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Structure of nylon 7 solution grown crystals

A. PRIETO, J. M. MONTSERRAT, S. MUÑOZ-GUERRA
*Departamento de Ingeniería Química, Universidad Politécnica de Cataluña,
ETS de Ingenieros Industriales, Diagonal 647, 08028 Barcelona, Spain*

Single crystals of nylon 7 prepared by crystallization from glycerine were studied by both X-rays and electron microscopy. Electron diffraction proved that they consist of a twinned layered α-structure with hydrogen bonds running parallel to their long dimension. Polyethylene decoration of such crystals showed that they are subdivided in folding domains so that both chain folding and hydrogen bonding take place along the same crystallographical planes.

1. Introduction

Although electron microscopy observations on nylon crystals grown in solution have been frequently reported [1], the molecular organization of such crystals remains still an open question. Conclusive structural studies on nylon crystals are usually hindered by difficulties encountered in the preparation of well developed morphologies suitable to correlate electron diffraction and bright field images. Additional drawbacks preventing an unmistakable interpretation of electron microscopy data arise from the pronounced trend displayed by polyamides to give polymorphs as well as from the occurrence of strong hydrogen bonding which may influence the nature of crystal growth.

No electron microscopy studies on odd nylons other than those dealing with nylons 3 [2] and 11 [3] are found in the literature. Elongated flat crystals comprised of chains organized in the common α-structure were reported but no evidence was given on the orientation of the lattice with respect to the crystal in either case. Unlike even polyamide chains, an odd polyamide chain is compatible with the formation of hydrogen bonded sheets with adjacent chains arranged in either parallel or antiparallel. This gives rise to a further structural ambiguity which adds difficulty to the determination of the chain organization in crystals made of odd nylons.

This paper reports evidence of twinned nylon 7 crystals made of a layered α-structure where chains are folded back and forth. Two models have been proposed for the α-modification of this nylon corresponding to hydrogen bonds formed between chains arranged either in parallel or antiparallel. The model given by Hasegawa *et al.* [4] consists of a unit cell of parameters $a = 0.98$ nm, $b = 1.00$ nm, $c = 0.98$ nm, $\alpha = 56°$, $\beta = 90°$, $\gamma = 69°$ and contains four chains in antiparallel arrangement. On the other side, the model put forward by Slichter [5] is a primitive lattice of parameters $a = 0.49$ nm, $b = 0.54$ nm, $c = 0.98$ nm, $\alpha = 49°$, $\beta = 77°$, $\gamma = 63°$. Although a very similar lattice geometry results from both models only the former appears to be compatible with the occurrence of adjacent chain reentry.

2. Experimental details

The nylon 7 sample used in this study was a kind gift received from Dr Sekiguchi (Universitè Pierre et Marie Curie, Paris). A 0.1% solution of this polymer in *m*-cresol has a reduced viscosity of $0.7\,\mathrm{dl\,g^{-1}}$ at 25° C which corresponds to an approximate molecular weight of 20 000 by comparison with the viscosimetric data reported for nylon 5 [6]. For crystallization, a small amount of nylon 7 was dissolved in refluxing glycerine to give a solution containing 0.01–0.5 wt % polymer and then quickly cooled to 160° C. Crystals appeared after several hours of incubation at such temperature and were isolated by centrifugation and then washed repeatedly with n-butanol.

Samples for electron microscopy were processed in the usual way and shadowed with Pt–C at an angle of 14°. Some specimens were decorated before shadowing, with a low molecular weight sample of polyethylene ($\approx 10\,000$) according to the technique introduced by Wittmann and Lotz [7]. Either a Philips EM-301 or a Hitachi TEM-200 were used for examination in both bright field and selected area electron diffraction modes. A thin film of gold was evaporated occasionally on the specimens in order to provide for internal calibration of the camera length.

3. Results and discussion

Morphologies shown in Figs 1a and b càn be regarded as representative of the precipitate obtained by crystallization. They appear mixed together and turn out to be indistinguishable from an electron diffraction standpoint. Significant features of these crystals are serrated front edges and fine striations and pleats oriented parallel to their long dimension. Whereas entities represented in Fig. 1a consist of large flat lamellae developed from a spherulitic core, those of Fig. 1b are actually individual crystals composed of rolled or folded lamellae closer in appearance to those described by Holland [8]. The thickness of both types of crystals is 7–9 nm as calculated from the length of their shadows and the known casting angle.

The X-ray diagram from dried down flakes of these crystals recorded with the beam parallel to the mat surface is represented in Fig. 2. The two intense

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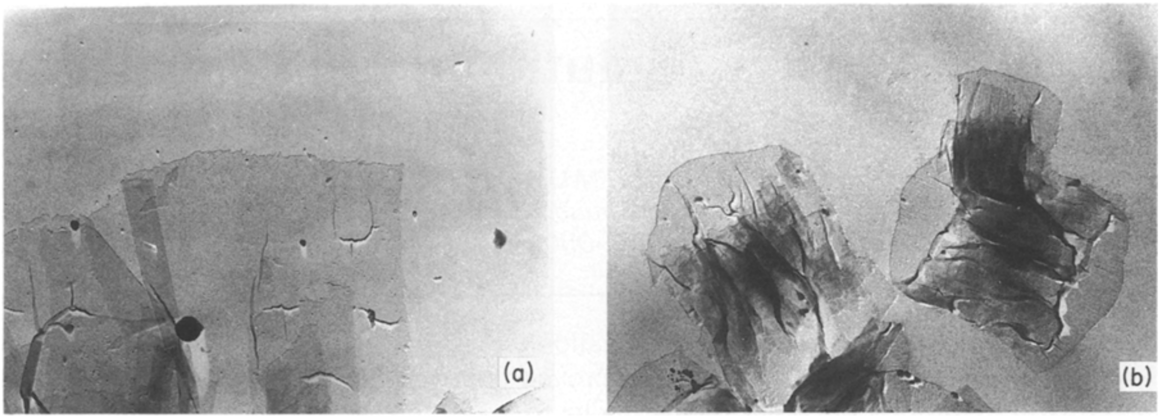

Figure 1 Nylon 7 crystals grown from glycerine solution at 160° C. (a) Flat lamellae, (b) Rolled or folded single crystals.

reflections with Bragg spacings at 0.442 and 0.372 nm observed in this diagram demonstrate that such crystals are made of α-structure. Wide angle X-ray scattering (WAXS) spacings along with those registered by electron diffraction are listed and compared with the calculated values in Table I. On the other hand, discrete low angle reflections with the maximum intensity centred on the meridian, i.e. on the direction normal to the flake, are observed at spacings of 8, 2.6 and 1.6 nm. This is in agreement with previous experiences of oriented mats of nylon crystals [9] and is consistent with the reflections being due to stacks of lamellae 8.0 nm thick lying with their basal planes horizontal. Furthermore, an arced reflection corresponding to a spacing of 0.78 nm is observed on the meridian with medium intensity. This is interpreted as arising from 0 0 1 planes of the α-structure lying with the c axis tilted about 30° from vertical. Therefore, around ten unit cells are contained within the lamellar thickness resulting in a Dreyfuss' factor of $R = 8$ in agreement with the period length of nylon 7. In spite of the good orientation displayed along the meridian, wide angle reflections located around the equator appear considerably spread. It should be noted that the angular spreading exhibited by the outermost reflection 0 2 0/2 2 0 is much wider than the corresponding to the inner 2 0 0 reflection. This is consistent with the chains being tilted mainly in the 1 0 0 planes and approximately 30° from vertical within the crystals.

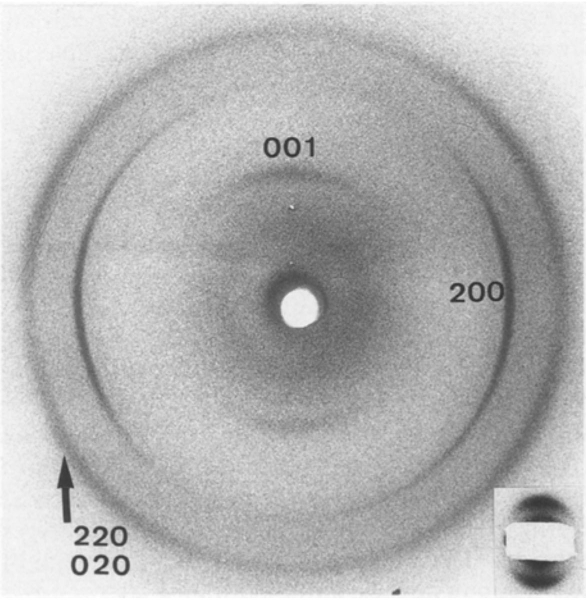

Figure 2 X-ray diagram from a mat of nylon 7 crystals as those shown in Fig. 1. The mat normal is vertical. Inset: low angle reflection corresponding to a spacing of 8.0 nm.

Selected area electron diffraction of crystals depicted in Fig. 1a gives diagrams confirming the existence of the α-structure. However the texture exhibited by the pattern largely depends on what area is selected for diffraction. Diagrams consisting only of one or two pairs of reflections are usually registered as should be expected from crystal chain tilting. Nevertheless, diagrams containing the *hk*0 reciprocal plane are occasionally observed which indicate that chains have been prevented from tilting, at least partially, in some areas of the crystal. The single crystal pattern shown in Fig. 3a was obtained from an area located on one half side of the lamella and near to the front edge. It can be satisfactorily indexed on the basis of the unit cell given by Hasegawa *et al.* [4] and oriented with the 0 1 0 axis parallel to the long dimension of the crystal. The same pattern but rotated 180° around an axis normal to the 0 1 0 direction was obtained instead from an equidistant area located on the counter half of the same crystal. As expected, a composed pattern as that shown in Fig. 3b was recorded from a large area centered in the middle of the crystal. These observations are in full agreement with the existence of a twinned texture in these crystals, with the composition plane being the 0 1 0 plane. In spite of the rounded

TABLE I X-ray and electron diffraction spacings observed and calculated on the basis of a triclinic unit cell with parameters $a = 0.98$ nm, $b = 1.0$ nm, $c = 0.98$ nm, $\alpha = 56°$, $\beta = 90°$, $\gamma = 69°$

Spacings, d (nm)				Index
Observed		Intensity	Calculated	
X-ray	ED			
0.78		medium	0.785	0 0 1
0.48		weak	0.483	2 1 0
0.442	0.438	v.s.	0.442	2 0 0
0.372	0.372	v.s.	0.377	2 2 0
	0.376	v.s.	0.374	0 2 0
0.238	0.240	strong	0.241	4 2 0

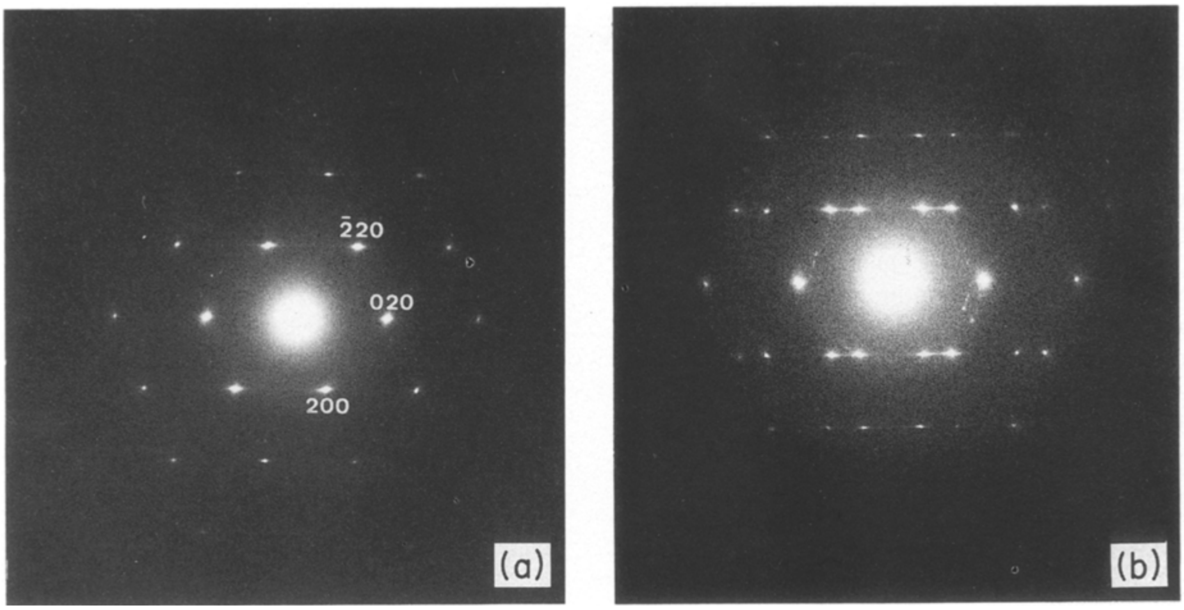

Figure 3 Electron diffraction patterns of nylon 7 crystals. (a) Single crystal pattern. (b) Twinned crystal pattern. Indexing has been made on the basis of a triclinic unit cell as defined by Hasegawa *et al.* [4] (see text).

contours exhibited by the crystals the apex angle shown in Fig. 1b can be roughly estimated to be about 140°. This figure fits well with that expected for the angle defined by the 1 0 0 planes corresponding to two associated twinning domains. A schematic picture of the twinned lattice illustrating how it becomes oriented with respect to the lamella is drawn in Fig. 4a.

The ratio of the average nylon 7 chain length used in this work to the thickness measured for the lamellae indicates that more than five folds are required to accommodate a molecule within the crystal provided that adjacent reentry takes place. According to the chain arrangement in the crystalline lattice, two different sets of planes, 0 1 0 and 1 1 0, are able to accommodate the folds. In fact, both of them are comprised of antiparallel chains separated by a similar distance of approximately 0.5 nm. To discern between these two possibilities, we have made use of the polymer decoration technique which has been proved to be a valuable tool to establish the local fold orientation on polymer crystal surfaces. Figure 5 shows nylon 7 crystals obtained under the same conditions as those of Fig. 1a but decorated with evaporated polyethylene before Pt–C shadowing. This material forms a dense population of tiny elongated rods all over the preparation but the population density is much higher on the lamellar surfaces indicating that nucleation has been much more effective on such a substrate. A preferred orientation of the rods is visualized on both sides of the crystals near to their long edges. Provided that the decorating polyethylene rods lie on the plane

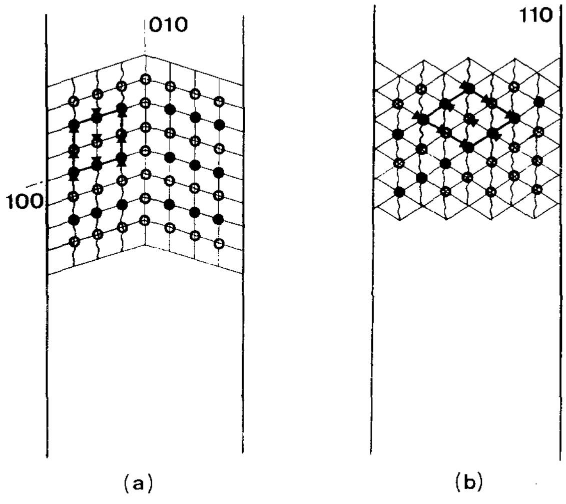

Figure 4 Schematic representation of the nylon 7 crystalline lattice arranged with the 0 1 0 planes (a) or the 1 1 0 planes, (b) parallel to the long axis of the crystals.

Figure 5 Nylon 7 crystals decorated with polyethylene vapours. Sharp change of orientation of the decorating rods is most apparent in areas near to the corners of the crystals (arrowed).

of the fold surface and normal to the folding direction it can be concluded that folds are contained in the 0 1 0 planes of the corresponding 0 1 0 growth sectors. Therefore, chain folding and hydrogen bonds must occur in the same crystallographical planes. On the contrary, a rather erratic orientation of the rods is observed on the filling 1 0 0 sectors. This strongly suggests a dendritic growth characterized by a considerable increase in the number of grown faces with the subsequent continuous changing in fold orientation.

An alternative model being able to account for most of our observations is generated by rotating the unit cell 65° around its *c*-axis, so that the 1 1 0 planes now become parallel to the long axis of the crystal (Fig. 4b). In this case, fold planes in 1 1 0 grown sectors would be 1 1 0 planes and would meet hydrogen bonded planes at an angle of approximately 65°. However such an arrangement would make it difficult to explain the existence of twinning domains. On the other hand, there are signs in disfavour of such a model, (i) crystal striations strongly suggest slippage of planes parallel to the side edges of crystals, a process which would become hindered by the existence of hydrogen bonds linking such planes, (ii) a crystal apex angle of about 130° would result from this arrangement which deviates significantly from the observed value. Furthermore, electron microscope observations reported by Geil [10] on nylon 66 single crystals in the α-modification suggest that hydrogen bonded sheets used to be parallel to the long axis of the crystals.

Finally we would like to note that evidence of chain folding in nylon 7 crystals presented here is incompatible with the unit cell proposed for this nylon by Slichter [5]. However a doubled unit cell including two chains in antiparallel arrangement would become a valid model provided that the unit cell is oriented in the crystal as indicated in the scheme of Fig. 4b. Otherwise indexing of electron diffraction patterns is not feasible unless a completely different chain arrangement in the unit cell is adopted.

Acknowledgements

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