are lamellae with more or less regularly folded chains¹. The basal planes of the lamellae are generally parallel to those crystallographic planes which have low Miller indices. In sedimented mats of polyamides, lamellar crystals are limited by folding planes which are parallel to the (001) planes and their lamellar thickness is an integer or a half-integer multiple of the d_{001} spacing²⁻⁴. The crystallographic c -axis is parallel to the chain axis. In the wide-angle X-ray pattern of sedimented mats of single crystals of polyamide 6/6, additional reflections, which are localized between the (001) reflections, cannot be indexed with the parameters of the unit cell⁵. These reflections, however, provide the following complementary information about the structure of lamellar crystals: the folds are short and the majority of these folds contain the acid group of the monomer unit⁶.

For samples crystallized from the melt, the situation concerning the occurrence of lamellar crystals is considerably more complicated⁷. No general relationship can usually be found between the orientation of the lattice and the angular positions of the small-angle X-ray scattering (SAXS) reflections for most oriented, bulk-crystallized polymers. However, in samples of low-density polyethylene (LDPE), a single texture, obtained by unidirectional rolling, is found where the folding planes of the lamellar crystals are parallel to the ($h01$) crystallographic planes⁸⁻¹⁰, where $h = 2-4$. Polyethylene is not a particularly good example for confirming whether

the folding planes of lamellar crystals in oriented samples are parallel, or otherwise, to the crystallographic planes, on account of the small length of its monomer unit. However, polyamides are useful materials in this respect because the length of their monomer unit is generally quite large. Polyamide 12 has been chosen for its low concentration of amide groups (i.e. 7.7 amide groups per 100 chain atoms). Polymorphism in nylon 12, which occurs on casting from a phenol-ethanol mixture, has been investigated by X-ray diffraction and infrared spectroscopy¹¹. Kollross and Owen¹² have studied the influence of hydrogen bonding on the mechanical behaviour of polyamide 12. It is only by thermal annealing in contact with formic acid, under well-defined conditions, that lamellar crystals in doubly oriented nylon 11 samples have their basal planes parallel to the (001) crystallographic planes, as found in single crystals^{13,14}. Oriented samples of the polyamide 6/2*n* series (where $n = 3-6$), which possess an almost single texture at the level of the lattice and a preferred orientation of the basal planes of the lamellar crystals, have been prepared by planar extrusion¹⁵. The limiting planes of the lamellae are parallel to the (001) crystallographic planes. The chain axes are along the extrusion direction, and the crystallographic a -axis is in the extrusion plane, perpendicular to the extrusion direction.

The relative orientation of the folding planes, with respect to the lattice, is investigated here in three types of polyamide 12 samples, i.e. sedimented mats of single crystals obtained from filtration, bulk samples oriented by unidirectional rolling, and samples extruded at 160°C .

EXPERIMENTAL

Granules of polyamide 12, obtained from BASF, are dissolved in boiling 1,4-butanediol under an inert nitrogen atmosphere. After the crystallization at 80°C is complete, the dilute solution (0.05 wt%) is slowly filtered using a Buchner glass funnel (porosity 4) maintained at 80°C, and after filtration, the funnel is kept at 50°C (under vacuum) to remove the last traces of solvent. Well-oriented sedimented mats are obtained from such a procedure. Unidirectional rolling of a polyamide 12 sheet is achieved by a four-fold thickness reduction procedure to give doubly oriented samples. The external shape of the rolled sheet is used as a reference; OY is the rolling direction and OX is normal to the YOZ rolling plane. Doubly oriented samples with an almost single texture are prepared by planar extrusion of a polyamide 12 sheet at 160°C, using a special device built in our laboratory.

Wide-angle X-ray scattering (WAXS) and SAXS patterns are obtained simultaneously with a modified Kiessig camera using a pinhole collimation; the distance between the sample and the registration plane is 400 mm for the SAXS experiments, with the latter using nickel-filtered Cu K α radiation. A cryokit (Air Products) is used for X-ray measurements at low temperatures. Silver is evaporated on both faces of the sample that are normal to the X-ray beam being used for calibration. Electron microscopy observations are performed on a CR10 Siemens microscope, with a thin layer of gold used as the calibration standard for the electron diffraction investigations.

RESULTS AND DISCUSSION

Polyamide 12 single crystals

Figure 1 shows typical single crystals of polyamide 12 and their electron diffraction pattern. The growing faces of these lamellar crystals are not so well defined as in the case of linear polyethylene single crystals^{16,17}. A least-squares fitting of 28 experimental Bragg spacings ((*h*00), (0*k*0) and (*hk*0)) gives the following parameters for the two-dimensional unit cell with a maximum deviation of 1%; $a = 1.027$ nm, $b = 0.5149$ nm and $\beta = 120.4^\circ$. These parameters are slightly larger than those previously reported in the literature¹⁸⁻²⁰ (see Table 1). Such discrepancies with respect to the unit-cell dimensions of polyamide 12 have previously been reported and have been traced to differences in the orientational symmetries of the particular samples under investigation²¹.

The WAXS and SAXS patterns of a sedimented filtration mat of single crystals of polyamide 12 are shown in Figures 2a and 2b, respectively. In the WAXS pattern (Figure 2a), the (001) reflections are concentrated on the mat normal (i.e. the meridian), with the (002) spots being the most intense. The (200) and (010) reflections are arced about the equator, i.e. parallel to the plane of the mat. The reflections are uniform rings when the X-ray incident beam is perpendicular to the plane of the mat. The normal to the plane of the mat is an axis of cylindrical symmetry around which the crystals are randomly oriented. In the SAXS pattern (Figure 2b), the reflections are arced with their maximum intensity on the mat normal, i.e. in the same angular position as the (001) reflections. The angular spread of the spots in the SAXS pattern is around 35–40°, which is the same as that of the (002) reflections of the WAXS pattern. The folding planes of the lamellar crystals

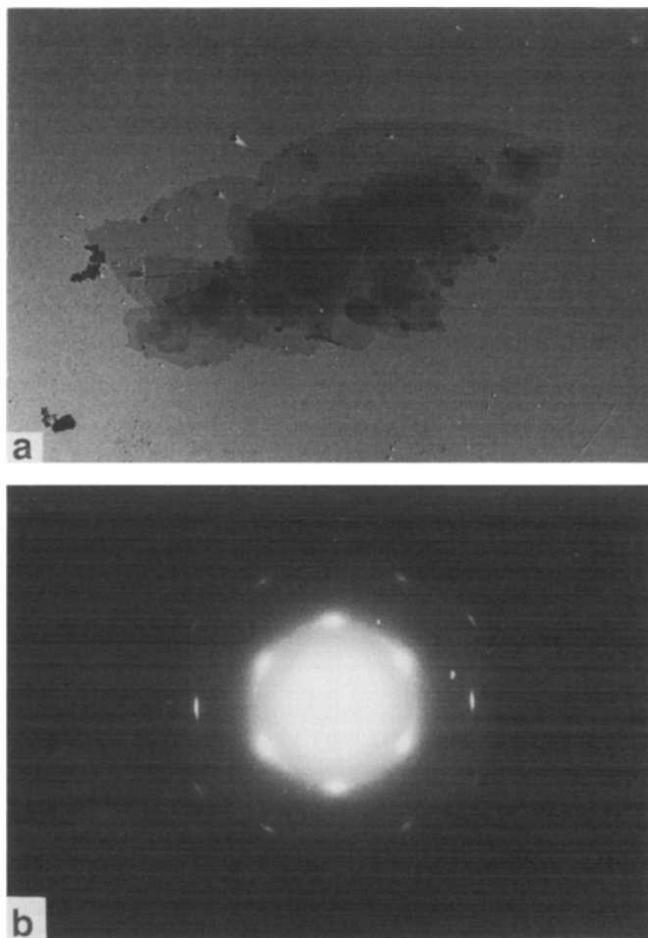


Figure 1 Polyamide 12: (a) typical single crystals grown from dilute solution in 1,4-butanediol at a magnification of 10 000, and; (b) the corresponding electron diffraction pattern

Table 1 Crystallographic unit cell parameters of polyamide 12, obtained by various authors

Crystal system	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	α (°)	β (°)	γ (°)	Reference
Hexagonal	0.47	0.47	3.10	90	90	120	18
Monoclinic	0.938	0.487	3.22	90	90	121.5	19
Monoclinic	0.958	0.479	3.19	90	90	120	20
Monoclinic	0.928	0.485	3.135	90	90	124.4	This work
Triclinic	0.928	0.529	3.135	59	90	60	This work

are parallel to the (001) crystallographic planes, as is generally observed in other polyamide single crystal samples²⁻⁴. The long spacing is 10.2 ± 0.2 nm, and the *R*-ratio is 3.25 (*R* being the ratio of the lamellar thickness to the d_{001} spacing corresponding to a repeat unit containing two amide groups). The 'mixed' WAXS and SAXS patterns of a sedimented mat of single crystals of polyamide 12, which have been annealed at 170°C is shown in Figure 3. Several diffractions localized normal to the mat plane are observed between the first order of the long spacing and the d_{002} Bragg spacing on the original pattern (see Table 2). Four orders of the long spacing are observed, which supports the uniformity of thickness of the lamellar crystals. There is some ambiguity, however, concerning the spacing equal to 1.65 nm, i.e. it does not correspond exactly to the sixth

Table 2 Bragg spacing values of the X-ray diffractions localized on the direction of the normal to the plane of a sedimented filtration mat of single crystals of polyamide 12^a

Spacing (nm)	10.54	5.28	3.54	2.74	1.65	1.54	1.27	0.794	0.539
Indexing	L_1	L_2	L_3	L_4	L_6	002	Extra	004	006

^a Obtained from a dilute solution in 1,4-butanediol at 80°C, and then annealed at 170°C

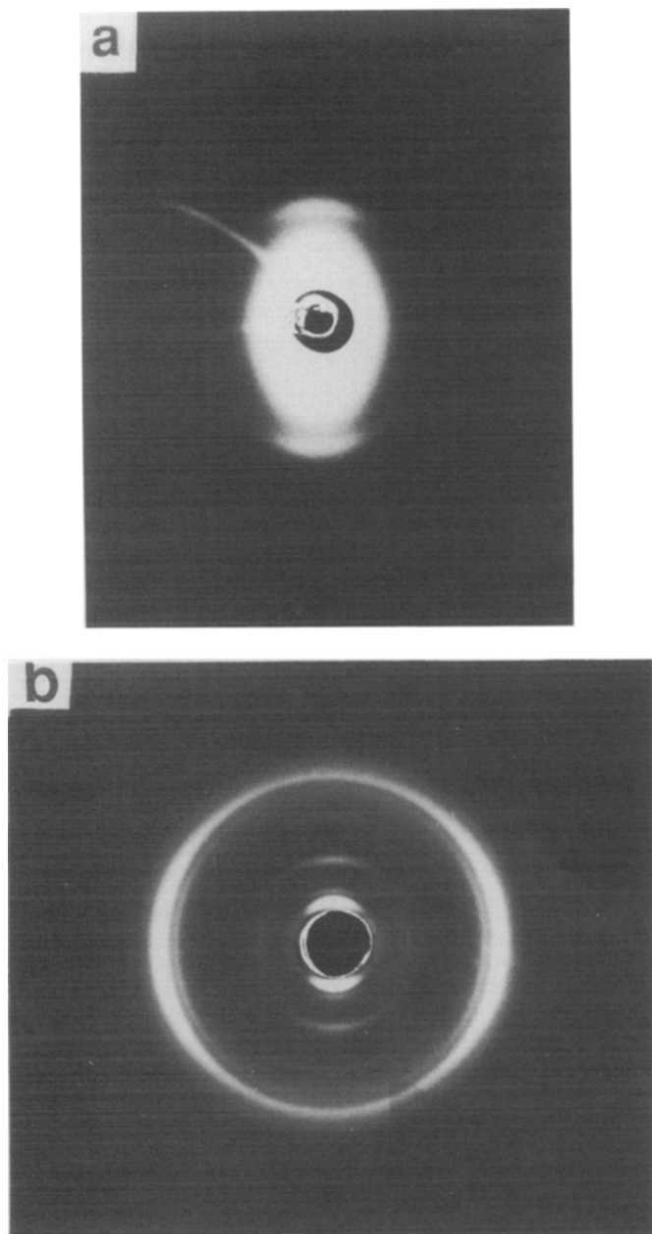


Figure 2 The WAXS (a) and SAXS (b) patterns of a sedimented mat of single crystals of polyamide 12, crystallized from a dilute solution in 1,4-butanediol (0.05 wt%) at 80°C. The incident X-ray beam is along the plane of the mat, with the mat normal vertical

order of the long spacing. Moreover, the reflection characterized by the spacing equal to 1.27 nm cannot be indexed with the parameters reported for the unit cell of polyamide 12 (see Table 1). The calculated structure factor of a single lamella which contains five or six monomer units has secondary maxima at 1.25 and 1.299 nm, values which agree well with this experimental value of 1.27 nm.

Doubly oriented samples of polyamide 12

The WAXS and SAXS patterns of a doubly oriented sample of polyamide 12, which has been obtained by

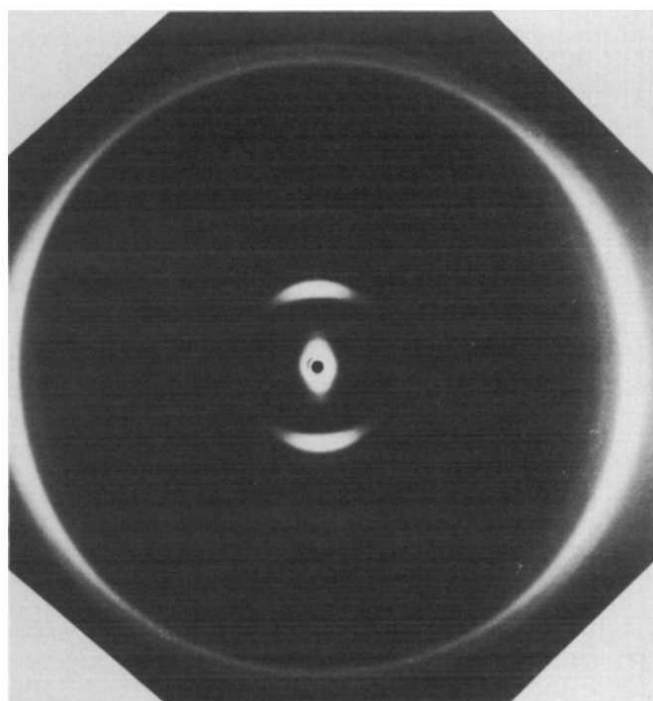


Figure 3 The 'mixed' WAXS and SAXS patterns of a sedimented mat of single crystals of polyamide 12, crystallized from a dilute solution in 1,4-butanediol at 80°C, and later annealed at 170°C. The incident X-ray beam is along the plane of the mat, with the mat normal vertical

unidirectional rolling and subsequent annealing at 130°C, are shown in Figures 4a and 4b, respectively; the incident X-ray beam is along the OZ axis. In the WAXS pattern (Figure 4a), the (001) arcs are concentrated on the OY rolling direction. A low-intensity reflection, also localized on the rolling direction, and having a Bragg spacing equal to 1.29 nm, is observed between the (002) and (004) reflections; this cannot be explained by using any of the proposed unit cells. The (200) reflections are arced about the equator, i.e. normal to the rolling plane: the (200) planes, containing chains which are linked by hydrogen bonds, are parallel to the YOZ rolling plane, as previously reported^{19,20}. In each such sheet, the directions of the neighbouring chains are antiparallel, as in the γ form of nylon 6²². The Bragg spacings of the WAXS pattern can be fitted to a monoclinic unit cell but our proposal differs mainly by a shorter value for the parameter along the chain axis (see Table 1). The orientation of the monoclinic unit cell is as follows: the chain axis is along the OY direction, with the a - and b -axes in the XOZ plane, perpendicular to the rolling direction, and at an angle of 120.4°. The proposed crystal structure contains four monomers (two chains per unit cell), i.e. with a two-monomer repeat unit along the molecular chain direction. In contrast, Owen and Kollross²¹ have proposed a 'primitive' basal plane for the unit cell of polyamide 12, implying that each crystal contains only 'parallel' chains. Northolt *et al.*¹⁸ have also reported an

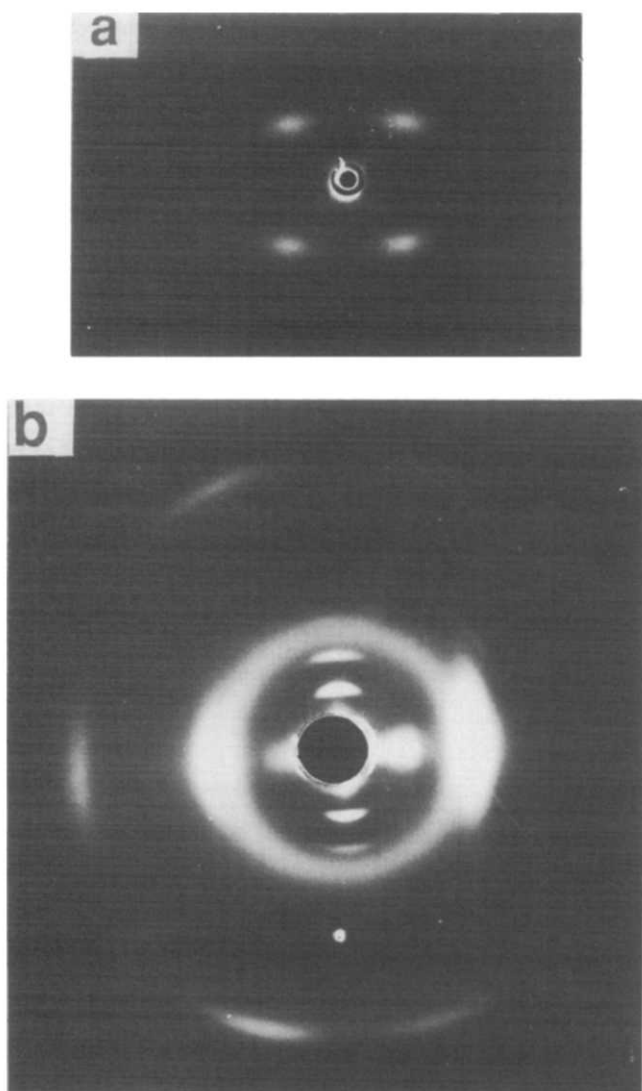


Figure 4 The WAXS (a) and SAXS (b) patterns of a rolled sample of polyamide 12 which had been annealed at 130°C. The incident X-ray beam is along the OZ axis, with the rolling direction (OY) vertical

Table 3 Values of the expansion coefficients in the plane perpendicular to the chain axis in a doubly oriented sample of polyamide 12 over different temperature ranges

Thermal expansion coefficient ($\times 10^3$) (K^{-1})	Temperature range ($^{\circ}C$)	
	-100 to 28	25 to 170
α_{200}	1.204 1.191	3.27
α_{010}	0.098 0.078	1.01

hexagonal primitive unit cell for a fibre drawn at room temperature. Expansion coefficients have been determined in the plane perpendicular to the chain axis (the a^*b^* plane in the reciprocal space) to check this proposal. Two temperature ranges were investigated, i.e. -100 to 28°C, and 25 to 170°C. Assuming a true hexagonal unit cell, the chains connected by hydrogen bonds should be localized in the (100), (010) or (110)

planes and the expansion coefficients along the normal to these crystallographic planes must be equal. In the temperature range from -100 to 28°C, the expansion coefficient is much larger along the normal to the (200) planes than along the normal to the (010) planes (Table 3). The expansion coefficient measured between 25 and 170°C along the same crystallographic directions gives qualitatively the same results (see Figure 5, which shows the temperature dependence of the corresponding Bragg spacings). These thermal expansion data confirm that the unit cell is not hexagonal in rolled samples of polyamide 12. The discrepancy between the values of the crystallographic parameters that have been reported for drawn and rolled polyamide 12 samples suggests that the method of preparation of the oriented samples leads to slightly different parameters for the unit cell.

The SAXS pattern is a four-point diagram, and the long spacing is 7.3 ± 0.2 nm. Two sets of lamellae normals, hence n_L poles, concentrated in the YOX plane, are separated by an angle of $43 \pm 2^{\circ}$ from the OY axis. Referring to the SAXS data obtained for single crystal mats, both axes connecting each pair of diffraction spots precisely determine both orientations of the normals to the limiting faces of the lamellar crystals in the doubly oriented polyamide 12. This means that the basal planes of the lamellae are parallel to the OZ axis and tilted by $43 \pm 2^{\circ}$, with respect to the OY axis. To bring about an agreement between the orientation of the unit cell and the lamellae normals, the lamellar crystals must be considered to be made up of blocks of four hydrogen bonded planes, with each plane shifted with respect to the next by one monomer unit (Figure 6). The limiting planes of the lamellar crystals are not parallel to any one of the crystallographic planes that have low Miller indices. Bulk polyamide 12 samples, oriented by unidirectional rolling, contain lamellar crystals having limiting planes whose orientation cannot be correlated with the orientation of the lattice. Upon rolling, the maximum tangential stresses occur in the YOX plane, along axes

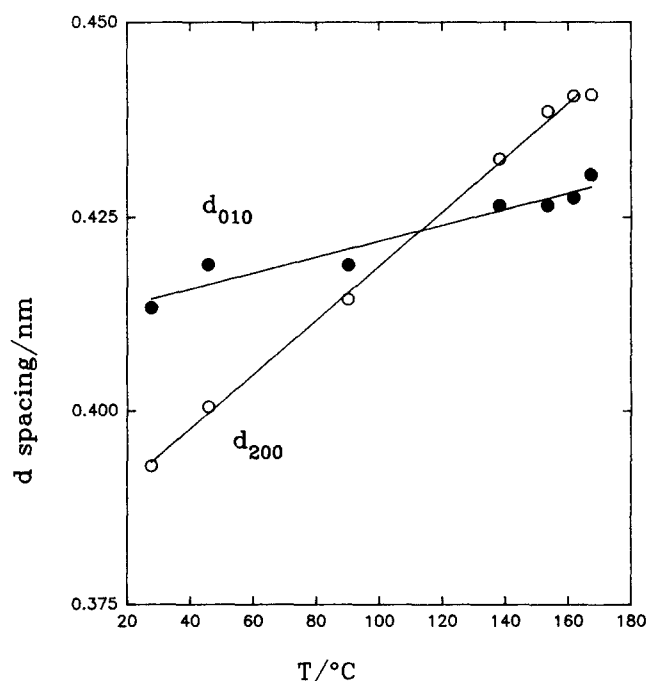


Figure 5 Variation of the (200) and (010) Bragg spacings as a function of temperature for a doubly oriented sample of polyamide 12

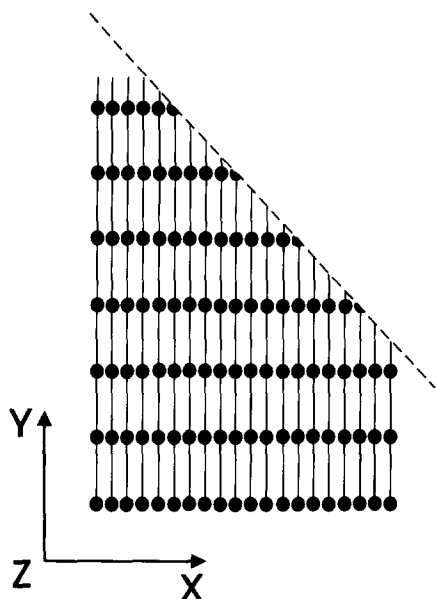


Figure 6 A schematic drawing of the orientation of the lattice and the limiting faces of lamellar crystals in a rolled sample of polyamide 12. The crystallographic c (chain axis)- and a -cell parameters are along the OY and OX axes, respectively. Planes containing hydrogen bonded chains are parallel to the YOZ plane, with folding occurring in the YOZ plane

at angles of 45° to the rolling direction. The crystalline-amorphous interface of the lamellar crystals is oriented perpendicular to both these directions where the strains are at a maximum. Such a proposal is attractive because rolled samples of several other linear polymers also display a four-point SAXS diagram. The angle, Φ , between the axis of the stacks of the lamellae (i.e. the rolling direction, OY) and the normal n_L to the limiting basal planes of these lamellar crystals, has values in the range from 40 to 45° (see *Table 4*). Values of ψ , the angle between c^* and the rolling direction OY, and the long-spacing distances, L , are also given in this table.

Doubly oriented polyamide 12 samples in contact with formic acid

The WAXS and SAXS patterns of a rolled polyamide 12 sample, annealed for 1 h in contact with formic acid at 78°C , are shown in *Figure 7*. This thermal annealing in contact with the acid significantly modifies the SAXS pattern, which now becomes a two-point diagram. The basal planes of the lamellar crystals are parallel to the (001) planes, since no modification in the orientation of the lattice is observed in the WAXS pattern. As with

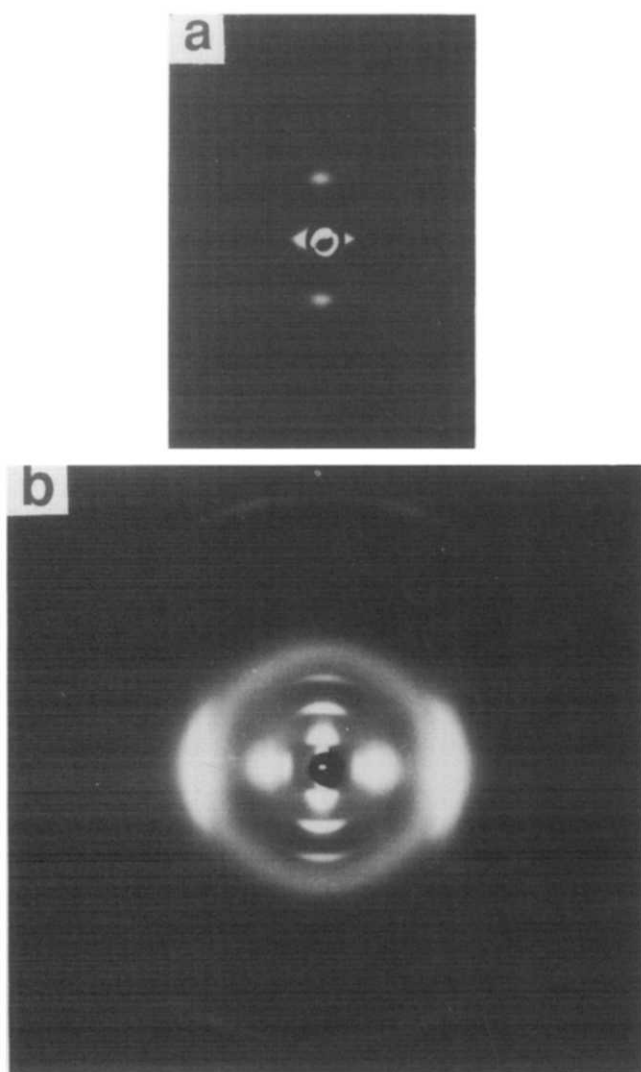


Figure 7 The WAXS (a) and SAXS (b) patterns of a rolled sample of polyamide 12 which has been annealed in contact with formic acid at 78°C . The incident X-ray beam is along OZ

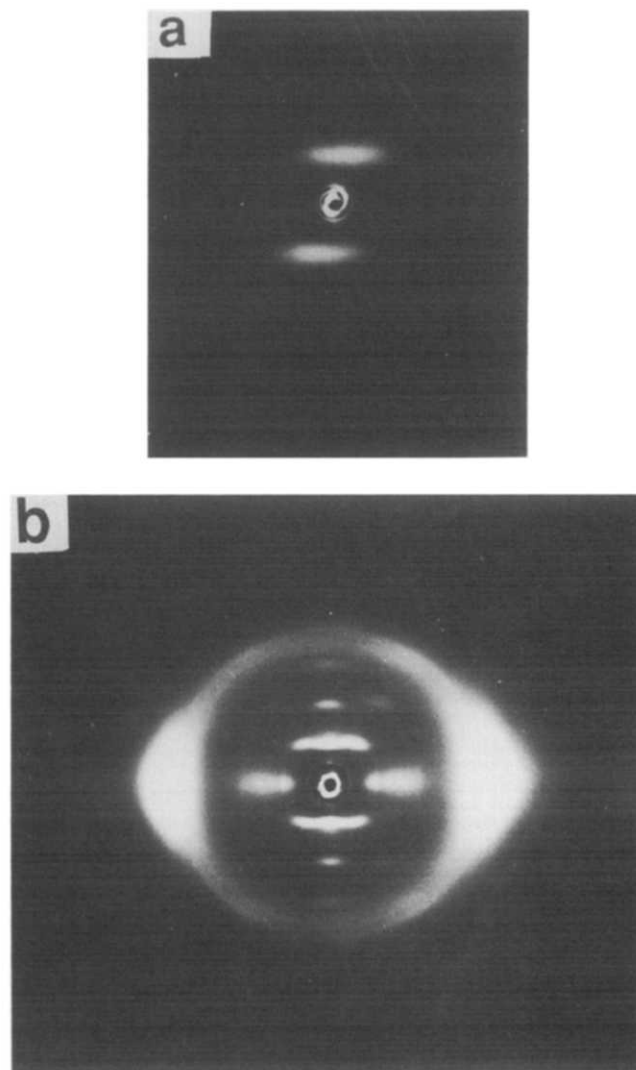


Figure 8 The WAXS (a) and SAXS (b) patterns of a polyamide 12 sample which has been extruded at 160°C . The incident X-ray beam is along OZ

doubly oriented samples of polyamide 11¹³, thermal annealing in contact with formic acid produces samples with the same structure as the sedimented mats of single crystals. The molecular reorganization resulting from thermal annealing is much easier in a swollen sample than in a 'dry' one. However two obvious differences must be noted here when compared to single crystal samples. First, the annealed sample keeps its double orientation, which is not the case for sedimented mats. Secondly, the long spacing of the annealed sample is 14.5 nm, which is larger than the lamellar thickness of

single crystals. Further details about the thermal annealing of oriented samples of polyamide 12 will be given elsewhere²³ and compared with other results^{24,25}. Such data for annealed samples will be used to check if the basal plane of the unit cell is 'primitive' or otherwise, in order to determine the type of packing of adjacent chains in hydrogen bonded sheets.

Doubly oriented polyamide 12 samples with an almost single texture

The WAXS and SAXS patterns recorded in the central zone of a polyamide 12 sample obtained by planar extrusion at 160°C are shown in *Figures 8a* and *8b*, respectively; the incident X-ray beam is along OZ. In the WAXS pattern, two types of (002) reflections are observed on the first layer line, namely the conventional (002) reflections belonging to the monoclinic unit cell and two pairs of reflections making an angle ψ with the OY axis and which have a Bragg spacing equal to 1.33 nm. These diffractions cannot be indexed on the basis of a monoclinic unit cell. Northolt *et al.*¹⁸ have published a similar WAXS pattern which was obtained on a sample drawn at a temperature below its melting point. These meridional reflections are characteristic of a triclinic unit

Table 4 Angular positions of the SAXS and (001) reflections with respect to the rolling direction for several rolled polymers^a

Polymer	Φ (°)	ψ (°)	L (nm)
LDPE	45–50	0	7.3 ± 0.2
Polyamide 6	41 ± 2	0	6.2 ± 0.3
Polyamide 11	42 ± 2	23	6.7 ± 0.3
Polyamide 12	43 ± 2	0	7.0 ± 0.2
PVDF	40 ± 2	0	7.2 ± 2

^a See text for definitions

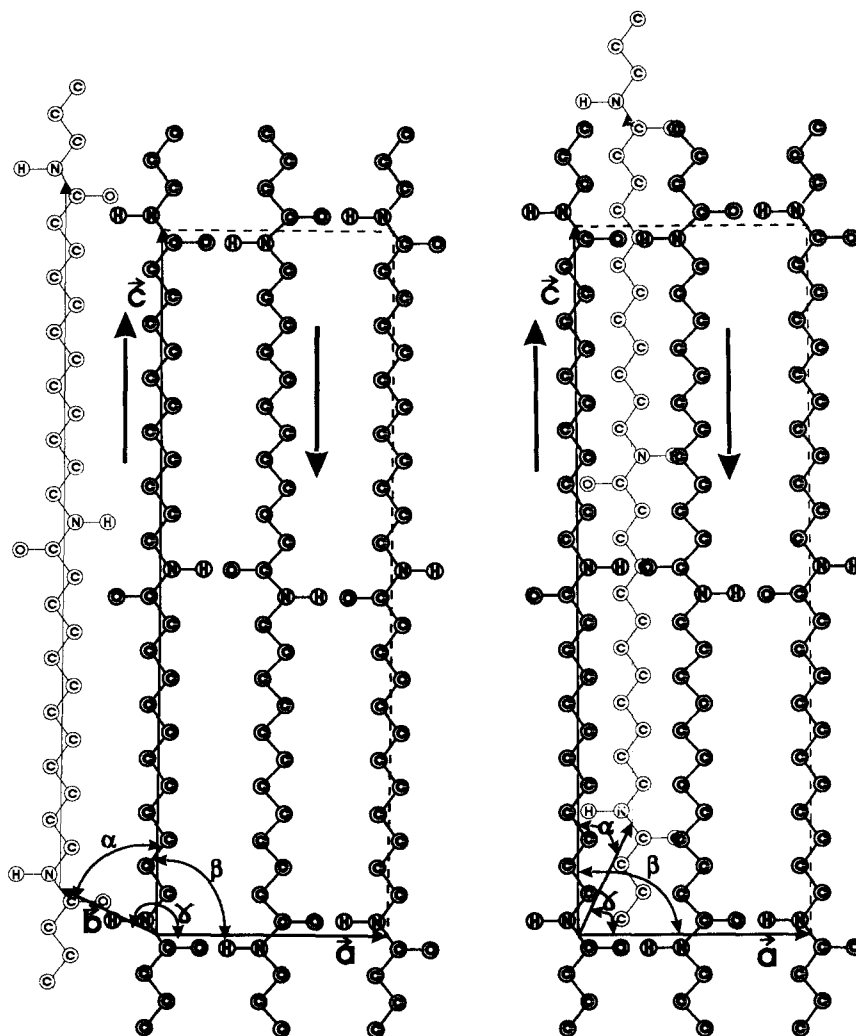


Figure 9 A schematic representation of the shear deformation of the monoclinic unit cell of polyamide 12 along the chain axis, in which deformation by an amount equivalent to two methylene units yields a triclinic unit cell. The arrows indicate the direction of NH-CO units, with the molecule of polyamide 12 being directionally polar

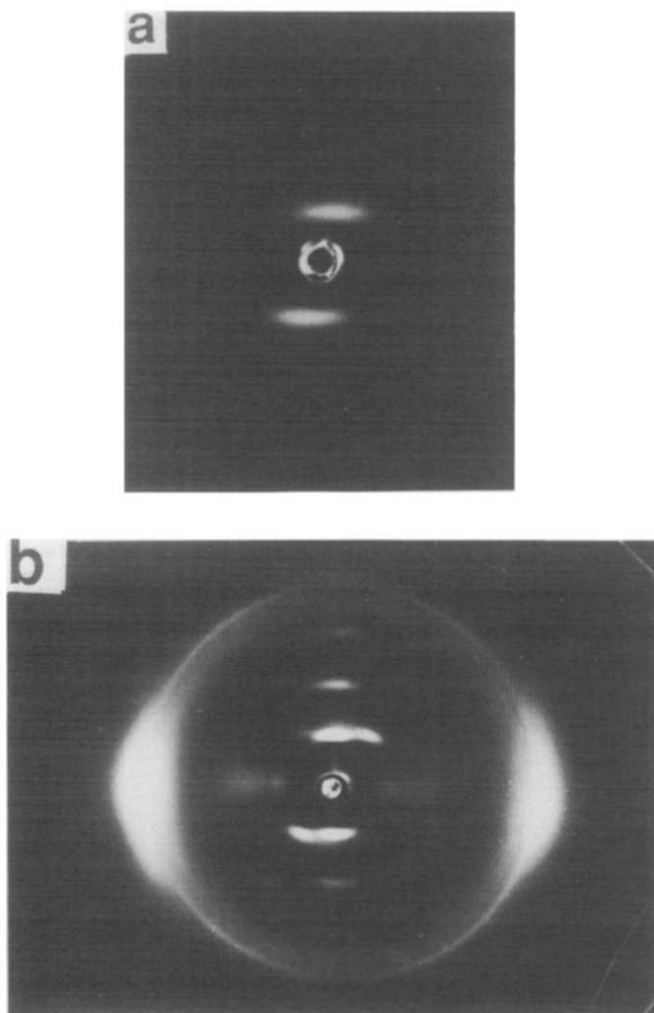


Figure 10 The WAXS (a) and SAXS (b) patterns of a doubly oriented polyamide 12 sample with an almost single texture. The incident X-ray beam is along OZ, with the rolling direction (OY) vertical

cell. From the WAXS patterns obtained with the incident X-ray beam along OZ, OY and OX, the following preliminary triclinic unit cell parameters are proposed: $a = 0.91$ nm, $b = 0.53$ nm, and $c = 3.18$ nm; $\alpha = 59^\circ$, $\beta = 90^\circ$, and $\gamma = 120^\circ$. The triclinic unit cell results from a shear of the sheets containing hydrogen bonded chains along the chain axis of the monoclinic unit cell by an amount equivalent to two methylene units (see *Figure 9*). In the monoclinic unit cell of polyamide 12, as seen in the α -form of polyamide 6, the adjacent segments in the hydrogen bonded sheets are inverted, which allows all hydrogen bonds to be easily formed. Such a shear of the lattice has been suggested as explaining the polymorphism observed in fibres of polyesters²⁶ and polyamides²⁷, and has been experimentally realized in rolled samples of polyamide 11²⁸. As the SAXS pattern is always a conventional four-point diagram, the triclinic lamellar crystals have the same limiting planes as the conventional monoclinic crystals.

The WAXS and SAXS patterns obtained at the periphery of the sample are shown in *Figures 10a* and *10b*, respectively. The (002) reflections of the WAXS pattern show that only one population of the triclinic crystal species is present in this part of the sample. The SAXS pattern contains essentially two diffraction spots;

the Φ angle between the lamellar surface normals n_L and the axis OY has a value of 38° . The peripheral part of the sample contains only one population of lamellar crystals, with basal planes parallel to the (001) crystallographic planes. The chain axes of these lamellar crystals, belonging to either the monoclinic or the triclinic phase, are along the axis OY. This sample possesses an almost single texture at the level of the lattice, as well as at the level of the limiting planes of the lamellar crystals. The long-spacing of this oriented sample with a single texture is 11.2 ± 0.3 nm.

CONCLUSIONS

Sedimented mats of single crystals of polyamide 12, crystallized from a dilute solution in 1,4-butanediol at 80°C contain lamellar crystals having basal limiting planes parallel to the (001) planes, with a lamellar thickness of 10.2 nm. In doubly oriented samples obtained by unidirectional rolling, the limiting planes of the lamellar crystals are not parallel to any one of the crystallographic planes that have low Miller indices. It is only by thermal annealing in contact with formic acid that lamellar crystals with folding planes parallel to the (001) plane can be restored. Bulk annealed samples differ from mats of single crystals: they remain doubly oriented and have a long-spacing which is larger than that found in single crystals. Doubly oriented samples prepared by planar extrusion contain two allotropic forms, namely the conventional monoclinic phase and a triclinic phase, with the limiting planes of the lamellar triclinic crystals parallel to the (001) crystallographic planes.

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