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Structural studies of odd-nylon crystals grown from solution

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Lamellar crystals of nylons 5, 9 and 13 in α-structure were grown from solution and systematically studied by electron microscopy and X-rays. Electron diffraction showed that they all consist of a twinned structure with hydrogen bonds running parallel to the long dimension of the crystals. Polyethylene decoration of such crystals revealed folding sectorization only in the case of nylon 9. Diffraction data from films both uniaxially and biaxially oriented were used to propose a unifying model for the α-structure of odd nylons based on the antiparallel model given by Tadokoro. In this model successive sheets are progressively sheared along the chain axis by approximately twice the interatomic height. Such a model is able to account well for most of the structural observations we have made on solution grown crystals.

1. Introduction

Knowledge of the crystalline structure of polyamide single crystals and how it is related to the lamellar morphology is still limited and by no means free of uncertainties. Although it is generally assumed that both hydrogen bonding and chain folding must play a decisive role in the crystal growth mechanism, evidence provided so far is not sufficient to describe in detail how the chains are organized within the crystal.

Electron microscopy studies on nylon single crystals are scarce, in particular those dealing with odd nylons [1]. Furthermore, interpretation of data from such studies is usually hindered by the occurrence of polymorphism as well as by the difficulties encountered in the preparation of well developed crystals. In the case of odd nylons an additional complexity arises from the ability of their chains to be arranged in perfectly hydrogen bonded sheets when aligned in either parallel or antiparallel directions.

We reported recently on the structure of nylon 7 solution grown crystals [2]. It was found that lamellar crystals of this nylon grown in glycerine at high temperature consisted of a twinned α-structure with 0 1 0 planes being the composition planes. It was also found that such crystals were subdivided in folding domains so that both chain folding and hydrogen bonding shared the 0 1 0 crystallographical planes in those sectors bounded by the lateral edges of the crystal (0 1 0 sectors). Although sectorization is a feature familiar to polymer single crystals, it had not previously been observed in those in which extensive intermolecular hydrogen bonding occurs. Some years ago we also carried out an electron microscopy study on nylon 3 single crystals [3]. In that case, neither twinning nor sectorization was observed although the latter aspect was not specifically investigated. To our knowledge no other detailed electron microscopy studies on odd nylons have been reported.

The relevant conclusions drawn from the study of nylon 7 stimulated us to extend the electron microscopy study to other members of the family. Lamellar crystals of nylons 5, 9 and 13 have now been grown from solution and investigated by electron diffraction and isochronous surface decoration with polyethylene vapours. In order to support the interpretation of data provided by this study, uniaxially and biaxially oriented films of these nylons were also examined by electron diffraction. The aim of this work is to give a comprehensive picture of the crystalline structure of odd-nylons lamellar crystals covering both molecular organization and morphology.

Data reported in the literature on the crystal α-structure of nylons subjected here to study are in clear disagreement. Two different crystal models have been put forward for nylon 9 according to what type of arrangement, parallel or antiparallel, is assumed for the neighbouring chains within the hydrogen bonded sheets [4, 5]. No conclusive crystal model exists either for nylon 5. In this case two structures, both of them made up of antiparallel hydrogen bonded chains but differing from each other in the relative orientation of adjacent sheets have been proposed [5]. On the other hand, no data at all have been published so far for nylon 13.

2. Experimental procedure

The nylon 5 sample used in this work was prepared by anionic ring opening polymerization of piperidinone in the presence of quaternary ammonium salt catalyst as described in detail elsewhere [6]. Samples of nylons 9 and 13 were a kind gift received from Dr Pryde (Department of Agriculture, Peoria, IL, USA). The reduced viscosities at 0.1% concentration in m-cresol at 25 °C were 0.86, 0.68 and 1.14 $\mathrm{dl\,g^{-1}}$ for nylons 5, 9 and 13, respectively, which correspond to molecular weights of about 7000, 5000 and 10 000 when those figures are compared with the viscosimetric data reported for nylon 5 [7].

Samples to be studied by electron microscopy were processed in three different ways. Films showing uniaxial orientation were prepared by stroking a 30% solution of the polymer in formic acid on a glass slide at room temperature. Doubly oriented films were obtained instead by epitaxial crystallization following the technique described by Wittmann and Lotz [8]. In both cases, film zones displaying high birefringency under the polarizing microscope were selected for subsequent electron microscopy observation. Single crystals were obtained by isothermal crystallization from dilute solutions in glycerine or triethyleneglycol. These samples were deposited onto carbon-coated grids and then shadowed with platinum–carbon at an angle of 15°. In some cases they were decorated with polyethylene vapours [9] before shadowing. A Philips EM-301 instrument operating at 80 and 100 kV for bright field and electron diffraction modes, respectively, were used throughout this work. Electron diffraction patterns were recorded under a minimum flux of electrons in the selected area mode and were internally calibrated with gold. Crystal mats to be studied by X-rays were prepared by slow filtering and diagrams recorded at room temperature with the beam inciding parallel to the mat surface. A modified Statton camera (W. H. Warhus, Wilmington, DE, USA) with graphite monochromatized copper radiation was used for these experiments.

3. Results

Crystallization of nylon 5 from glycerine at 120 °C rendered a wide diversity of morphologies differing in complexity but all of them consisting of a more or less tightened bundle of fairly large platelets about 8 to 9 nm thick. Two extreme illustrative examples are given in Fig. 1. Crystallizations of nylons 9 and 13 were carried out in triethyleneglycol at 180 °C and 250 °C, respectively. In both cases, a rather homogeneous population of crystals with a thickness of about 8 nm was obtained, representative examples of which are shown in Fig. 2. A significant feature common to all these crystals and shared also by those previously reported for nylon 7 is the serrated shape displayed by the front edges, a feature which also affects the side edges in the case of crystals of nylon 13. On the other hand, fine striations parallel to the long dimension of the lamella are observed for nylon 5 (as was the case for nylon 7), whereas a smooth surface is exhibited by the crystals made of nylons 9 and 13 instead.

X-ray diagrams showing moderate orientation were recorded from sedimented mats of these crystals (Fig. 3). They contain two intense equatorial (nylon 5) or quasi-equatorial (nylons 9 and 13) reflections with Bragg spacings close to 0.44 and 0.38 nm which strongly suggest the presence of the α-structure in each case. The pattern along the meridian in both, wide and low angle regions, is also similar for the three nylons provided that differences in the length of the respective repeating units are taken into account. In fact, a rather intense reflection appears centred on the meridian

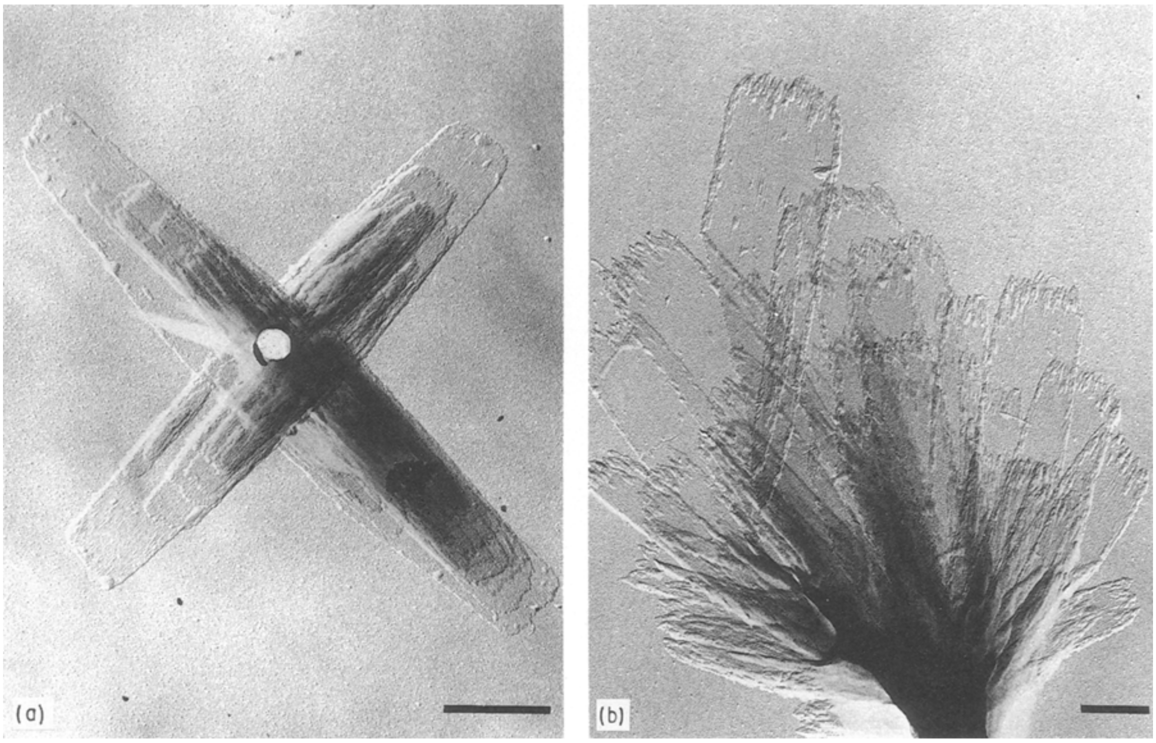


Figure 1 Lamellar crystals of nylon 5 grown in glycerine at 180 °C. (a) Isolated morphology showing overgrowths and fine striations parallel to the long edges. (b) Sheaf-like morphology with irradiated lamellae displaying serrated tip edges. Bars denote 1 μm.

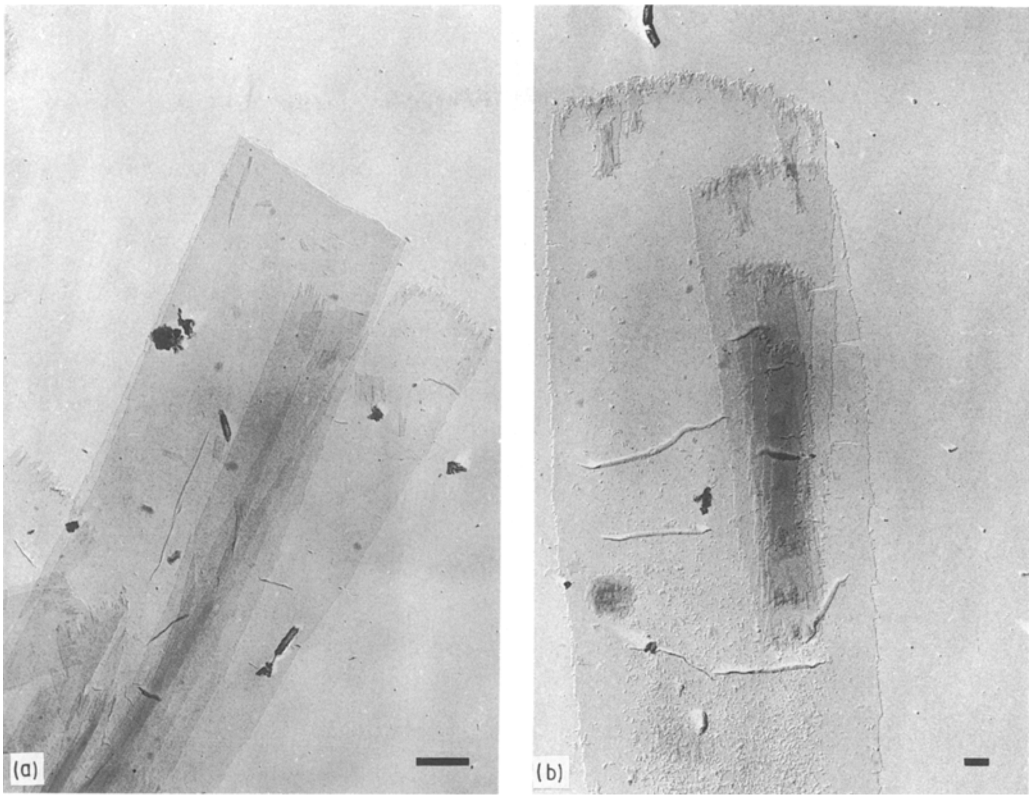


Figure 2 Lamellar crystals of (a) nylon 9 and (b) nylon 13 grown from triethylene glycol at 180 and 250 °C, respectively. Note the serrated morphology affecting the long edges of nylon 13 crystals. Bars denote 1 μm.

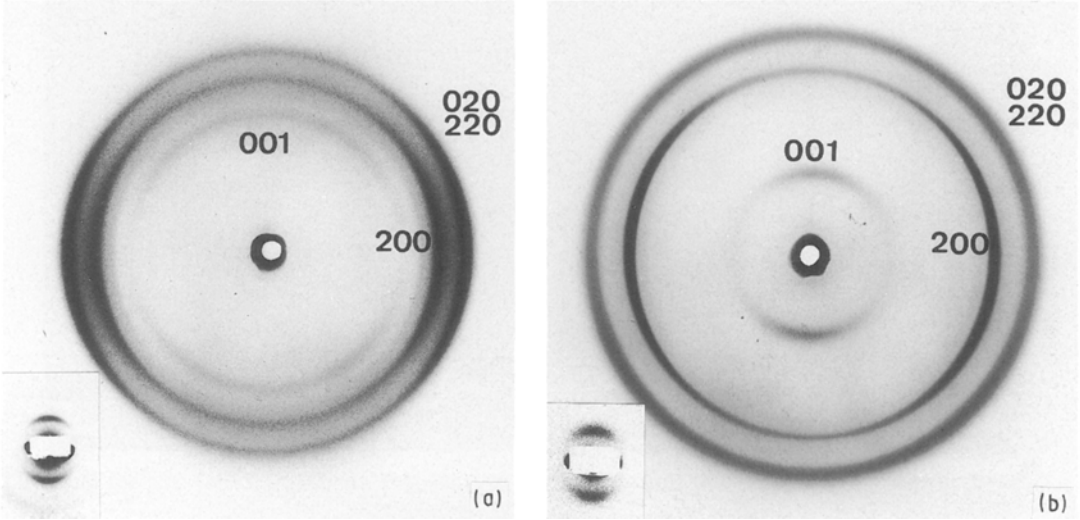


Figure 3 X-ray diagrams from sedimented solution grown crystals of (a) nylon 5 and (b) nylon 9. The lamellar plane is horizontal. Low angle reflections observed in each case are inserted in the corresponding insets.

(nylons 9 and 13) or near the meridian (nylon 5) with a spacing such as expected for the 0 0 1 distance given in the literature for each particular nylon in the α-structure. In the small angle region an intense reflection with a spacing around 7 to 9 nm and a few others corresponding to its higher orders are common to all three nylons. In agreement with previous experiences gained with oriented mats of other nylon single crystals [10] these reflections may be interpreted as arising from the stacking of lamellae 7 to 8 nm thick lying horizontally. Chains within the lamellae must be oriented either normal (nylon 5) or at an angle near 60° (nylons 9 and 13) to the basal plane of the sedimented mat.

Selected area electron diffraction of all these crystals produced similar results. A single crystal diagram was obtained when a rather small area located on the side of the crystal was selected to diffract. Such a pattern consists of an oblique array of reflections defining two basic spacings around 0.44 and 0.37 nm. It may be straightforwardly interpreted on the basis of a monoclinic lattice such as that described by Tadokoro [11] for the α structure of odd nylons. In such a crystalline model, hydrogen-bonded sheets are made up of fully extended chains in an antiparallel arrangement so that a figure ranging between 0.95 and 1.0 nm and corresponding to the double of the interchain distance results for the ***a*** parameter of the lattice. Sheets are separated by a distance near to 0.38 nm and shifted along the ***a*** axis so that a γ angle ranging between 65° and 70° results. The reciprocal γ^* angle measured in these diagrams is 67° for nylons 7, 9 and 13 (the same value was observed for nylon 7 as reported [2]) whereas a slightly lower value, 63°, was found for nylon 5. The orientation of the lattice with respect to the crystal, as deduced from the relative orientation of the electron diffraction pattern, is such that hydrogen bonds run parallel to its long dimension.

A composed diagram is obtained instead when the size of the diffracting area is not restricted. The pattern is in full agreement with the existence of a twinned structure with the composition plane being the 0 1 0 plane. Reproductions of the single and twinned diagrams recorded from nylons 5 and 13 are shown in Fig. 4. Those corresponding to nylon 9 are almost identical in both spacings and intensities to those obtained from nylon 13 and have not been included. It should be remembered that a similar result was attained in the case of nylon 7. It appears, therefore, that the existence of twinning is a common feature shared by all odd nylon lamellar crystals. A schematic representation of such diagrams indexed according to the Tadokoro's crystalline model is depicted in Fig. 5.

The ratio of crystal thickness to average length of the polyamide chains used in this work is low enough to presume that chain folding takes place in each case. About ten folds are actually required to accommodate such chains in extended conformation within the height of the lamella. In order to disclose how these foldings are organized in the crystals we have made use of the valuable decoration technique developed by Wittmann and Lotz to analyse the surface topography of polymer crystals [9]. In this method, condensation and subsequent crystallization of polyethylene vapours on a crystalline substrate results in the formation of small elongated crystals, the orientation of which provides insight into the surface structure, and more precisely into the fold orientation in the case of a substrate consisting of folded polymer chains. Different decorating patterns were obtained for crystals of nylons 5, 9 and 13 when subjected to decoration under identical experimental conditions (Fig. 6). Nylon 9 crystals display a well outlined sectorization resembling that observed for nylon 7 [2]. In these crystals, sectors bounded by the long growth faces, which were identified as 0 1 0 sectors by electron diffraction, exhibit a unique orientation for the decorating rods, normal to the 0 1 0 direction. We conclude

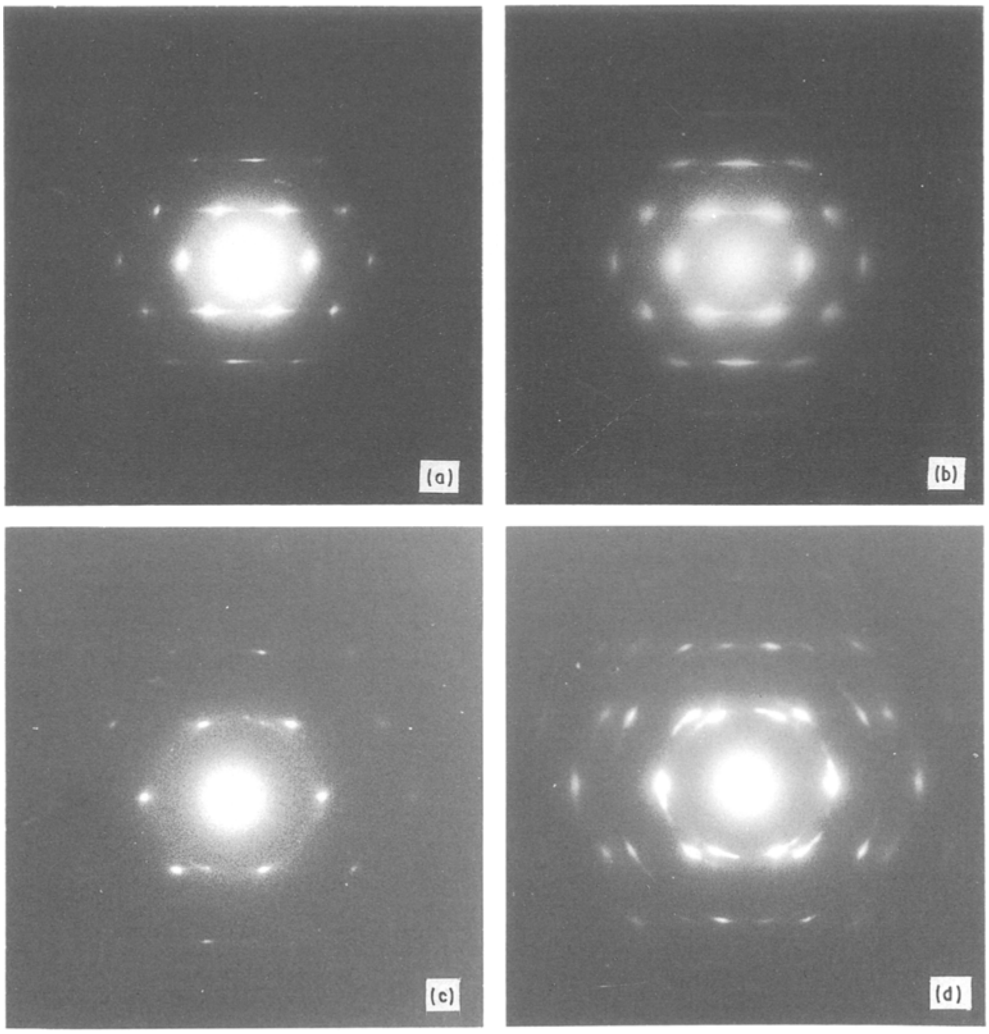
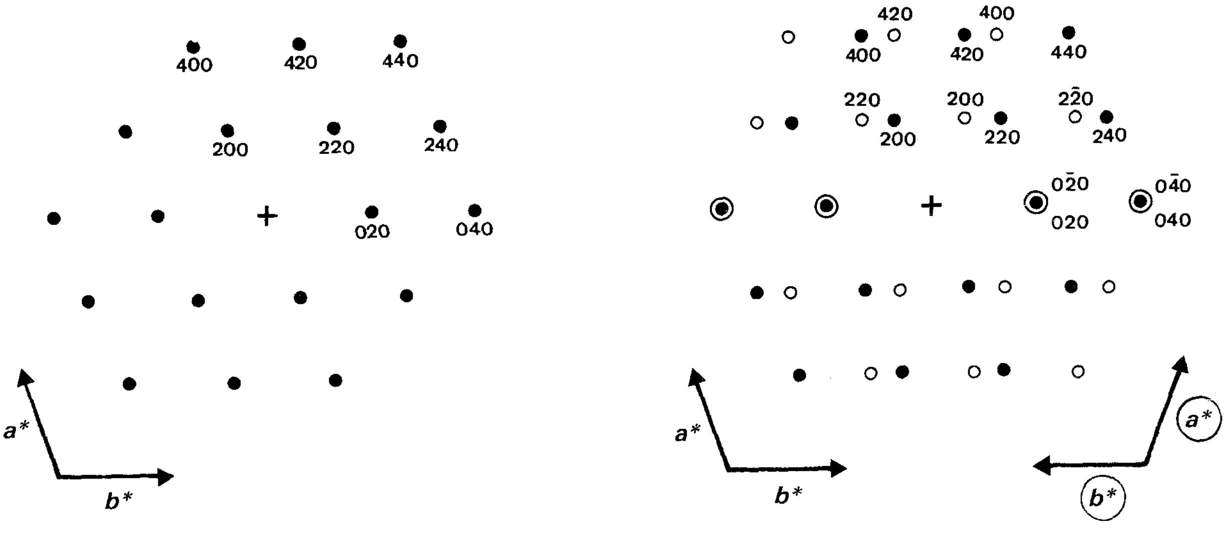


Figure 4 Electron diffraction patterns recorded from crystals of (a) single nylon 5 (b) twinned nylon 5 (c) single nylon 13 and (d) twinned nylon 13.



(a) (b)

Figure 5 Schematic representation of the single and twinned electron diffraction patterns of odd nylon crystals indexed according to the unit cell model given by Tadokoro (see Table I and text).

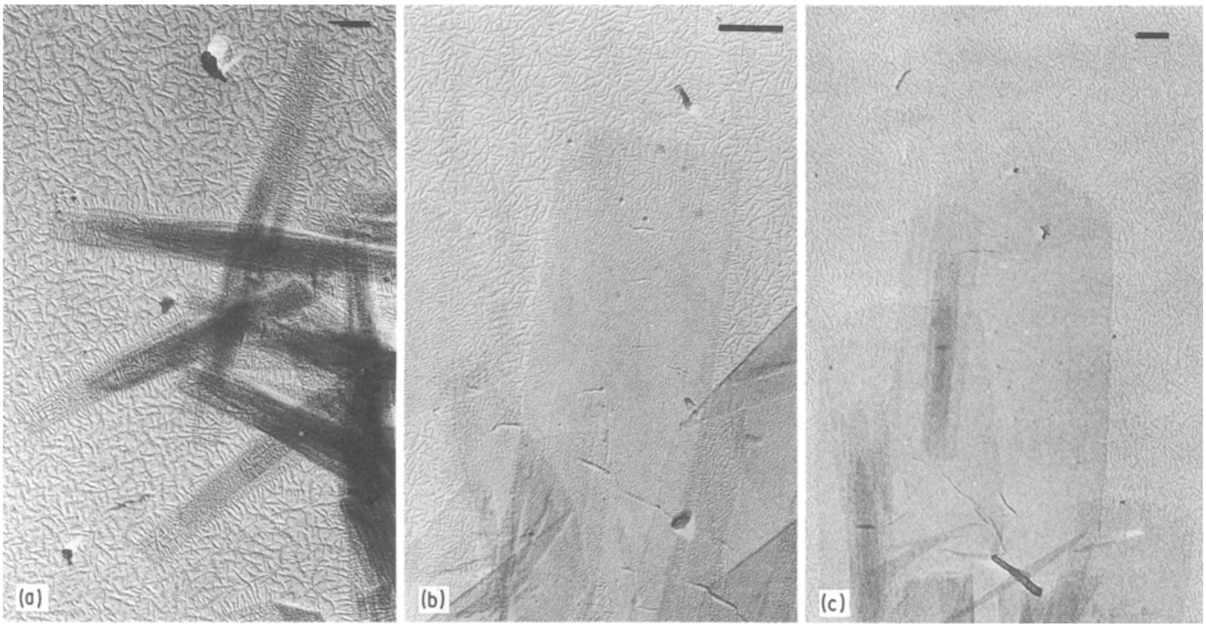


Figure 6 Lamellar crystals of (a) nylon 5, (b) nylon 9 and (c) nylon 13 decorated with polyethylene vapours before shadowing. Note in (a) as the decorating rods are frequently centred near to the long edges. A sharp change of orientation of the decorating material is apparent in nylon 9 crystals. No preferred orientation of the rods is detected in nylon 13 crystals. Bars denote 1 μm.

from these observations that both folding planes and hydrogen bonds in 0 1 0 sectors run parallel to the long dimension of the crystals. On the contrary, a range of orientations is observed in those sectors bounded by the front growth edges, namely filling sectors. Such a pattern is interpreted as being indicative of microsectorization according to previous studies carried out in polyethylene single crystals [9]. On this basis the front growth faces will be made up of multiple 0 1 0 and 1 1 0 microfacets as reflected by the serrated morphology of their edges. On the other hand, a unique orientation of the polyethylene rods, normal to the long crystal edges, was observed all over the surface of decorated nylon 5 crystals. A careful inspection of the decorating picture reveals, however, that nucleation giving rise to rods, took place mostly near the long crystal edges. It can be thought, therefore, that chain foldings are structured in nylon 5 in a similar way to nylons 7 and 9. As opposed to these cases, no preferred orientation at all was detected on the decorating patterns produced by the nylon 13 crystals.

In order to substantiate the interpretation of the results obtained with solution grown crystals, a systematic electron diffraction analysis was carried out on films of nylons 5, 9 and 13. Uniaxially oriented films were prepared by stroking whereas those displaying a biaxial texture were obtained by epitaxial crystallization. The patterns recorded in each of these two textures were very similar to those for the three nylons under study. The couple corresponding to nylon 9 is depicted in Fig. 7 to illustrate the general appearance displayed by both types of diagrams. Features of such diagrams relevant to the crystalline structure are the following.

(a) The well defined meridional reflection appearing in both uniaxial and biaxial diagrams with a spacing of 0.120–0.125 nm. This spacing is made to correspond to the mean rise of the interatomic bond along the chain in extended zigzag conformation.

(b) The intense equatorial pair of reflections appearing in uniaxial diagrams with spacings at 0.44 and 0.37 nm characteristic of the α-structure.

(c) The group of reflections appearing along the equator of diagrams were recorded from doubly oriented films. They may be indexed as $2k0$ with $k = 2n$ (n being an integer) indicating that the crystal lattice in these films is lying with the 0 1 0 planes normal to the electron beam. Such planes are in contact with the substrate and contain the hydrogen bonds. This is in agreement with all previously reported observations made on epitaxial crystallization of polyamides [8, 12].

(d) The outstanding layerline appearing in both types of diagrams and corresponding to a repeating distance of 0.24–0.25 nm. This reveals that a periodicity along the chain axis equivalent to twice the interatomic backbone height must be a structural feature common to all odd nylons.

These observations in conjunction with others made on solution grown crystals, clearly demonstrate that all the samples studied in this work adopted a layered structure. They reveal further that the geometry of such structures should be almost identical for all members of the odd nylon family.

Diffraction data are not sufficient to discriminate between the two alternative models that are currently considered for the crystal α-structure of odd nylons. If, however, morphological observations made on lamellar crystals are taken into account, the antiparallel model turns to be clearly favoured. It is obvious that an antiparallel arrangement of hydrogen-bonded chains is the only one compatible with the occurrence of planes containing both chain foldings and hydrogen bonds as observed in the folding sectors of nylon 7 and 9 crystals. Furthermore, we have tested the two models in detail by using their respective reported crystal data to explain our diffraction data. A better correspondence was found in fact, when the antiparallel model was considered. We have noticed in addition that a model with hydrogen-bonded sheets progressively shifted by approximately 0.25 nm along the chain axis can be assumed for the whole series if the lattice parameters given in the literature for each particular nylon are slightly modified. Such a model not only explains even better our electron diffraction data but gives a better account for the striking 0.25 nm layerline that without exception appears in the oriented diffraction patterns.

The model can be straightforwardly applied to other odd nylons not investigated in this work, as is the case of nylons 3 and 11, if their respective crystal data are modified in a similar manner. A comprehensive description of structural data embracing the whole odd-numbered family is given in Table I. It includes figures reported in the literature as well as those calculated on the basis of the results given in this work. A schematic representation of the molecular organization assumed in our model as well as its disposition in relation to the crystal morphology are given in Figs 8 and 9.

4. Discussion

Up to six different arrays of chains may be conceived for the α-structure of odd numbered nylons. They differ either in the relative upside-down orientation adopted by adjacent chains in the sheets or in the relative orientation of the sheets themselves. As such differences are not clearly reflected in the diffraction

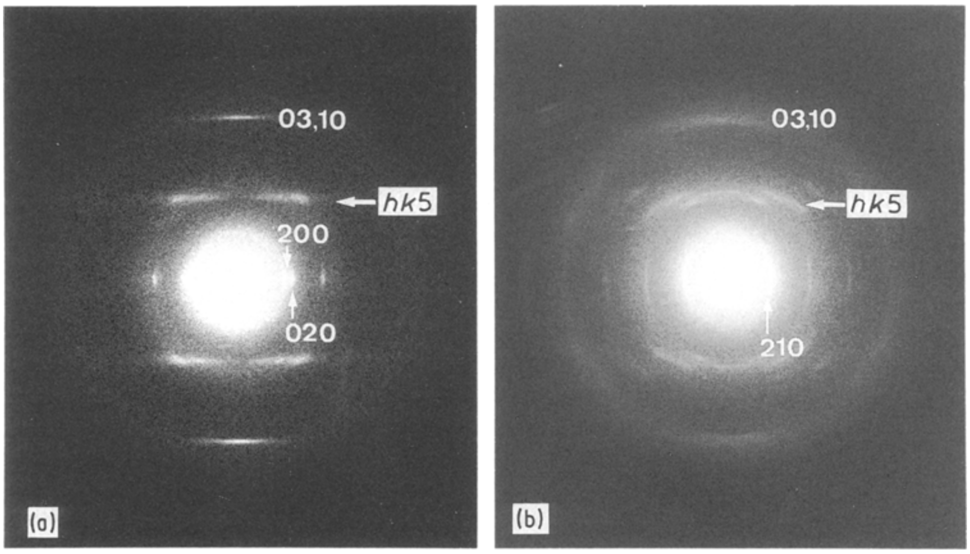


Figure 7 Electron diffraction diagram of oriented films of nylon 9: (a) Uniaxially oriented film obtained by stroking. (b) Biaxially oriented film prepared by epitaxial crystallization onto benzoic acid. The chain axis is vertical in both cases.

TABLE I

Nylon	Observed data[a]		Δ*a*[b]	Unit cell[c]	Unit cell[d]	Calculated values[e]	
	200	020		*a*, *b*, *c*	*a*, *b*, *c*	200	020
	γ*			α, β, γ	α, β, γ	γ*	Δ*a*
3	0.405	0.378	0.240	0.96, 0.896, 0.48[f]	0.960, 0.102, 0.480	0.405	0.378
	57.5			90, 90, 57.5	61.80, 90.0, 61.8	57.6	0.240
5	0.430	0.380	0.194	0.95, 0.840, 0.75[g]	0.965, 0.978, 0.726	0.430	0.379
	63			90, 90, 64	60.4, 90.0, 66.7	63.0	0.193
7	0.440	0.376	0.160	0.98, 1.00, 0.98[h]	0.970, 0.965, 0.984	0.444	0.377
	67			56, 90, 69	58.6, 90.0, 70.0	66.4	0.165
9	0.440	0.376	0.160	0.97, 0.97, 1.26[h]	0.970, 0.960, 1.242	0.443	0.375
	67			64, 90, 67	58.5, 90.0, 70.0	66.3	0.164
13	0.441	0.372	0.158		0.970, 0.955, 1.722	0.443	0.372
	67				58.2, 90.0, 70.0	66.3	0.163

[a] Observed electron diffraction data from crystals (nm).

[b] Calculated from observed data by 020/tan γ*.

[c] Unit cell parameters reported in the literature.

[d] Unit cell parameters modified according to the text. Modifications are made by refining the respectively reported unit cell against our observed data and keeping Δ*c* = 0.25 nm as an approximately constant value.

[e] Calculated data on the basis of the modified unit cells.

[f] [3].

[g] [5].

[h] [11].

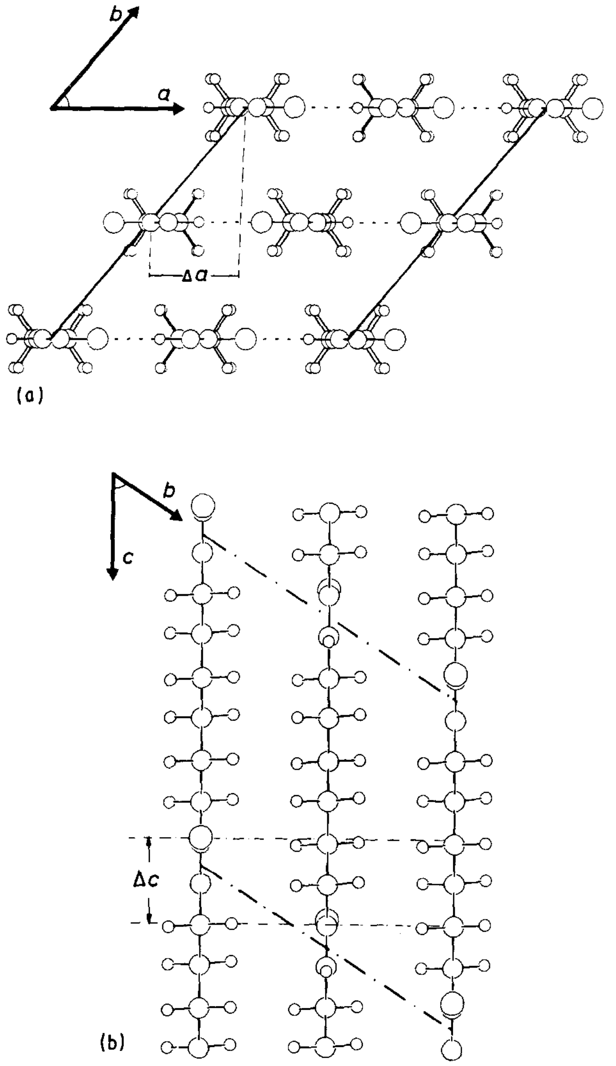


Figure 8 Schematic representation of the molecular organization in the crystal structure of odd nylons. (a) Unit cell viewed along the *c* axis. Chains are in an up-and-down arrangement along the ***a*** axis, and successive sheets alternate in polarity along the ***b*** axis. (b) View along the ***b*** axis showing three adjacent chains. For explanation of (a) and (c) see text and Table I.

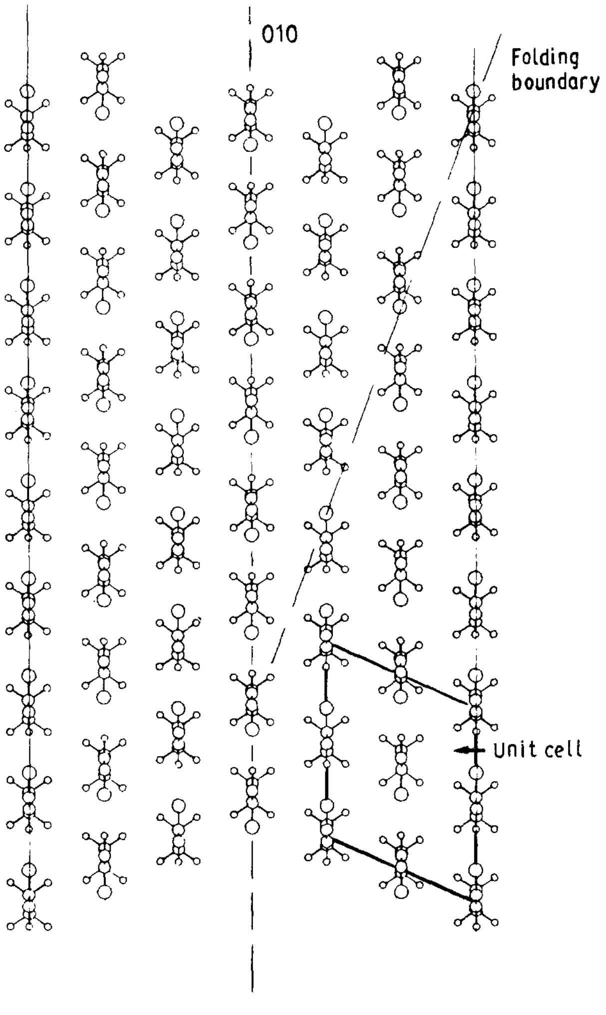


Figure 9 Crystal lattice of an odd nylon viewed along the ***c*** axis and oriented with respect to the lamella. 0 1 0 planes are parallel to the long dimension of the crystal.

diagrams, more than one interpretation of the experimental data is possible. Nevertheless, only two models are currently considered as alternatives. (a) The antiparallel model, which appears to be the most widely accepted, is similar to that given for the β structure of nylon 6 [13]. (b) The parallel model, which is thought to favour the interaction of amide dipoles, resembles the α form of nylon 66. The former is the only one compatible with the occurrence of chain reentry in the crystal.

We have gained substantial evidence in support of an antiparallel structure with successive sheets alternating in orientation along the ***b*** axis in agreement with the model put forward by Tadokoro [11] for nylons 5, 7, 9 and 11. We have found in addition that a better correspondence with our experimental results is attained if the unit cell parameters given by those authors are properly adjusted in an extent within the limits admitted by experimental errors. In this manner a unifying model results for odd nylons in general, which is characterized by a staggered shear of the sheets equal to $2c/m$ where m is the number of backbone atoms contained in the repeating unit of each respective chain. Such a model also fits well with the diffraction data obtained for nylon 13 (studied for the first time in this work) and is directly usable with nylon 3 for which a layered structure involving a staggered shear of $c/2$ had been earlier reported [3].

Bunn *et al.* [13, 14] found that successive hydrogen bonded sheets were displaced about three backbone interatomic heights in the layered structure of nylons 6 and 66. Such shearing value appeared to be reasonable on the basis of packing considerations as a favourable crossed side-by-side arrangement is thus achieved for the polymethylene chains. We note that a similar favourable arrangement is obtained by a displacement of an even number of interatomic heights provided that successive sheets alternated in polarity along the ***b*** axis. As this is actually the disposition assumed in the α structure of odd nylons, a shear of approximately 0.25 nm, as proposed, is not at all in disagreement with the conclusions drawn from the study of even numbered nylons.

Another aspect concerning the geometry of the α structure of odd nylons which deserves particular comment is that related to the shift of the sheets along the ***a*** axis (Δa). As reflected in Table I a value of 0.24 nm corresponding exactly to the half of the interchain distance within the sheets results for nylon 3. This value decreases to about 0.20 nm for nylon 5 and reaches a fairly constant value of about 0.16 nm for all the others. Such regular variation does make sense if the influence of the polar amide group is considered to be decisive in fixing the distance between chains. Nylon 3 stands out as an extreme case resembling polypeptides, in particular to the β-form of poly-L-alanine [15].

As regards the structure of solution grown crystals, the results obtained by polyethylene decoration demonstrate that sectorization implying the occurrence of folding domains, is a frequent feature amongst polyamide crystals. It has become clear that folding planes and hydrogen bonds run parallel within those sectors bounded by the long edges of the crystal, whereas such coincidence is abandoned in the filling sectors. The resulting model assumes an organization of both folds and hydrogen bonds which is fully consistent with all accepted mechanisms of crystal growth. As no information is provided to ascertain which crystallographical planes are those containing the folds in the filling sectors, no satisfactory explanation can be given either for the variation observed in the sector angle when different members of the series are concerned. The fact that sectorization could not be brought out in the case of nylon 5 is thought to be due to the extremely narrow morphology developed by the crystals in this case as well as to the overwhelming nucleating effect exerted by the foldings contained in the lateral sectors. A similar explanation was offered for the case of the nylon 7/5/3 single crystals for which an identical decorating pattern was observed [16]. The opposite situation is found for the case of nylon 13 whose fairly wide crystals produce a decorating pattern showing no sign of preferred orientation. A plausible explanation may be given in this case if the dendritic growth leading to microsectorization is assumed to take place as soon as crystallization starts. With such mechanism operating a filling sector develops which occupies the whole crystal space. The apparent serrated morphology affecting the long edges of this nylon crystal is in support of such interpretation.

Electron diffraction from solution grown crystals revealed that twinning along 0 1 0 planes is a feature common to the whole odd-nylon family. According to observations made on samples decorated with polyethylene vapours, such twinning involves a change in the orientation lattice rather than in the orientation of the folds. The fact that no composed diagrams were reported in the study of nylon 3 [3] should be looked at not as an exception but as a logical consequence of the particular geometry adopted by the crystal lattice in this case. Shifting of the sheets by exactly one quarter of the ***a*** axis generates an arrangement such that twinning domains, if they exist, become undistinguishable when projected along the ***c*** axis of the structure. It should be noted that a similar type of twinning concerning odd nylons had already been observed in the case of even nylons 4 [17] and 6 [18] in α-structure. This is appreciated as additional evidence of the structural resemblance between these two families of nylons.

The last point which deserves comment is that related to the orientation of the chains with respect to the basal plane of the lamellae in sedimented samples. X-ray diagrams indicate that chains are tilted about 30° to the normal in sediments of nylons 7, 9 and 13. This is the situation which should be expected from a triclinic structure with $\alpha \approx 60^\circ$ and $\beta = 90^\circ$ that collapses on sedimentation. Nylon 5, however, deviates from such behaviour so that chains keep normal to the basal plane after sedimentation. The apparent fine striations observed in these crystals indicate an accordion-pleated shape which may be able to prevent flattening on sedimentation. Such a structure would arise as a consequence of the continuous change in the orientation of 0 0 1 planes subsequent to the existence of frequent twinning along 0 1 0 planes. Such increase in the twinning frequency will imply a general misalignment of the whole crystal along the ***a*** axis, a feature which becomes evident in the rather diffuse electron diffraction diagrams produced by crystals of this nylon.

Acknowledgements

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