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Structures for monodisperse nylon 6 oligomers. Two different intersheet shears for 5- and 9-amide oligomer crystals

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Abstract

Crystals of the monodisperse 5-amide nylon 6 oligomer (4.6 nm long), grown from solution, have been investigated using X-ray diffraction and electron microscopy. If the crystals are prepared by adding the miscible non-solvent 1,4 dioxane to a solution in trifluoroethanol the usual nylon 6 monoclinic α-structure occurs, i.e. a structure where the hydrogen-bonded sheets shear in an alternating fashion with respect to the chain (*c*-axis) direction. If, however, crystals are grown isothermally from *N*,*N*-dimethylformamide at 70–80°C a progressive *c*-axis intersheet-sheared triclinic structure is found. These crystals are three-dimensional in character, owing to the crystallographic stacking of successive molecular layers (3.4 nm thick due to chain tilt), and the diffraction signals index on a triclinic unit cell with parameters: $a = 0.980 \pm 0.002$ nm, $b = 0.545 \pm 0.002$ nm, $c = 4.60 \pm 0.02$ nm, $\alpha = 50.4 \pm 0.5°$, $\beta = 90°$ and $\gamma = 71 \pm 0.5°$. A model is proposed for this triclinic structure and the calculated diffraction pattern is compared with experimental data. In both monoclinic and triclinic polymorphs the 5-amide molecules exist in an all-*trans* non-folded conformation.

Crystals of the 9-amide nylon 6 oligomer have also been prepared using 1,4 dioxane/trifluoroethanol mixtures. In this case, these longer 9-amide molecules (8.06 nm) are once-folded but again crystallize in hydrogen-bonded sheets that stack in the usual nylon 6 monoclinic α-structure. When these crystals are annealed at 140°C, a solid state transformation occurs into a triclinic structure with progressive *c*-axis intersheet shear. © 2001 Published by Elsevier Science Ltd.

Keywords: Nylon oligoamides; Crystal structures; Crystallization

1. Introduction

We have recently described and discussed the crystalline structures obtained from a series of nylon 6 and nylon 6 6 monodisperse oligoamides with a range of specified lengths [1–3]. These molecules, precisely defined in both length and chemistry, were synthesized by Dr G. Brooke and colleagues[2] [4–7] at the University of Durham. The oligoamides are terminated with short alkane segments, specifically designed to minimize the disturbance to the crystal lattice. In the case of nylon 6, we have undertaken studies on the 3-amide [1–3], 5-amide, 9-amide and 17-amide oligomers [2,3]. In the all-*trans* conformation, these four oligoamides span the length range 3–15 nm. In the early stages of the investigation, we were interested in the onset of chain folding [2]. Under the crystallization conditions used, we found that the two shorter molecules remained non-folded, the 9-amide (length 8.06 nm) could be crystallized in both a non-folded conformation and a once-folded (hairpin) conformation, and the longer 17-amide oligomer crystallized in a twice-folded conformation. Nylon 6 oligomers were also investigated by Zahn and Pieper [8] and Balta Calleja and Keller [9] in the 1960s. Their nylon 6 oligomers were terminated with a bulky aromatic group and a carboxyl group at either end, respectively. The lack of orientation and poorer quality X-ray diffraction data did not allow the chain tilt to be determined and no detailed interpretation of the results was undertaken, however, the overall pattern of behavior was consistent with our recent findings.

The monoclinic nylon 6 α-structure, proposed by Holmes et al. [10] in 1955, was based on X-ray fiber diffraction data.

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[2] The chemical synthesis of these high-pedigree monodisperse oligoamides by Dr G. Brooke and his colleagues at the Chemistry Department, University of Durham, Durham, UK, was in response to a desire by Prof. E. Atkins at the Physics Department, University of Bristol for high-fidelity oligo- and polyamides that are necessary for studying fundamental aspects of polymer physics; in this case the subtle interplay between van der Waals interactions, hydrogen bonding, chain-folding and crystallization. We appreciate the foresight of the Engineering and Science Research Council, UK in supporting this collaborative venture.

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The unit cell contains two pairs of antiparallel chain segments in the all-*trans* extended conformation and the unit cell parameters are: $a = 0.956$ nm, $b = 0.801$ nm, c (chain axis) $=$ 1.724 nm, $\alpha = \beta = 90°$ and $\gamma = 112.5°$. A slightly modified structure was subsequently proposed by Malta et al. [11] and a space group $P2_1$ assigned. In nylon 6, the array of antiparallel chains allows adjacent –C=O···H–N– hydrogen bonds to be fully saturated and linear, producing a planar hydrogen-bonded sheet (*ac*-plane with $\beta = 90°$) as shown in Fig. 1(a). In the α-structure [10,11], the sheets stack together via van der Waals interactions and successive sheets shear progressively parallel to the *a*-direction (Fig. 1(b)) in the *ac*-plane. In addition, there is an alternating intershear ($\pm\Delta c$) parallel to *c*, as shown in Fig. 1(c). The originally reported Δc value for nylon 6 fibers [10] was $3c/14$ or 0.37 nm, based on comparison with nylon 6 6 [12]. Recently it has been argued [13], that the actual value is closer to 0.14 nm, and certainly less than 0.21 nm. Leon et al. [14] have also reported on potential energy calculations associated with intersheet shear in nylon 6.

In the monoclinic nylon 6 α-structure, since the *c*-axis intersheet shear is alternating, the *c*- and c^*-axes are coincident and the two strong characteristic interchain diffraction signals at spacings 0.44 nm (200) and 0.37 nm (020) occur in the equatorial plane (a^*b^*-plane) of the X-ray fiber diffraction pattern.

In the course of our studies we also discovered that the type of nylon 6 crystal structure that formed could be influenced by both the conditions of crystallization and by annealing at elevated temperature [3]. In the case of the non-folded

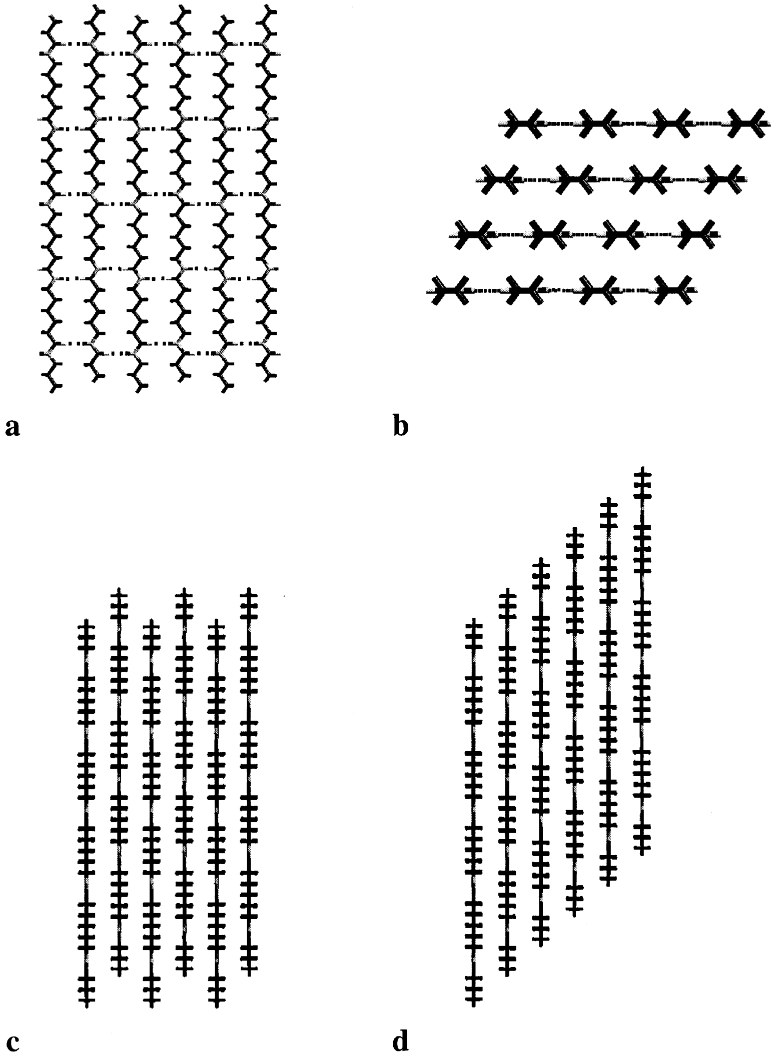

Fig. 1. (a–c) The nylon 6 monoclinic α-structure, using the 5-amide oligomer as the example. (a) Projection orthogonal to a single hydrogen-bonded sheet (*ac*-plane). Adjacent chains need to be antiparallel for all the hydrogen bonds to be saturated. (b) View looking down the chain, or *c*-axis, illustrating the progressive intersheet shear parallel to the *a*-axis in the *ac*-plane. (c) Projection parallel to the *b*-axis to show the alternating intersheet shear parallel to the *c*-axis in the *ac*-plane. (d) The proposed triclinic structure for the 5-amide nylon 6 crystals. Projection parallel to the *b* axis highlighting the progressive intersheet shear parallel to the *c*-axis in the *ac*-plane. The other projections are similar to (a) and (b). Color code: white, hydrogen; light gray, carbon; dark gray, nitrogen; black, oxygen; hydrogen bonds, dashed lines.

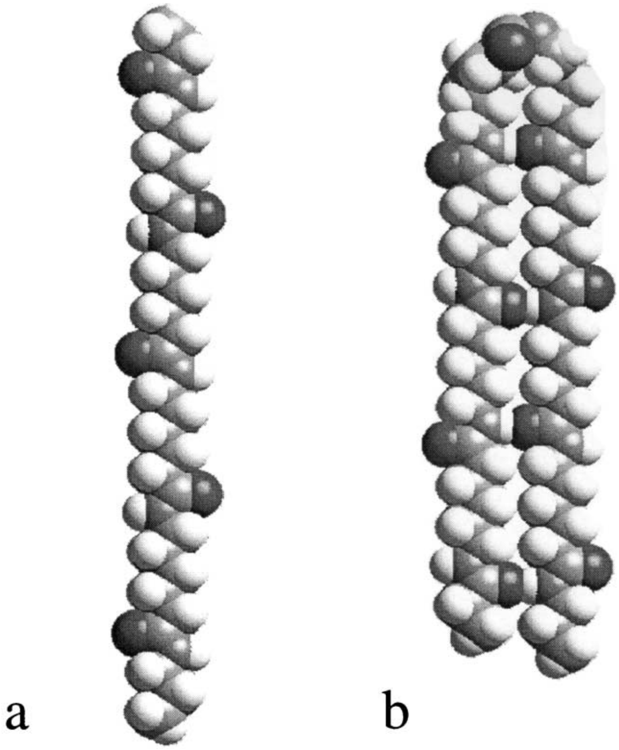

Fig. 2. Space filling models of nylon 6 monodisperse oligoamides. (a) The non-folded 5-amide molecule in the all-*trans* conformation (4.6 nm long). Note the $-CH_2CH_3$ and $-CH_2\ CH_2CH_3$ at the carbonyl and amine ends of the molecule, respectively. (b) The once-folded 9-amide hairpin-like molecule. It is considered that the hydrogen-bonded sheets are composed of an antiparallel arrangement of these hairpin entities [2].

5-amide nylon 6 oligomer (Fig. 2(a)), two different crystalline phases were identified [3]. The fundamental difference between the two structures is the nature of the intersheet shear. In the first phase, that is similar to the α-structure for nylon 6 [10,11], the intersheet shear parallel to the molecular axis (*c*-axis) is alternating [2]; in the second phase it is progressive [3], as shown in Fig. 1(d). In the case of the once-folded 9-amide oligomer (Fig. 2(b)) a transformation between the monoclinic and triclinic polymorphs was induced wholly within the solid state, by annealing at elevated temperature, but well below the melting point [3].

To our knowledge, the first detailed model of constant progressive *c*-axis intersheet shear in even nylons[3] was reported in 1985 by Cojazzi et al. [16] for nylon 10; it was called the α^*-structure and it was suggested that it also occurred in nylons 8 and 12. However in a subsequent paper [17] two years later by the same research group, the originally proposed nylon 10 α^*-structure was modified; it was argued to be a disordered phase with two different values for the *c*-axis intersheet shear and also with paracrystalline order in the intersheet stacking. Thus, according to this work [17], the α^*-structure in nylon 10 appears to be a mixed crystalline phase. Jones et al. [18] have reported a triclinic structure for chain-folded crystals of nylon 8, with constant progressive *c*-axis intersheet shear, and called it the λ-structure. A similar structure has been recently found for chain-folded nylon 6 polymer crystals [19].

In this contribution, we shall consider the occurrence of the two different crystalline phases for the 5-amide and 9-amide oligomers of nylon 6, with respectively alternating (monoclinic) and progressive (triclinic) intersheet shears, in relation to the crystallization conditions and, in addition, provide a more detailed structure for the progressively *c*-axis intersheet-sheared three-dimensional structure for the non-folded 5-amide oligomer.

1.1. Comment on the 9-amide nylon 6 oligomer

We have already shown [2] that the molecules in the 9-amide oligomer lamellar crystals, to be discussed in this contribution, exist in a once-folded hairpin-like conformation; as illustrated in Fig. 2(b). This result was established by sedimenting the lamellae to form a mat in which contiguous lamellar normals are aligned and directed parallel to the mat normal. The wide-angle X-ray diffraction pattern of the mat, with the incident beam orthogonal to the mat normal (vertical), from Ref. [2] is reproduced in Fig. 3(a). The diffraction pattern is similar to the nylon 6 α-structure [2,10,11,13] with the *hk*0 diffraction signals on the equator; thus, the chain (all-*trans* conformation) direction is orthogonal to the lamellar crystal surfaces. The length of the all-*trans* conformation of this 9-amide molecule is 8.06 nm. However, the first order of the lamellar stacking periodicity (LSP) was found to be only 4.60 nm [2], a value consistent with lamellae composed of the once-folded model shown in Fig. 2(b). These results have been discussed in more detail previously [2]. If crystals of this type (in the form of a sedimented mat) are annealed at 140°C in a vacuum oven for 24 h, then cooled to room temperature, the wide-angle X-ray diffraction pattern changes to that shown in Fig. 3(b) (reproduced from Ref. [3]). The most obvious changes are: (1) the rotation, off the equator, of the outer 020 diffraction arc by ≈50° and the inner 200 by ≈10°, and (2) a value of 0.64 nm for the measured spacing of the meridional 002 diffraction signal (arrowed in Fig. 3(b)); a reduction by 26% of the all-*trans* value of 0.86 nm, and suggesting a molecular tilt of 42°. The low-angle diffraction region has considerable diffuse scatter making it difficult to establish a LSP value with confidence.[4,5]

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[3] There have been earlier reports, of triclinic phases, in this particular case nylon 12 [15], which would indicate that progressive *c*-axis shear can occur in even nylons.

[4] These experiments were undertaken and the X-ray diffraction results obtained by EA while on a Visiting Professorship at the Department of Polymer Science and Engineering, University of Massachusetts, Amherst, USA.

[5] In the annealing experiment, although we are confident that the starting 9-amide lamellar crystals were composed of once-folded molecules we cannot be certain that they remained precisely once-folded after annealing at 140°C in a vacuum oven for 24 h.

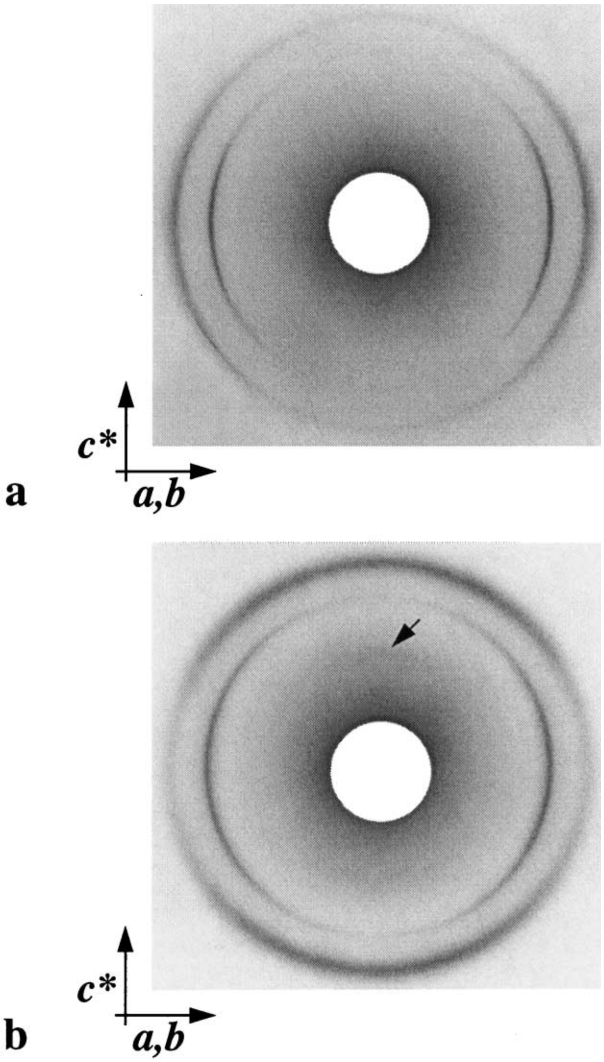

Fig. 3. X-ray diffraction patterns obtained from sedimented mats of the 9-amide nylon 6 oligomer. Incident X-ray beam parallel to the mat surface and with the mat normal vertical. (a) Crystals obtained by adding the miscible non-solvent 1,4-dioxane to the 9-amide oligomer in a solution of trifluoroethanol; reproduced from Ref. [2]. The 9-amide molecules are in a once-folded hairpin conformation; viz, the α-structure. (b) After annealing the sample produced in (a) at 140°C in a vacuum oven for 24 h. The spacing of the 002 diffraction signal (arrowed) is 0.64 nm, suggesting a molecular tilt of 42°.

1.2. Nature of the fold in the 9-amide nylon 6 oligomer

Hairpin turns in nylon 6 have been discussed in some detail previously [2,20,21].[6] On the current evidence we have available we do not judge that it is of direct relevance to the main aspect of this contribution which focuses on the progressive intersheet *c*-axis shear in nylon 6 monodisperse oligomer crystals, and its relationship to alternating intersheet *c*-axis shear.

2. Experimental

2.1. Materials

The starting materials, in the form of purified powders, were kindly provided by Dr G. Brooke and coworkers, University of Durham, UK. The chemical synthesis and detailed characterization, including NMR, of these and related monodisperse oligoamides have been reported by Brooke et al. [4–7]. The chemical structure of the nylon 6 oligomer family is given by: $CH_3CH_2CO[NH(CH_2)_5CO]_n NH(CH_2)_2CH_3$, where $n = 4$ and $n = 8$ for the 5-amide and 9-amide oligomers, respectively (see Fig. 2).

2.2. Methods of crystallization

Two different types of crystallization procedure were employed.

2.2.1. Solvent/non-solvent

The oligoamide powder was dissolved in trifluoroethanol to make 0.7% (w/v) solution. The miscible non-solvent 1,4-dioxane was added until the solution became slightly turbid. This method was used for both the 5-amide and 9-amide oligomers.

2.2.2. Isothermal crystallization

A 0.7% (w/v) solution of the 5-amide oligomer was prepared in *N*,*N*-dimethylformamide (DMF) at 100°C, followed by isothermal crystallization at 70–80°C for 12 h.

2.3. X-ray diffraction

X-ray diffraction patterns were obtained from sedimented mats of the oligoamide crystals. The sedimented mats were prepared by filtering the crystal suspensions using a glass syringe onto a 0.2 μm filter contained in a stainless-steel filter holder. The filter holder was then attached to a compressed air line to compact the crystals. The wide angle X-ray patterns were obtained at room temperature using a nickel-filtered CuKα radiation of wavelength 0.1542 nm from a Phillips sealed tube X-ray generator operating at 35 kV and 40 mA. The X-ray diffraction patterns were recorded on film, using a point-collimated, evacuated flat-plate camera and with the incident beam parallel to the surface of the mats and the mat normal vertical. Calcite ($d_B = 0.3035$ nm) was dusted onto selected samples for calibration purposes.

2.4. Transmission electron microscopy

Samples for transmission electron microscopy (TEM) were prepared by depositing drops of the crystal suspension onto carbon-coated grids and allowing the solvent to

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[6] The crystal structure of a cyclic dimer of nylon 6 has been reported [20]. The molecules form a square-like structure and the hairpin turn(s) are similar to the turn shown in Fig. 2(b), i.e. with the plane of the amide unit approximately orthogonal to the plane in which the connecting (anti-parallel) alkane segments lie.

evaporate. The samples were examined at room temperature in both imaging and diffraction modes using a Phillips 400T TEM operating at 100 kV. Some crystals were decorated with platinum/palladium to calibrate the diffraction patterns and to shadow the images.

2.5. Computational modeling

The software package Cerius 2 version 3.8 (Biosym/ Molecular Simulations Inc.) was used in the structural modeling. In the simulated X-ray diffraction patterns, the appropriate Lorentz and polarization factors were included and the intensity and degree of arcing were chosen to match the experimental patterns.

3. Results and discussion

3.1. X-ray diffraction

3.1.1. 5-Amide nylon 6 oligomer

The X-ray diffraction pattern obtained from a sedimented mat of the 5-amide nylon 6 oligomer crystallized by addition of non-solvent (Fig. 4(a)) exhibits the classic nylon 6 α-structure [10,11,2,13]. The characteristic pair of interchain diffraction signals, the 200 (0.44 nm) and 020 (0.37 nm), occurs on the equator (a^*b^*-plane) as discussed in the Introduction. A set of four orders of 4.79 nm on the meridian (coincident *c*- and c^*-axes) represent the stacking of the 5-amide molecular layers (the molecular length is 4.60 nm).

In contrast, when the 5-amide nylon 6 oligomer is isothermally-crystallized at 70–80°C in DMF a distinctly different X-ray diffraction fingerprint is obtained, as shown in Fig. 4(b). The characteristic 200 and 020 interchain diffraction signals occur, but not on the equator. The center of the outer 020 diffraction arc is observed $\approx 50°$ relative to the equator and the inner 200 is $\approx 10°$ off the equator. The 020 diffraction signal directly represents the intersheet distance and therefore the only plausible interpretation of the X-ray diffraction data is that substantial *progressive* intersheet shear, parallel to the molecular axis (*c*-axis), exists in this isothermally-crystallized 5-amide nylon 6 structure. This explanation is supported by other features in the diffraction pattern. On the meridian, a strong diffraction signal at 3.40 nm is observed, together with a set of four sharp orders. This result suggests that the molecular *c*-axis is tilted by approximately 42° [$\cos^{-1}(3.40/4.60)$] relative to the equatorial plane. The pattern also exhibits numerous other sharp and closely spaced *hkl* diffraction signals. The combined new features evident in the X-ray diffraction fingerprint suggest the following basic structure.

1. The 5-amide molecules hydrogen bond in an antiparallel fashion to form the classical nylon 6 hydrogen-bonded sheets,

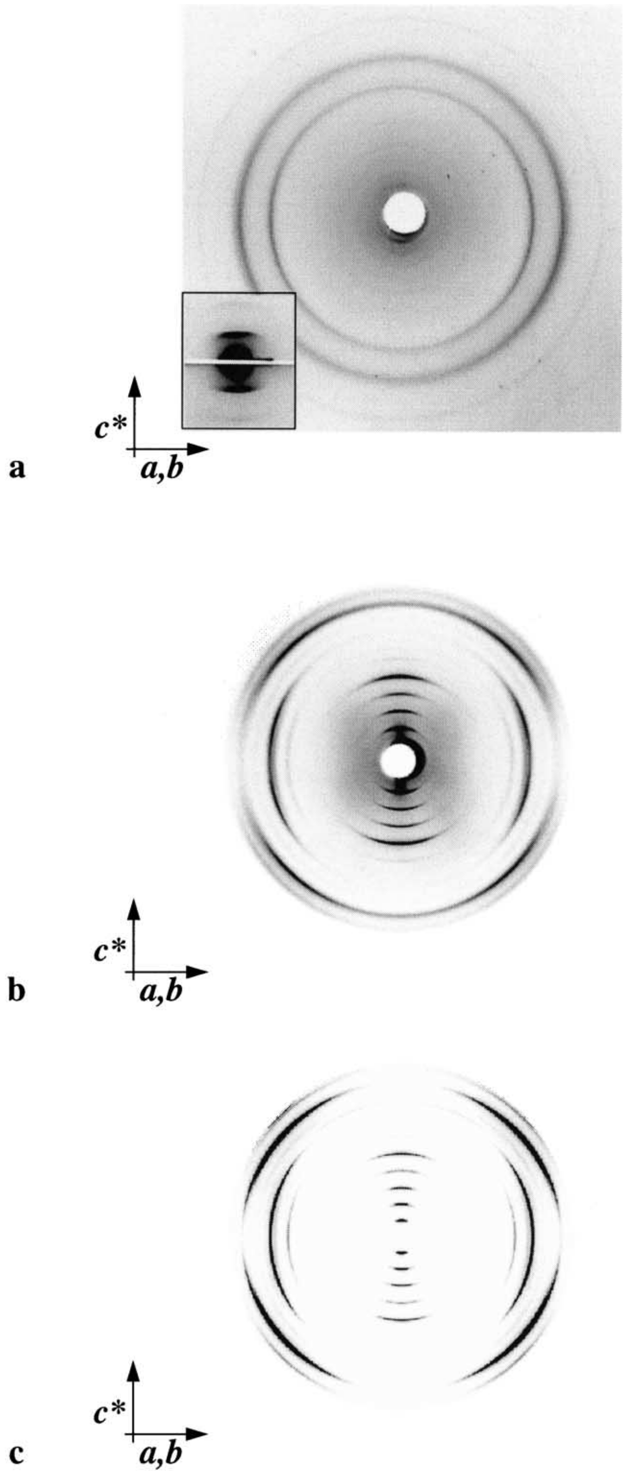


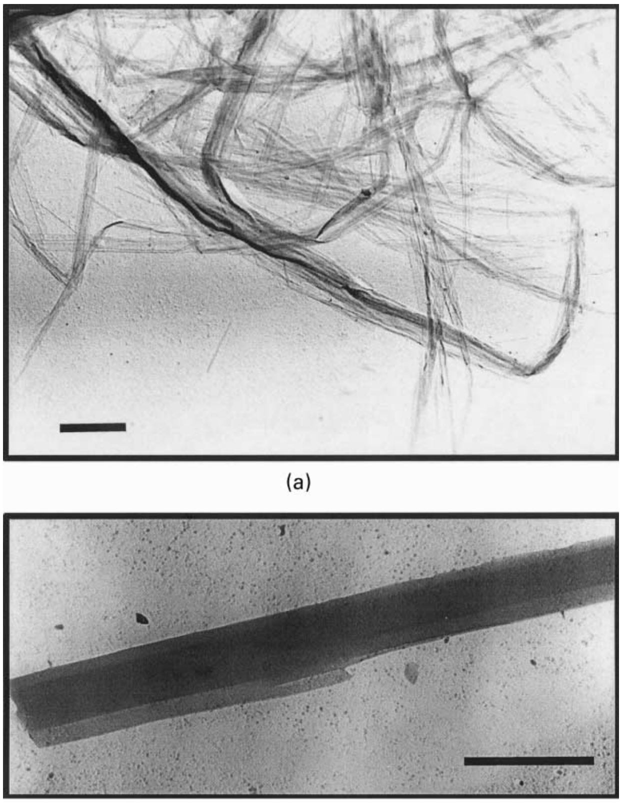
Fig. 4. (a and b) X-ray diffraction patterns obtained from sedimented mats of the 5-amide nylon 6 oligomer. Incident X-ray beam parallel to the mat surface and with the mat normal vertical. (a) Crystals obtained by adding the miscible non-solvent 1,4-dioxane to a solution of the 5-amide oligomer in trifluoroethanol; the α-structure. The meridional 001 at 4.60 nm, and orders, are shown in the lower left inset. (b) Crystals obtained by isothermal crystallization at 70–80°C in DMF. (c) Simulated X-ray diffraction pattern of the proposed structure of the crystals obtained in (b). This figure can be compared with the experimental X-ray diffraction pattern (same scale) shown in b.

2. The sheets (*ac*-planes) stack with progressive shear in both *c*- and *a*-directions,
3. Taking the usual nylon 6 hydrogen-bonded sheets to be a fundamental ingredient in this structure, then $\beta = 90°$, $a = 0.980$ nm and $c = 4.60$ nm.

Starting with these three initial parameters (and keeping $\beta = 90°$ invariant throughout), the measured *hkl* diffraction signals can be indexed on a two-molecule triclinic unit cell, incorporating the whole molecular length, with the following parameters: $a = 0.980 \pm 0.002$ nm, $b = 0.545 \pm 0.002$ nm, $c = 4.60 \pm 0.02$ nm, $a = 50.4 \pm 0.5°$, $\beta = 90°$ and $\gamma = 71 \pm 0.5°$. A list of the measured interplanar spacings and estimated relative intensities, together with the calculated spacings and indexing is given in Table 1. The determination of the triclinic unit cell parameters allows a more accurate value of 40° for the chain tilt to be calculated.

3.2. Transmission electron microscopy

Fig. 5(a) shows the long, ribbon-like crystals obtained when the 5-amide oligomers are crystallized from solvent (triflouroethanol)/non-solvent (1,4 dioxane) mixtures [2]. Electron diffraction, with the incident beam parallel to the ribbon surface normal [001], shows the classic strong *hk*0 diffraction signals of the nylon 6 α-structure. This shows that the molecular axes are parallel to the ribbon surface normal and the hydrogen bond direction is parallel to the long axis of the ribbons [2]. The morphology of the crystals is different when the 5-amide oligomers are isothermally crystallized at 70–80°C in DMF (Fig. 5(b)); the crystal appear as discrete entities with a smaller length to width ratio. The thickness is ≈60 nm, as estimated using metal shadowing. In this case, electron diffraction with the incident beam parallel to the basal (001) crystal face normal does not give the *hk*0 reciprocal net, but rather weaker higher order indices, suggesting that the molecular axis is inclined to the basal crystal face normal.



(a)

(b)

Fig. 5. Transmission electron micrographs of crystals obtained from the monodisperse 5-amide nylon 6 oligomer. (a) Crystallized by adding the miscible non-solvent 1,4-dioxane to a 5-amide oligomer trifluoroethanol solution; reproduced from Ref. [2] for direct comparison with figure b. (b) Crystallized isothermally from DMF at 70–80°C. The scale bar represents one micron.

3.3. Structural modeling

Although both the 5-amide and 9-amide nylon 6 oligoamides have been obtained in crystal structures in which the hydrogen-bonded sheets progressively *c*-axis intersheet shear, the 5-amide structure provides by far the richer set of X-ray diffraction data, as shown in Fig. 4(b). Thus, it is logical to use this data as the basis for modeling the structure. The 5-amide molecules are tilted relative to the vertical as shown in Fig. 1(d). In the three-dimensional crystalline structure these 5-amide layers (Fig. 1(d)) stack to generate the triclinic lattice given in Table 1. Fig. 4(c) shows a simulated X-ray diffraction pattern calculated for this triclinic 5-amide nylon 6 structure (Fig. 1(a), (b) and (d)). The positions and relative intensities of the diffraction signals match well the experimental X-ray diffraction pattern, as shown in Fig. 4(b) and listed in Table 1.

4. Discussion and conclusions

The usual α-structure for nylon 6 [10,11,13] consists of hydrogen-bonded sheets (*ac*-plane) with progressive intersheet shear parallel to the hydrogen bond (*a*) direction but alternating parallel to the chain (*c*-axis) direction, thus generating a monoclinic structure. In the case of the two nylon 6 oligomers described above, it is clear that a different type of *c*-axis intersheet shear can occur, viz a progressive intersheet shear. As a consequence of this progressive *c*-axis intersheet shear, the structure becomes triclinic. In the case of the progressively *c*-axis intersheet sheared 9-amide nylon 6 oligomer crystals, the molecular layers (parallel to *ab*-plane) do not stack with crystallographic register. We believe this is because of the surface folds in the lamellae. Indeed, it is characteristic behavior of the type of lamellar stacking in chain-folded polymers in general, i.e. the layers stack with random orientation about the stacking direction to form a one-dimensional lattice, but usually with only fundamental order occurring [23,24]. In the case of the non-folded 5-amide crystals, with progressive *c*-axis

Table 1
Comparison of observed and calculated X-ray diffraction spacings for the 5-amide nylon 6 oligomer crystallized from DMF*

Index[a] *hkl*	Observed spacings ±0.003 nm	Calculated spacing[a] (nm)	Observed relative intensity	Calculated relative intensity	Azimuthal Orientation
0 0 1	3.400[b]	3.398	vs	vs	M
0 0 2	1.697	1.699	vs	vs	M
0 0 3	1.135	1.133	vs	vs	M
0 0 4	0.851	0.849	s	s	M
0 0 5	0.679	0.680	vs	vs	M
0 0 6	0.567	0.566	w	w	M
0 0 11	0.307	0.309	w	w	M
1 1 19	0.228	0.220	w	w	Near-M
1 2 19		0.229			Very broad
$\bar{1}$ 1 19		0.232			
0 1 1	0.409	0.410	w	w	Off-E
2 1 1		0.395			
0 1 0	0.380	0.381	vs	vs	Off-E
2 1 0		0.379			Broad
0 1 $\bar{1}$	0.353	0.353	m	m	Off-E
2 1 $\bar{1}$		0.360			Broad
0 1 $\bar{2}$	0.325	0.327	vw	vw	Off-E
2 $\bar{1}$ 0	0.245	0.243	m	m	Off-E
					Broad
2 0 0	0.443	0.444	vs	vs	Near-E
2 1 6	0.406	0.405	m	m	Near E
4 0 0	0.221	0.222	m		Near-E
0 1 5	0.512	0.509	m	m	E
2 0 $\bar{2}$	0.461	0.463	m	m	E
2 0 $\bar{3}$		0.460			
4 0 $\bar{3}$	0.235	0.231	m	m	E
4 0 $\bar{4}$		0.232			Broad
4 0 $\bar{5}$		0.231			

[a] Based on a triclinic unit cell with parameters: $a = 0.980 \pm 0.002$ nm, $b = 0.545 \pm 0.002$ nm, $c = 4.60 \pm 0.02$ nm, $\alpha = 50.4 \pm 0.5°$, $\beta = 90°$ (chosen value) and $\gamma = 71 \pm 0.5°$.

[b] Low-angle signal obtained using synchrotron X-ray radiation source [3]. E = equator; M = meridional; vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

[*] Crystals prepared at higher crystallization temperatures have been reported [22] together a detailed structure determination.

intersheet shear, crystallographic stacking does occur to form crystals many times thicker ($\geq \times 20$) than the 3.40 nm layer thickness. As a consequence, a structure analysis could be undertaken for this triclinic 5-amide nylon 6 crystal and projections of the proposed structure are shown in Fig. 1(a), (b) and (d).

The triclinic structure and the traditional monoclinic nylon 6 α-structure share basic common features. Both are composed of fully saturated hydrogen-bonded sheets with adjacent molecules arranged in an antiparallel fashion (Fig. 1(a)) and the hydrogen-bonded sheets shear parallel to the hydrogen bond direction (*a*-axis) in a progressive fashion, to optimize interchain interactions between the sheets. However, here the similarity ends. Whereas the *c*-axis intersheet shear in the α-structure is alternating, in the case of the triclinic structure the *c*-axis intersheet shear is progressive.

We have found that this triclinic crystalline nylon 6 phase can be obtained by crystallizing under different conditions. In the case of the 5-amide oligomer, this was achieved by isothermally crystallizing at elevated temperatures, rather than by crystallizing from solution at room temperature by addition of miscible non-solvent, a process that results in the α-structure. For the 9-amide oligomer, the progressive *c*-axis intersheet sheared crystalline phase was induced by heat annealing previously prepared α-structure crystals. Thus in this case, a condensed state crystalline transformation, from alternating to progressive intersheet shear, was accomplished. We have recently called this progressive *c*-axis intersheet sheared crystalline polymorph the λ-structure [25], and observed the structure in chain-folded lamellar crystals obtained from both nylon 8 [18] and nylon 6 polymers [19].

The relationship between the α- and λ-phases in nylon 6 bears a strong resemblance to the two crystalline polymorphs: I_β and I_α, that occur in native cellulose [26]. In the cellulose structures, the polysaccharide chains hydrogen bond together to form sheets, and in both crystalline polymorphs there is progressive intersheet shear parallel to the hydrogen bond direction (*a*-axis).[7] However, in the chain (*c*-axis) direction the intersheet shear is alternating in the I_β-structure but progressive in I_α-structure. In many common forms of native cellulose both the monoclinic I_β and the triclinic I_α crystalline phases occur, but can vary in relative proportions; thus, sometimes it is difficult to delineate between the two phases.[8] A similar mixed phase structure might well have occurred in the past for nylon 6, but was not specifically recorded.

Acknowledgements

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[7] Again to relieve interchain interactions between neighboring sheets.

[8] It took nearly 60 years for the I_α-structure to be recognized in cellulose and, as a consequence of this discovery, it is now realized [26] that most cellulose structures are mixtures of two polymorphs.