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Structural and morphological investigations of nylon 8 chain-folded lamellar crystals

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The structure and morphology of nylon 8 chain-folded lamellar crystals have been studied using transmission electron microscopy including selected area electron diffraction. Solution grown lamellar crystals are lathe-like in appearance. Two types of diffraction pattern have been identified, indicating two crystal forms. The normal room temperature form is monoclinic with $a=0.964$ nm, $b=0.803$ nm, c, the chain axis $=2.24$ nm and $\gamma=115°$. This is similar to the α form reported for fibres. Crystals quenched into non-solvent from the crystallization temperature show a different structure for which we propose a pseudo-hexagonal unit cell with $a=b=0.965$ and $\gamma=120°$. When monoclinic crystals are heated in the hot stage of the transmission electron microscope the diffraction pattern changes, gradually transforming towards the pseudo-hexagonal phase. For crystals prepared under some conditions the transformation is completed, but in others melting takes place before the full pseudo-hexagonal phase is reached. It is argued that the low temperature phase of nylon 8 single crystals is monoclinic and the pseudo-hexagonal phase is the stable form at high temperatures. Crystals transform from monoclinic towards pseudo-hexagonal on heating. The crystals grow in the high temperature, pseudo-hexagonal phase and this can be obtained at room temperature by quenching from the crystallization temperature into non-solvent below the glass transition temperature.

(Keywords: polyamides; nylon 8; lamellar crystals)

INTRODUCTION

Two crystalline structures have been reported for nylon 8[1] and Vogelsong[2] has proposed models for both based on X-ray fibre diffraction patterns from uniaxially oriented monofilaments. The Bragg diffraction signals of one form, called the α-phase, index on a monoclinic unit cell with dimensions $a=0.98$ nm, $b=0.83$ nm, c (chain axis: fibre direction) $=2.24$ nm and $\gamma=115°$. The structure consists of hydrogen-bonded sheets with adjacent chains of opposite polarity (antiparallel). The sheets are progressively sheared in a direction perpendicular to the chain axis and parallel to the sheet plane (ac plane). The sheets also stagger alternately in the c direction (bc plane). Thus the unit cell incorporates two sheet segments or four chain segments. The (200) and (020) high electron density planes give rise to two prominent equatorial diffraction signals at spacings 0.44 and 0.36 nm, respectively. This pair of diffraction signals is characteristic of a number of sheet-like nylon structures such as those proposed for nylon 6[3], nylon 46[4] and nylon 4[5].

Although the monoclinic α-phase is the usual phase for nylon 6, nylon 46 and nylon 4 single crystals, it does not appear to be the usual phase in nylon 8 fibres[1]. In fact the first structure reported for nylon 8[1,6,7] was a pseudo-hexagonal phase, called the γ-phase. Vogelsong[2] proposed a structure for this pseudo-hexagonal phase (observed in fibres) based on a one-chain hexagonal unit cell with $a=b=0.48$ nm, c (chain axis: fibre direction) $=2.17$ nm and $\gamma=120°$. Cojazzi *et al.*[8] also proposed a model for the γ-phase. In both models[2,8] a slight reduction in the value of c was noticed when compared with the value for the α-phase of nylon 8. Annealing the nylon 8 γ-phase converts it to the α-phase. The α-phase can also be obtained by hot-drawing nylon 8 or by crystallizing from dilute formic acid[2].

The α- and γ-phases of nylon 8 bear a similarity to the reported α- and γ-phases[2,9] of nylon 6. Indeed, the detailed structure proposed for the monoclinic α-phase of nylon 8[2] is based on the α-phase structure determined for nylon 6[3].

In many even-nylons, the α-phase can be systematically converted into the γ-phase (or vice versa) or both can coexist in various proportions[10]. In particular, transformations can be engineered by solvent or swelling agent[10,11], rates of fibre spinning[12], temperature[13] or combinations of all three. Transformation to the γ-phase as a function of temperature (especially for nylon 66) is often referred to as the Brill transition, although we believe[14] that no *sudden* transition actually occurs.

Lamellar crystals of nylon 6, which we expect to be similar to nylon 8, have been reported and an electron diffraction pattern recorded[15]. However there is no discussion of the results in terms of crystal structure. So, rather than use fibres, we have prepared chain-folded

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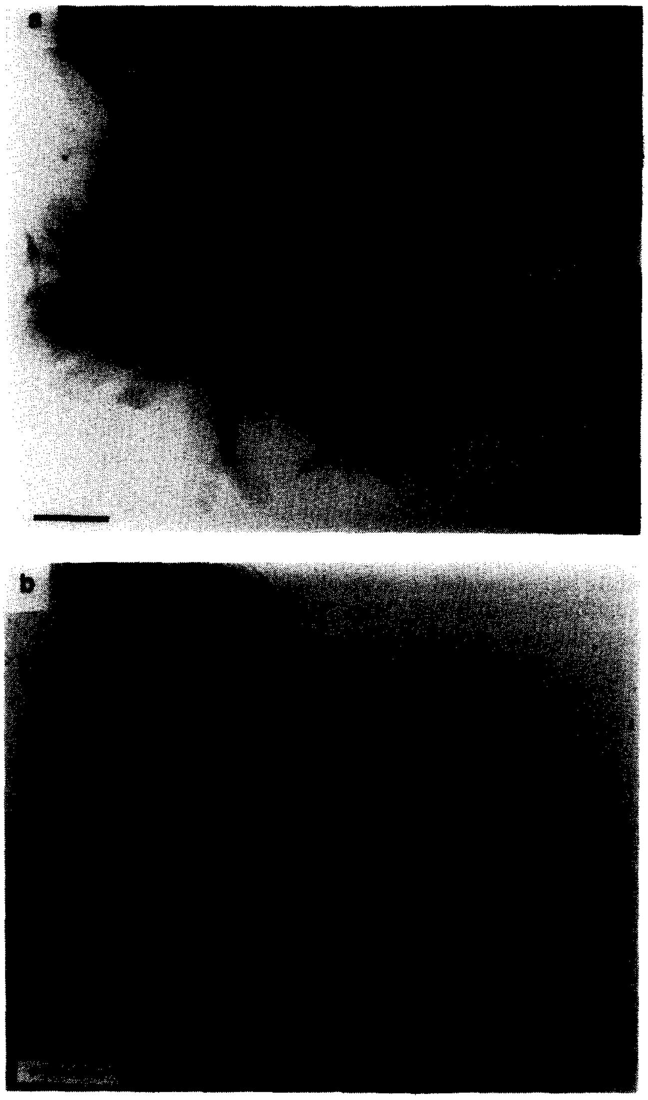

Figure 1 Electron micrographs of nylon 8 lamellar crystals: (a) crystallized during cooling from the dissolution temperature; (b) crystallized for 36 h at 125°C after seeding at 140°C. Scale bar = 1 μm

lamellar crystals of nylon 8 and reinvestigated the relationship between the low and high temperature phases using electron diffraction. The demands that folding with adjacent re-entry place on the straight stem crystallography enable us to rule out some of the particular models proposed for fibres when considering single crystals. For example, a one-chain unit cell[2] is not a model that can be seriously entertained in a structure with chains running with opposite polarity. In this investigation we have found two structures in single crystals of nylon 8, and followed the transformation as a function of both solvent environment and temperature.

EXPERIMENTAL

Single crystal preparation

The nylon 8 samples were a gift from DSM. A melting temperature of 197°C was recorded using d.s.c. (heating at 10°C min^{-1}). A solution of nylon 8 in 1,4-butanediol (0.025% w/v) was prepared by continuously stirring under reflux conditions for 2 h at 190°C. The crystals were grown isothermally and the optimum conditions were found to be 125°C for 36 h after the originally slowly cooled solution had been seeded by holding at 140°C for 20 min.

After isothermal crystallization the crystals were treated in a number of different ways:

1. The solution was cooled to room temperature. Crystals were placed on TEM grids and dried, either by leaving for a few hours in the laboratory, or in a vacuum oven overnight, in some cases at elevated temperature.
2. (i) The solution was 'quenched' from the crystallization temperature into acetone at room temperature. The quenching method was as follows. After the full crystallization time the crystals, suspended in the solvent, 1,4-butanediol, were poured into a Buchner funnel. The solvent was sucked rapidly through filter paper using a water vacuum. At the same time cold acetone was poured into the funnel and sucked through the filter paper with the excess solvent. This process gave rise to very rapid quenching from the crystallization temperature into cold non-solvent. After filtration the crystals were removed from the filter paper and resuspended in acetone. The crystal suspension was placed on TEM grids and allowed to air dry in the laboratory at room temperature.
   (ii) As in (i), but 'quenched' into methanol rather than acetone.
   (iii) As in (i), but subsequently dried overnight in a vacuum oven at room temperature.
   (iv) As in (iii), but dried at 65°C in a vacuum oven.

Electron microscopy

Samples were examined, both in real space and in diffraction mode, using a Philips 301 TEM operating at 80 kV. Some crystals were shadowed, and others were lightly decorated with gold to calibrate the diffraction patterns. Some crystals were heated to melting in a hot stage. The temperature of this hot stage could be controlled to within ±2°C. Relative measurements were accurate to 2°C and absolute measurements to within ±5°C. The hot stage was calibrated by observing the melting of substances of known melting point.

X-ray diffraction

An extruded fibre was used for the X-ray experiment. It was found that annealing at 125°C for 2 days noticeably improved the degree of crystallinity. X-ray diffraction patterns were obtained using point collimated monochromatized CuKα radiation from an Elliott GX-20 rotating target X-ray generator and the information collected using a Siemens GADDS two-dimensional detector.

RESULTS

Morphology

All the crystals were clumped to a greater or lesser degree and were ribbon-like. Crystals grown at high temperatures and for longer times were seen to be larger and more often monolayer; the maximum observed width was 0.5 μm and the lengths several micrometres. Many of the crystals had straight sides. Examples of crystals grown under different experimental conditions are shown in *Figure 1*. Crystals 'quenched' from the crystallization temperature looked the same as those that had been slow-cooled.

Electron diffraction

Two types of diffraction pattern were observed in unheated samples; the crystals giving rise to these patterns were not identifiable as being different in appearance. The patterns are shown in *Figure 2*, and are described below.

Monoclinic phase. *Figure 2a* shows the selected area diffraction pattern from a lamellar crystal obtained at room temperature after crystallizing from 1,4-butanediol and allowing the solution to cool to room temperature.

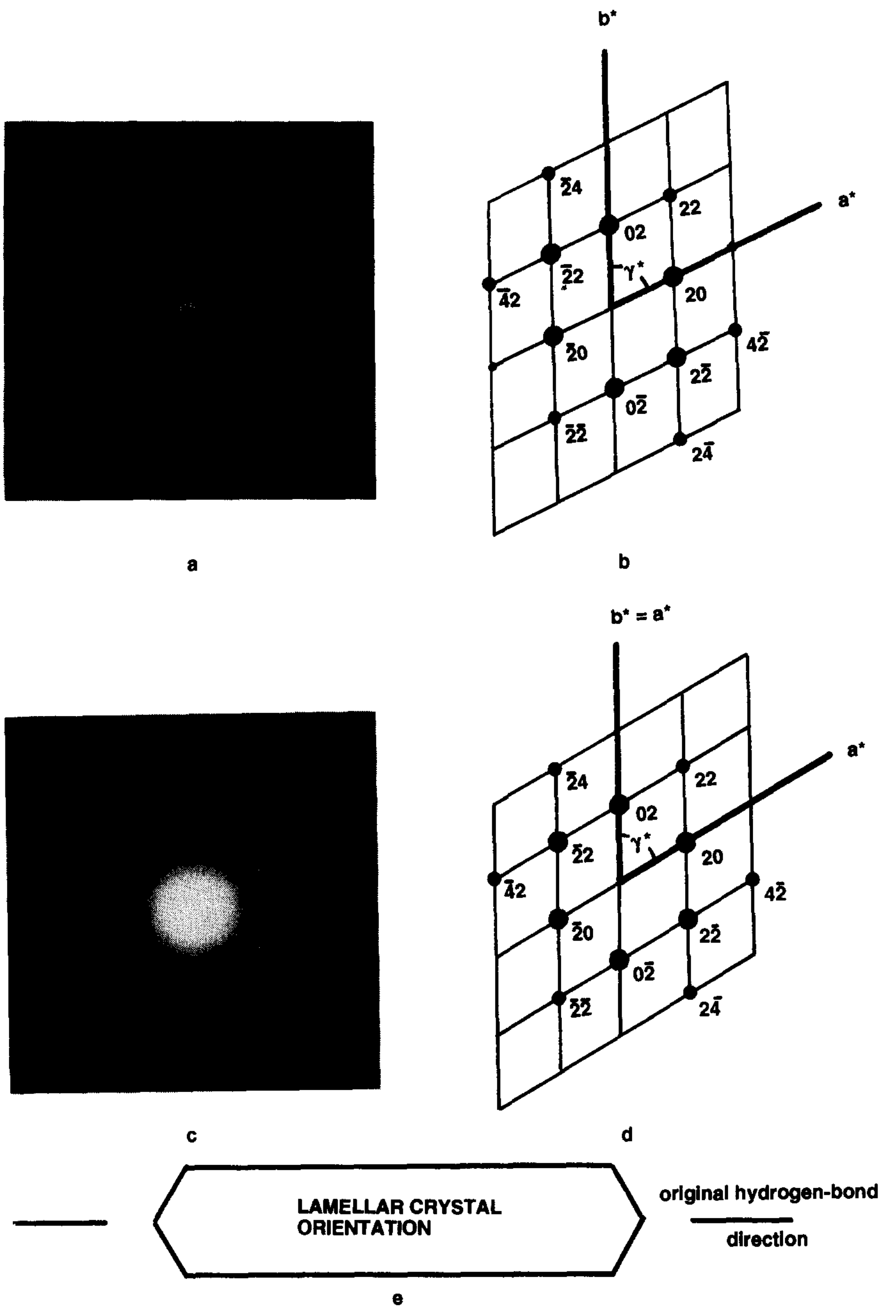

Figure 2 Selected area electron diffraction patterns from lamellar crystals of nylon 8. (a) Electron diffraction pattern obtained at room temperature from crystals prepared as those in *Figure 1b*. The pattern represents the *hk*0 reciprocal net of a monoclinic unit cell. (b) Scale drawing of the reciprocal net. The areas of the filled circles give an indication of recorded intensity and they all index on a reciprocal lattice (*hk*0) with $a^* = 2.29\,\mathrm{nm}^{-1}$ ($d_{10} = 0.437$ nm) and $b^* = 2.75\,\mathrm{nm}^{-1}$ ($d_{01} = 0.364$ nm) and $\gamma^* = 65°$, or, in real space, $a = 0.482$ nm and $b = 0.402$ nm and $\gamma = 115°$. In the three-dimensional unit cell the values of a and b will need to be doubled (see text). (c) Electron diffraction pattern of the pseudo-hexagonal phase. This phase was obtained by seeding at 140°C in 1,4-butanediol and crystallizing at 130.6°C for 8 h before rapidly quenching into acetone at room temperature. (d) Scale drawing of the reciprocal lattice net. The areas of the filled circles gave an indication of recorded intensity and they all index on a hexagonal reciprocal lattice (*hk*0) with $d_{10} = 0.418$ nm, or $a = 0.483$ nm. The orientation of the pattern is identical to that of (a) and (b). (e) Drawing of a single lamellar crystal and its orientational relationship with (a), (b), (c) and (d)

The observed reflections, together with an indication of their intensity, are listed in *Table 1*. The two strong signals, at spacings of 0.437 and 0.364 nm, are characteristic of room temperature nylon structures and represent a projection of the interchain distance within the hydrogen-bonded sheet and the intersheet distance, respectively; they lie at an angle of 65° to one another. The reflections index on a *hk*0 reciprocal lattice net of a monoclinic unit cell (*Figure 2b*) with lattice parameters $a=0.482$ nm, $b=0.402$ nm and $\gamma=115°$. By looking at the orientation of the electron diffraction pattern with respect to the real space image of the diffracting crystal, we find that the hydrogen-bonded sheets run parallel to the long axis of the crystal and lie in the *ac* plane. The values of a and b are degenerate and submultiples of the true values for a full three-dimensional structure. X-ray diffraction patterns, which give access to *hkl* reflections, show that the a and b values need to be doubled. The necessity to chain-fold would, quite independently, demand that a is doubled. This is illustrated in the chain-folded hydrogen-bonded sheet shown in *Figure 3*. Thus the true monoclinic unit cell, taking the value of c from X-ray fibre diffraction, is $a=0.964$ nm (± 0.002), $b=0.803$ nm (± 0.002), c (chain axis) $=2.24$ nm (ref. 2) and $\gamma=115°$. The a and b values are very close to those of the α structure reported by Vogelsong[2] who used fibre X-ray diffraction ($a=0.98$ nm, $b=0.83$ nm). Apart from the c value, which is specific to each nylon, the unit cell is similar to that reported for nylon 6[3] and nylon 4[5]. *Figure 4* shows a diagrammatic representation of the structure projected along the chain axis. The unit cell contains four chain segments. The doubling of the a dimension is a consequence of the changing polarity of the chains in the hydrogen-bonded sheets. The doubling of b emanates from the close packing of hydrogen-bonded sheets. In nylons, the sheets either shear in the *ac* plane progressively (e.g. nylon 66[16,17]) or alternately (e.g. nylon 46[4], nylon 6[3], nylon 4[5]). In the present case of nylon 8 we can conclude that the shear is alternating because the chains run normal to the crystal surfaces. This is clear from the observation of so many *hk*0 reflections in electron diffractions. Where the shear is progressive, as in nylon 66, very few *hk*0 reflections can be seen unless the crystals are tilted[18]. This is why the index values in *Figure 2b* and *Table 1* are doubled. Twinned crystals were often obtained when crystallization was rapid, and the composition plane is indexed as (010). We calculate the density of the monoclinic unit cell to be 1.19 g cm^{-3}.

Table 1 Data from electron diffraction of monoclinic phase of nylon 8 chain-folded single crystals. The *hk*0 net indexes on a lattice with $a=0.964$ nm, $b=0.803$ nm and $\gamma=115°$

Spacing (nm)		Estimated	
Measured	Calculated	relative intensity[a]	Index
0.437	0.437	VS	20
0.364	0.366 0.364	VS	$2\bar{2}$ 02
0.234	0.237 0.235	M	$4\bar{2}$ 22
0.219	0.219	W	40
0.198	0.201	W	$2\bar{4}$
0.182	0.182	VW	04

[a] VS, very strong; M, medium; W, weak; VW, very weak

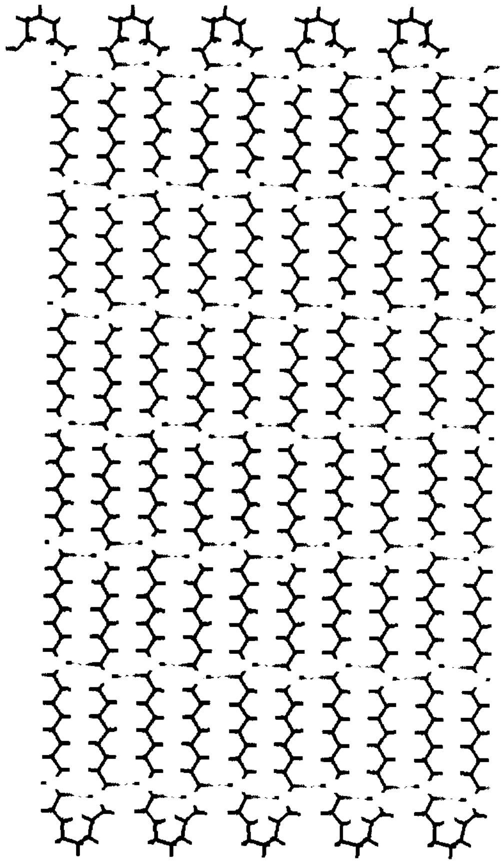

Figure 3 View of the chain-folded sheet of nylon 8, c axis vertical, a axis horizontal. The hydrogen bonds are shown as dashed lines

Table 2 Data from electron diffraction of pseudo-hexagonal phase of nylon 8 chain-folded single crystals. The *hk*0 net indices on a lattice with $a=b=0.965$ nm and $\gamma=120°$

Spacing (nm)		Estimated	
Measured	Calculated	relative intensity[a]	Index
0.418	0.418	S	20
0.243	0.241	M	22
0.209	0.209	W	40, 44

[a] S, strong; M, medium; W, weak

Pseudo-hexagonal phase. *Figure 2c* shows the selected area diffraction pattern from a lamellar crystal obtained by 'quenching' in acetone. The reflections index on a hexagonal lattice with dimensions $a=b=0.483$ nm, $\gamma=120°$. Again, for reasons to be discussed later, we believe the a and b values need to be doubled to 0.965 nm and therefore the indexing of the reflections in *Figure 2d* and the listings in *Table 2* are based on this larger unit cell. The six strong diffraction signals in *Figure 2c* are the {200} reflections spaced at 0.418 nm; other reflections observed are indicated in *Figure 2d*. A schematic diagram of the [001] projection of the pseudo-hexagonal phase is shown in *Figure 5*. It can be seen from *Figures 2a* and *c* or *b* and *d* that the two lattices are related. The angle changes by only 4.3% from 115° (monoclinic phase) to 120° (pseudo-hexagonal phase) and the length of b increases by 20%. Vogelsong[2] reported a reduction

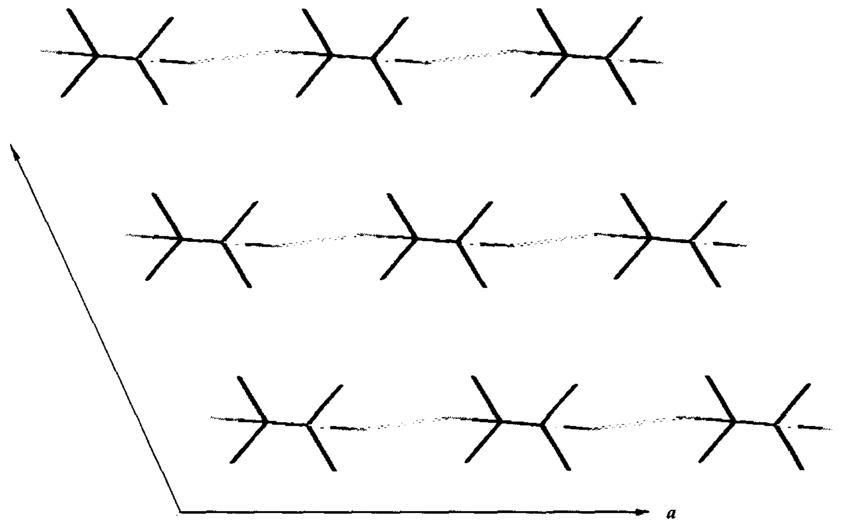

Figure 4 [001] projection of the monoclinic phase of nylon 8 single crystals. The monoclinic unit cell has parameters $a=0.964$ nm, $b=0.803$ nm, c (chain axis)$=2.24$ nm and $\gamma=115°$. The strongly diffracting planes (200) and (020) are shown and give rise to the characteristic spacings of 0.437 and 0.364 nm, respectively. Hydrogen bonds are shown dotted. The hydrogen-bonded sheets lie parallel to the ac plane. The centre sheet is displaced parallel to c and its exact location in the ac plane can only be established by structure determination from high resolution diffraction data

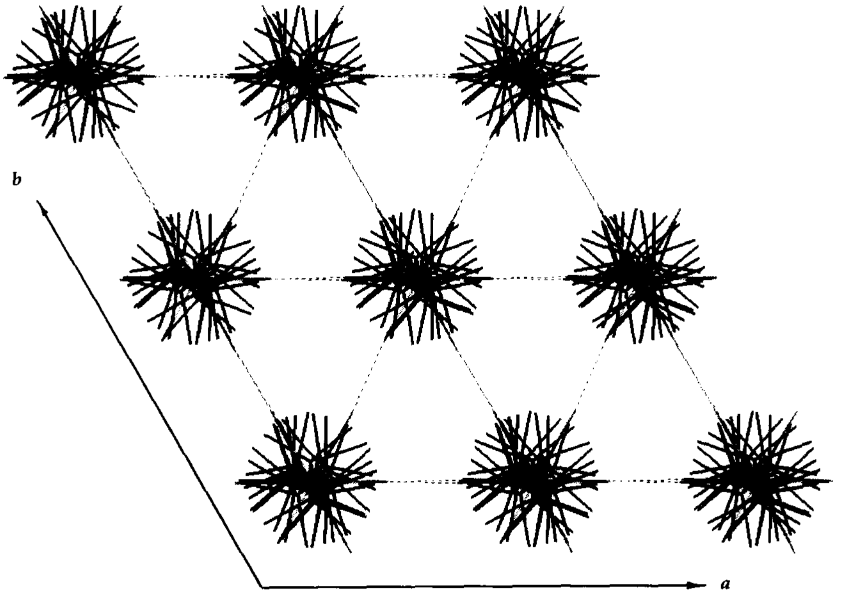

Figure 5 [001] projection of the pseudo-hexagonal phase of nylon 8. This is not a detailed model. It is meant to represent the lattice sites of the molecules which we believe are held together by hydrogen bonds lying in the three principal axes of a hexagonal (trigonal) net. A proportion of the chains will have displacements parallel to the c axis and therefore the larger unit cell with $a=b=0.965$ nm is drawn

of 3% in the value of c between the monoclinic and pseudo-hexagonal structures from his X-ray fibre diffraction patterns. Allowing for a similar slight reduction in the value of c, for our single crystals, the density of the pseudo-hexagonal phase (based on our $hk0$ unit cell measurements) would be $1.08\,\mathrm{g\,cm^{-3}}$, which is 9% less than for the monoclinic phase. If there were no change in c, the difference in densities would be greater.

Experimental conditions to produce monoclinic and pseudo-hexagonal crystals

Monoclinic crystals were obtained after crystallization in 1,4-butanediol and cooling to room temperature with no solvent exchange, as outlined in preparation method 1. Monoclinic crystals were also obtained following specimen preparation method 2(iv), i.e. when the crystals had been quenched from the crystallization temperature into acetone and subsequently dried in vacuum at 65°C.

Pseudo-hexagonal crystals were obtained by preparation methods 2(i), (ii) and (iii), i.e. when crystals were examined after crystallization in 1,4-butanediol, followed by quenching [see Experimental 2(i)] from the crystallization temperature into acetone or methanol and, if subsequently vacuum dried, not heated during drying.

Behaviour on heating

Three types of behaviour were recorded on heating, all essentially similar but differing in detail. The changes in spacing of the two prominent electron diffraction reflections for monoclinic crystals, at 0.44 and 0.36 nm, are shown in *Figures 6* and *7*. The data are displayed in two different ways: *Figures 6a* and *7a* show the actual spacings and *Figures 6b* and *7b* the ratio of these spacings. *Figures 8a* and *b* show the analogous data for pseudo-hexagonal crystals.

We show two cases for monoclinic crystals, grown in 1,4-butanediol and allowed to cool to room temperature. In both cases the two strong reflections moved nearer as heating progressed. When the crystals were grown isothermally, at elevated temperature, the strong diffraction signals moved towards each other on heating but did not actually meet before the melting point (*Figure 6*). The lowest ratio of the spacings was, in this case, 1.08.

When the crystals under investigation had been grown rapidly at low temperature (for instance by allowing the solution to cool in air from the dissolution temperature) the two diffraction signals met before the crystals melted; the same behaviour was noted when monoclinic crystals were not properly dried, but contained some solvent. Brill observed broadly similar behaviour in nylon 66[13], a pattern characterized by two strong reflections gradually changed with temperature in such a way that the strong reflections came together and met before the melting point was reached. This change, in nylons, from one phase to another on heating, has come to be termed as the 'Brill transition', and the temperature at which the reflections meet at the 'Brill temperature'. Note that when the Brill transition took place in nylon 8 single crystals the resulting strong diffraction signal was at the spacing characteristic of the pseudo-hexagonal crystals. Ramesh *et al.*[19] have recently recorded a similar variation in Brill temperature with crystallization temperature in nylon 66 bulk samples. In nylon 66 the Brill temperature is always reached before the melting point; for nylon 8 single crystals the structure always changes towards the pseudo-hexagonal on heating, but the Brill transition is not always achieved.

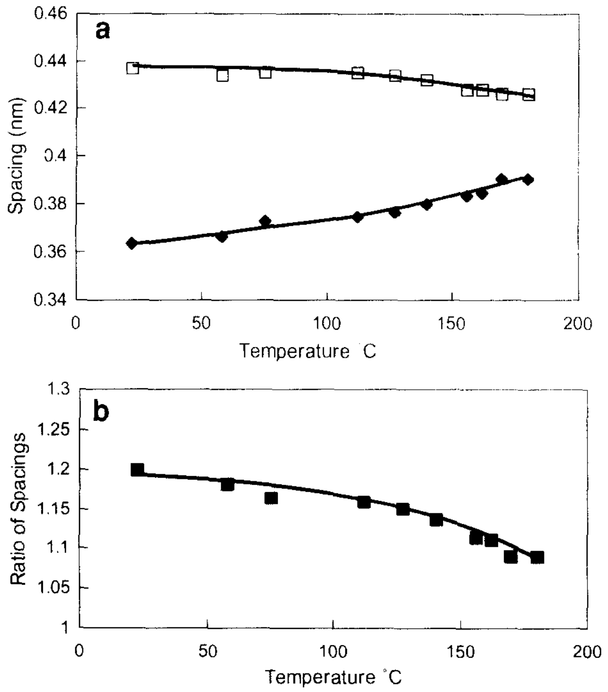

Figure 6 Changes in spacing of the two prominent electron diffraction signals on heating isothermally crystallized nylon 8 crystals of the monoclinic phase: (a) actual spacings; (b) ratio of spacings

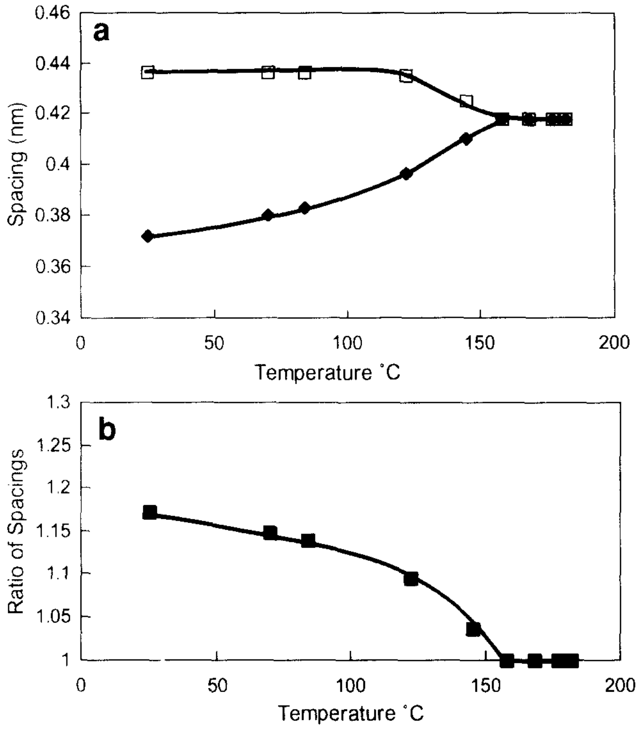

Figure 7 Changes in spacing of the two prominent electron diffraction signals on heating poorly crystallized nylon 8 crystals of the monoclinic phase: (a) actual spacings; (b) ratio of spacings

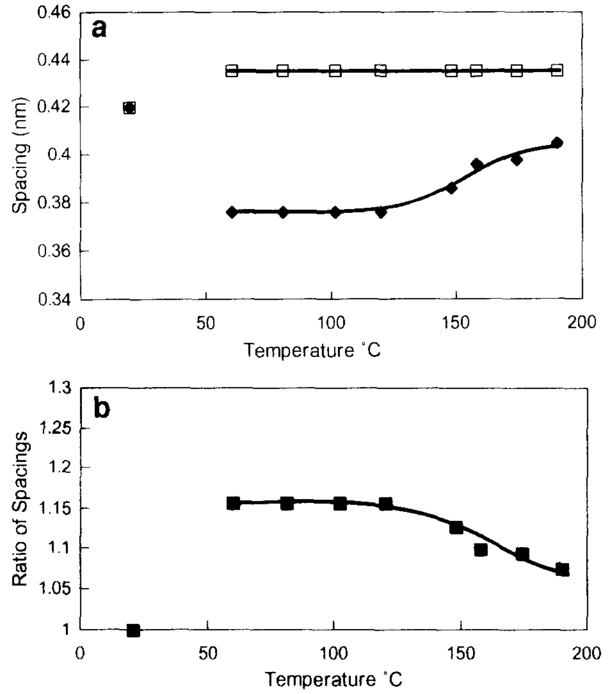

Figure 8 Changes in spacing of the two prominent electron diffraction signals on heating nylon 8 crystals obtained at room temperature in the pseudo-hexagonal phase by drastic quenching: (a) actual spacings; (b) ratio of spacings. The initial point, at 25°C, comes from the 'quenched in' pseudo-hexagonal phase. As soon as the crystals are heated above T_g (50°C) the structure reverts to monoclinic with two, and not one, strong diffraction signals

When 'quenched-in' pseudo-hexagonal crystals were heated in the transmission electron microscope they reverted to the monoclinic form on heating to above 50°C. On subsequent heating (*Figure 8*) the strong signals moved together but did not meet; the lowest ratio of spacings, obtained just before melting, was again 1.08. The way in which the diffraction signals moved together was different in detail from the changes seen in crystals which had never been through the pseudo-hexagonal phase; this can be seen by comparing *Figures 6a* and *8a*.

Summary of methods of preparation of pseudo-hexagonal crystals

We have obtained single crystals in the pseudo-hexagonal phase by three routes: (1) heating monoclinic crystals which had been crystallized rapidly at low temperature in 1,4-butanediol; (2) by removal of 1,4-butanediol at the crystallization temperature and simultaneous quenching into cold acetone; (3) as (2), but with cold methanol, rather than cold acetone, as the non-solvent.

DISCUSSION

In our studies of chain-folded crystalline lamellae we observe both the monoclinic and pseudo-hexagonal crystalline phases and are able to convert from one phase to the other. Since the chains must run with opposite polarity (antiparallel) the minimum number of chains per unit cell must be two for both phases. Thus one-chain unit cells, such as that proposed by Vogelsong[2] for the γ-phase (in fibres) are not commensurate with our data on chain-folded single crystals, although such cells are possible for fibres.

We believe that the pseudo-hexagonal phase, as seen in single crystals, is based on a model where the amide units flip $\pm 60^\circ$ out of the planar chain conformation found in the monoclinic phase. Chains which were neighbours in the monoclinic phase will need to slip parallel to each other (parallel to c) to enable a pseudo-hexagonal, or more correctly pseudo-trigonal, array of hydrogen bonds to form. In the pseudo-hexagonal phase there is a trigonal array of hydrogen bonds, rather than the system of hydrogen-bonded sheets held together by van der Waals packing which is the basic model for the monoclinic phase. A consequence of the trigonal arrangement of hydrogen bonds is that the pseudo-hexagonal phase is a lower density structure and this is borne out by the unit cells deduced from experiment.

The pseudo-hexagonal phase is the high temperature structure towards which the monoclinic phase transforms on heating; it is reached before melting for some, but not all, crystallization conditions. The pseudo-hexagonal phase can be obtained directly by rapid quenching from the crystallization temperature into a non-solvent. This shows that the crystals grow in the pseudo-hexagonal phase and that this phase can be 'frozen in' by quenching from the crystallization temperature to below the glass transition temperature (T_g) at 50°C[20]. However, if the crystals are raised above T_g they revert to the monoclinic phase which is the thermodynamically stable phase at low temperatures. If the temperature is increased further, the alkane segments increase their mobility (which accounts for the observed decrease in the c spacing[2]) and the structure starts to transform towards the pseudo-hexagonal phase. If the crystals are well formed and no solvent is present the complete transformation from monoclinic to pseudo-hexagonal is not accomplished before the melting point (isotropization temperature). We believe this pseudo-hexagonal, high temperature phase is the phase in which the single crystals form. It is similar to the hexagonal phase of polyethylene[21,22] obtained at high pressures. Very recently Ramesh *et al.*[19] have shown that bulk nylon 66 grows in a similar pseudo-hexagonal form and changes to triclinic (the usual form for room temperature nylon 66) on cooling.

Although isothermally crystallized, dry crystals melt before the pseudo-hexagonal phase is reached; *Figure 7* shows that the pseudo-hexagonal phase has been obtained on heating monoclinic crystals which had been prepared in particular ways. One group of crystals was poorly crystalline, having been crystallized on cooling, in air, from above the dissolution temperature. The imperfect nature of these crystals is reflected in the low ratio of the strong spacings at room temperature, 1.17 (*Figure 7b*) compared with 1.22 for isothermally crystallized monoclinic crystals (*Figure 6b*). We suspect that not all the possible hydrogen bonds were formed during this rapid crystallization and the crystals were unable to perfect on storage at room temperature (below the T_g, 50°C[20]). The disorder of these crystals presumably allowed greater mobility of the alkane segments at comparatively low temperatures, leading to an early build up of the trigonal hydrogen bonded array characteristic of the pseudo-hexagonal phase. The second group of crystals is more interesting. If solvents or swelling agents are present the temperature needed to drive a transformation is lowered. In general terms the phase behaviour is dictated by two variables: temperature and solvent effects. Adding solvents introduces a lyotropic element into the overall thermotropic behaviour.

The transformation, in single crystals, from the monoclinic to pseudo-hexagonal or vice versa must be conformationally and topologically straightforward. Thus, on average there should be equal numbers of amide groups flipping $+60^\circ$ and -60° as the change takes place. The type of structure formed will also depend on other parameters, in addition to temperature and solvent, such as pressure and strain.

CONCLUSIONS

From our studies of solution grown single crystals of nylon 8 we draw the following conclusions.

1. We have crystallized nylon 8 in the form of chain-folded crystal lamellae and observed two crystal phases. At room temperature single crystals are usually found in the monoclinic phase, for which $a = 0.964$ nm, $b = 0.803$ nm, c (chain axis) $= 2.24$ nm and $\gamma = 115^\circ$. This is the α structure described by Vogelsong[2].
2. We propose a new structure for the high temperature form of nylon 8 single crystals and found in single crystals which have been drastically quenched from the crystallization temperature. We propose a pseudo-hexagonal structure in which the projection parallel to the chain axis is $a = b = 0.965$ nm and $\gamma = 120^\circ$. Other authors have observed γ-phases in fibres; these phases

have similar diffraction patterns to the one that we see, but the structures previously proposed for fibres are not commensurate with chain-folded crystallization.

3. We have recorded changes in structure on heating single crystals from room temperature to melting. The monoclinic structure gradually transforms towards the pseudo-hexagonal structure. The process varies in detail with the crystal preparation before heating; the transformation is only completed if the crystals were originally imperfect and/or contained solvent.
4. The monoclinic phase is the low temperature phase and the pseudo-hexagonal phase the high temperature structure. We conclude that single crystals grow in this high temperature pseudo-hexagonal phase, but usually transform into the monoclinic phase on cooling to room temperature. The high temperature pseudo-hexagonal phase can, however, be 'frozen in' by quenching very rapidly from the crystallization temperature to below the T_g (50°C); such 'frozen' crystals revert to the low temperature, monoclinic phase on heating above 50°C.

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