The Three-Dimensional Structure of Monodisperse 5-Amide Nylon 6 Crystals in the λ-Phase

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Received February 20, 2001; Revised Manuscript Received April 11, 2001

ABSTRACT: Monodisperse 5-amide nylon 6 oligomers have been isothermally crystallized at 95 °C from *N*,*N*-dimethylformamide. The crystals have been investigated using optical microscopy, X-ray diffraction, electron microsopy (imaging and diffraction), atomic force microscopy and computational modeling. The diffraction signals index on a two-molecule triclinic unit cell with the parameters: $a = 0.967 \pm 0.002$ nm, $b = 0.540 \pm 0.002$ nm, c (molecular axis) $= 4.56 \pm 0.02$ nm, $\alpha = 49.3 \pm 0.5$ °, $\beta = 90.0°$ and $\gamma = 71.4 \pm 0.5°$. The calculated density is 1.15 g cm^{-3}. A structure refinement was undertaken based on the experimental electron and X-ray diffraction data. The results show that the molecules are in the all-trans conformation and hydrogen bond to antiparallel neighbors to form the usual nylon 6 hydrogen-bonded sheets. However in this structure, which has been called the λ-structure, the sheets stack with progressive *c*-axis shear, and consequently, the molecular layer thickness is noticeably reduced. Successive molecular layers associate in crystallographic register with a periodicity of 3.31 nm to form three-dimensional prismatic crystals that can be seen using conventional optical microscopy. The λ-structure is distinctly different from the traditional recuperative *c*-axis intersheet-sheared nylon 6 monoclinic α-structure. The 5-amide nylon 6 λ-structure is a relative of the triclinic nylon 10 α*-structure and indeed, in some respects, bears an architectural resemblance to the nylon 6 6 triclinic α-structure.

Introduction

The monoclinic α-structure, determined originally by Holmes et al.[1] from X-ray fiber diffraction patterns, is the more common crystalline phase for nylon 6. The unit cell contains two 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 and $\beta = 112.5°$. A slightly modified structure was subsequently proposed by Malta et al.[2] and space group $P2_1$ assigned.[3] In the nylon 6 α-structure,[1,2] an array of antiparallel chains allows adjacent interchain −C=O···HN− hydrogen bonds to be fully saturated and linear, which in turn generate a planar hydrogen-bonded sheet (*ac*-plane with $\beta = 90°$), as shown in Figure 1a. These hydrogen-bonded sheets stack together via van der Waals interactions and successive sheets shear progressively (see Figure 1b) along the *a*-direction in the *ac*-plane by $\approx a/6$. In addition, there is an alternating shear ($\pm\Delta c$) parallel to the *c*-axis. The originally reported[1] Δc value was $3c/14$ (0.37 nm) based on a comparison with nylon 6 6;[4] this value was also maintained by Malta et al.[2] Leon et al.[5] have reported on potential energy calculations associated with intersheet shear in nylon 6 and more recently it has been shown,[6] that the actual value is closer to 0.14 nm, and certainly <0.21 nm. Irrespective of the actual Δc value, because the *c*-axis intersheet shear in the nylon 6 α-structure is *alternating (or recuperative*[5]) the two strong characteristic interchain diffraction signals, at spacings of 0.44 nm (200) and 0.37 nm (020), respectively, occur in the equatorial plane (*a***b**-plane) of a X-ray fiber diffraction pattern.

Two other crystalline polymorphs have been proposed. (i) The first is a γ-structure, where the amide units tilt and rotate out of the *ac*-plane to form hydrogen bonds between parallel chains.[7−10] The characteristics of the γ-structure are a merging together of the 0.44 and 0.37 nm spacings, and a reduction of ≈ 5% in the *c*-repeat as a consequence of the twisted backbone conformation. (ii) The second is an unstable β-structure, where the *c*-direction shear is zero and possibly the hydrogen-bonded sheets consist of parallel chains and nonlinear hydrogen bonds.[1] Other interpretations of the β-structure have been reported and discussed, for example, by Murphy[11,12] and Auriemma et al.[13]

We have recently described and discussed the crystalline structures of particular nylon 6 monodisperse oligoamides.[14−18] These precisely defined molecules (in length and chemistry)[19−23] are terminated with short alkane segments (see Figure 1c) to minimize the disturbance to the crystalline lattice. The mondisperse 5-amide nylon 6 oligomer in the all-trans conformation has a length of 4.60 nm (Figure 1c). Three-dimensional crystals in the classic nylon 6 α-structure[1,2] are obtained when crystallized from solution by adding a miscible nonsolvent;[15] the molecules form smectic A-like layers with a periodicity of 4.79 nm (see Figure 2a). However, when the 5-amide oligomer was isothermally crystallized (70−80 °C) from *N*,*N*-dimethylformamide (DMF),[24] the crystals formed exhibited a progressive *c*-direction intersheet shear (≈49°), i.e., smectic C-like layers with a reduced layer stacking periodicity. More recently, we have obtained improved experimental data by raising the crystallization temperature to 95 °C. We have chosen to call this crystalline phase the λ-structure[18] (see Figure 2b) and found it occurs in chain-folded polymeric crystals of both nylon 8[25] and nylon 6.[26] Indeed, this structure bears a noticeable resemblance to the nylon 6 6 α-structure (*c*-direction intersheet shearing angle ≈ 50°) found in lamellae[27] and fibers.[4] Progressive *c*-axis intersheet shear has been discussed in other nylons, for example nylon 4 6,[28] and chain tilt in monodisperse cyclic trimers of nylon 11.[29]

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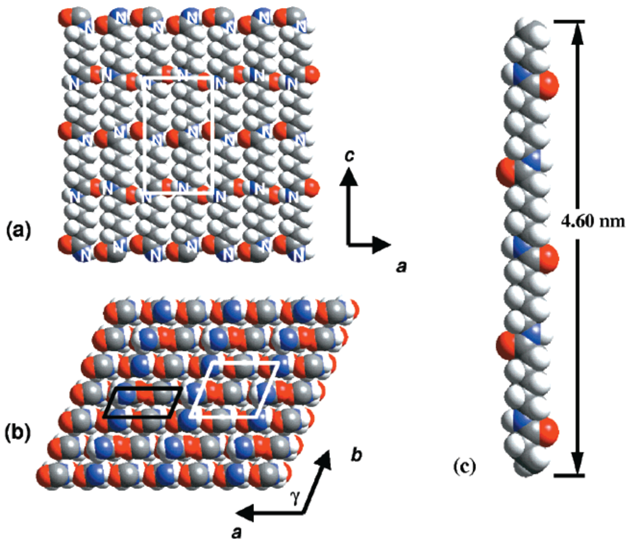

Figure 1. Space-filling models relating to the 5-amide nylon 6 oligomer. Note, in parts a and b the terminal $-C_3H_7$ and $-C_2H_5$ top and bottom groups, respectively, have been removed to allow the hydrogen-bonding scheme to be more clearly seen. (a) Projection, orthogonal to the sheet surface, of a single hydrogen-bonded sheet composed of antiparallel 5-amide nylon 6 molecules. Note the $-C{=}O\cdots HN-$ hydrogen bonds running parallel to the *a*-axis. The white rectangle is the repetitive unit and represents a basic structural entity in both the nylon 6 α-structure and the proposed 5-amide nylon 6 λ-structure. (b) View parallel to the chain (*c*-axis) showing the sheets with progressively intersheet shearing parallel to the *a*-axis. The white box represents the repetitive (monoclinic) unit cell for the recuperative *c*-axis intersheet sheared nylon 6 α-structure, and the appropriate *a* and *b* directions and γ-angle are inserted. In the case of the of the proposed 5-amide nylon 6 λ-structure, the black box represents a projection of the two-chain triclinic unit cell on a plane (a^*b^*-plane) orthogonal to the *c*-axis (indeed the obtuse angle is equivalent to γ^*). (c) Complete 5-amide nylon 6 oligomer in the all-trans conformation. The amine end (top) is terminated with a $-CH_2CH_2CH_3$ unit and the carbonyl group (bottom) is terminated with a $-CH_2CH_3$ unit. Color code: carbon, gray; nitrogen, blue; oxygen, red; hydrogen, white.

To our knowledge, a constant progressive *c*-axis intersheet shear in even nylons was first reported in 1985 by Cojazzi et al.[30] for nylon 10. We shall comment further on the nylon 10 α*-structure and on the relationship between the even nylon α*- and λ-phases in the Discussion section later.

In chain-folded lamellar crystals, of both nylon 6 and nylon 8, although each individual lamella is a crystal (~5 nm in thickness), the lamellae stack with random azimuthal orientation about their lamellar normals (c^*-axis). As a consequence, the quality of the diffraction data is restricted. In the case of the crystals of this high-fidelity, monodisperse 5-amide nylon 6 oligomer, many lamellae stack with crystallographic register in the lamellar normal direction to form a three-dimensional crystal; these crystals further stack with cylindrical symmetry about the lamellar normal. Thus, in this contribution, we are able to undertake a structural analysis to a level of accuracy not normally achievable for polyamides and describe this recently discovered nylon 6 λ-structure in detail.

Experimental and Modeling Section

Materials. The starting material, in the form of a purified powder, was generously provided by Dr. G. Brooke, University of Durham. The chemical synthesis and characterization of this family of monodisperse oligoamides have already been reported in detail by Brooke et al.[20−23]

Crystal Preparation. The 5-amide nylon 6 oligomer powder was dissolved in *N*,*N*-dimethylformamide (DMF) at 110 °C (temperature maintained in an oil bath) to make a 0.5% (w/v) solution. The temperature was slowly lowered (1 h) to 95 °C and isothermally crystallized for 14 h before being allowed to cool to room temperature. Oriented crystal mats suitable for X-ray diffraction were prepared by draining the crystal suspension through a 0.2 μm filter.

X-ray Diffraction. X-ray diffraction patterns were obtained at room temperature using nickel-filtered Cu Kα radiation of wavelength 0.1542 nm, from a Philips sealed tube X-ray generator operating at 35 kV and 40 mA. A point-collimated beam was directed parallel to the surface of the sedimented mats and the X-ray diffraction patterns were recorded using an evacuated flat-plate camera. Calcite ($d_B = 0.3035$ nm) was dusted onto selected samples for calibration purposes.

Optical Microscopy. Optical photographs were obtained using conventional polarizing optical microscopy. Samples were prepared by placing a drop of crystal suspension (as crystallized) between a glass slide and a coverslip. Observations were made on both crystals still in suspension and where the solvent was allowed to evaporate.

Atomic Force Microscopy (AFM). Drops of the crystal suspension were placed on freshly cleaved mica and allowed to dry. The thickness and surface morphology of the crystals were examined using a Digital Instruments Extended Multimode AFM. Simultaneous registration was performed in the contact mode for height and deflection images.

Transmission Electron Microscopy (TEM). Drops of the crystal suspension were placed on carbon-coated transmission electron microscopy (TEM) grids and the solvent allowed to evaporate in a vacuum oven at room temperature. Some samples were shadowed with Pt/Pd to enhance the contrast of TEM images and to calibrate the electron diffraction patterns. TEM images and electron diffraction patterns were recorded at room temperature using a Philips EM400T microscope operating at 100 kV.

Model Building and Analyses of Structure. The software package Cerius2, version 3.8 (MSI) was used for both the structural modeling and diffraction simulations. The basic strategy was to determine the molecular conformation, hydrogen bonding and the packing schemes within the unit cell determined from the diffraction data. After the initial model building stage, a combination of energy minimization (EMin), using the CVFF force field, and simulations of diffraction patterns was used. It was ensured that the model was stereochemically sound and that the simulated diffraction patterns were in good agreement with the experimental data. The X-ray fiber diffraction patterns were simulated in two stages. (1) A powder diffraction pattern was simulated in Cerius2 with the intensities of all the nonmeridional diffraction signals appropriately corrected using the fiber Lorentz correction factor, and (2) the calculated diffraction signals were superimposed on the experimental diffraction pattern as circles, with the diameters proportional to the calculated intensity. The positions of the diffraction signals were calculated from the experimental unit cell parameters. The intensities of meridional diffraction signals were not simulated but are plotted to show that their positions are correct.

Results and Discussion

Optical Microscopy. Figure 3a shows an array of prismatic crystals obtained from the 5-amide nylon 6 oligomers crystallized in the λ-structure and demonstrating their relatively large size: approximately 10 μm long by 1−2 μm in width. We know from electron microscopy that the long axis is the hydrogen bond direction (*a*-axis).

Atomic Force Microscopy. Figure 3b shows an AFM height image of 5-amide nylon 6 crystals solution-grown from DMF. A deflection image, highlighting

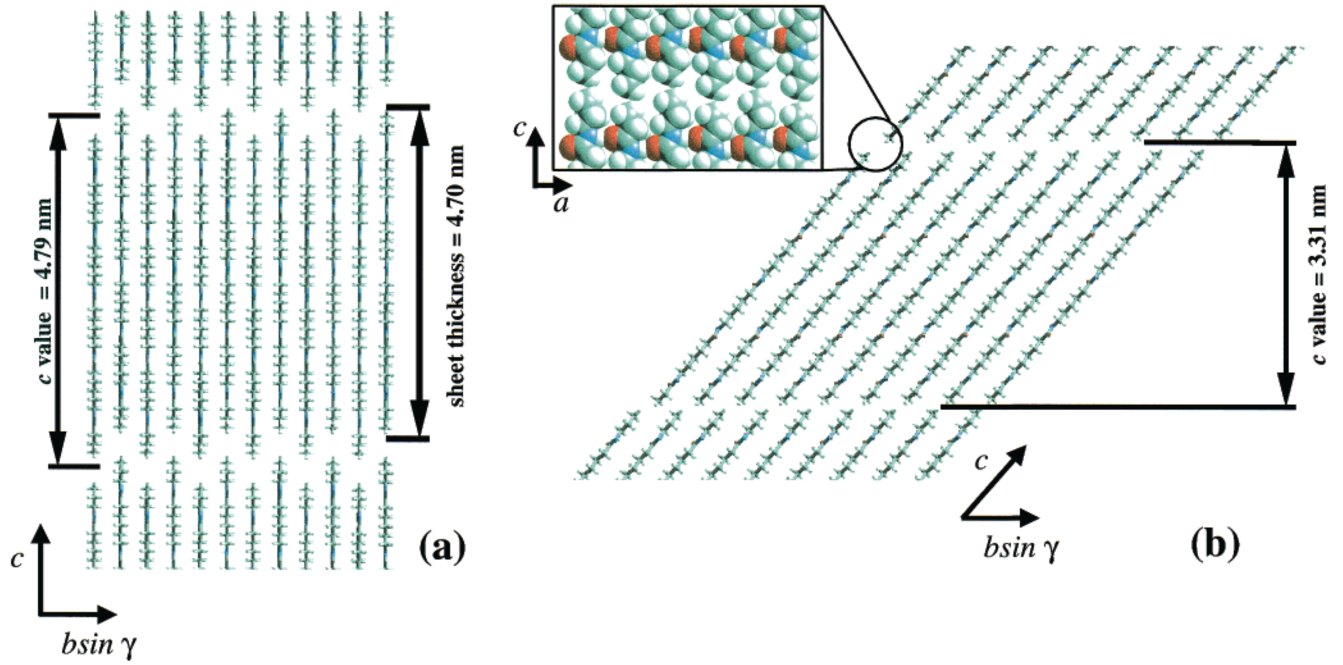

Figure 2. Projections (parallel to *a*-axis) of the 5-amide nylon 6 structures: (a) the α-structure and (b) the *λ*-structure. Note successive lamellae are off-set; they also interdigitate slightly (0.1 nm) as shown in by the space-filling model (upper left inset). Color code: carbon, gray; nitrogen, blue; oxygen, red; hydrogen, white.

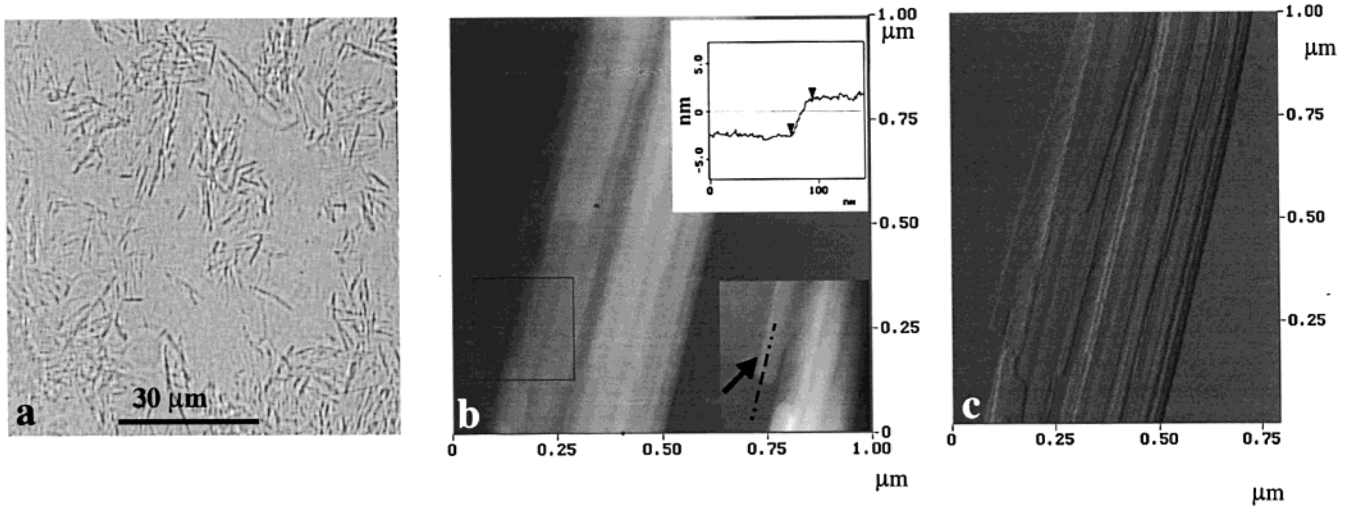

Figure 3. (a) Optical micrograph obtained from a drop of the 5-amide nylon 6 *λ*-form crystals between coverslips. (b) AFM height image of 5-amide nylon 6 crystals showing that the overall crystal thicknesses are in the region of 50−100 nm. The lower right inset shows a view near the edge of the crystal (boxed) and a height scan along the dashed line (arrowed) is shown in the upper right inset. The step jump in the line scan is 3.6 ± 0.4 nm. This is commensurate with the lamellar thickness of 3.41 nm. (c) AFM deflection image highlighting the longitudinal terracing.

surface morphology of the crystals, is shown in Figure 3c. Traces taken across the whole crystal give thicknesses in the range 75−100 nm, considerably greater than the thickness of individual lamella (3.41 nm) or the length of the 5-amide nylon 6 molecule (4.60 nm). The lower inset in Figure 3b shows a fragment of the crystal near its edge where the thickness of just one lamella can be measured. The measured value of 3.6 ± 0.4 nm is consistent with the value of 3.41 nm for the lamellar thickness measured by X-ray diffraction and estimated from electron microscopic images.

X-ray Diffraction. The X-ray diffraction pattern from a mat of sedimented crystals, where each 5-amide nylon 6 crystal is a stack of in-register lamellae, taken with the X-ray beam parallel to the mat surface and with the mat normal vertical, is shown in Figure 4. The pattern is basically a rotation crystal photograph about c^*-axis. The diffraction signals can be indexed on a triclinic unit cell containing two complete (antiparallel) molecules and with parameters: $a = 0.967 \pm 0.002$ nm, $b = 0.540 \pm 0.002$ nm, c (chain axis) $= 4.56 \pm 0.02$ nm, $\alpha = 49.3 \pm 0.5$ °, $\beta = 90.0°$, and $\gamma = 71.4 \pm 0.5°$; the Miller indices, interplanar spacings, and estimated relative intensities are tabulated in Table 1a. Note that the $c = 4.56$ nm value[31] is commensurate with the length (4.60 nm) of the 5-amide nylon 6 oligomer (Figures 1c and 2b).

The most dramatic feature in the wide-angle X-ray diffraction is the substantial azimuthal angular displacement (±43.4° [α^* −90°]) of characteristic nylon 6 intersheet (0.370 nm) diffraction signal (see Figure 4) from the equatorial axis. Care was exercised in the

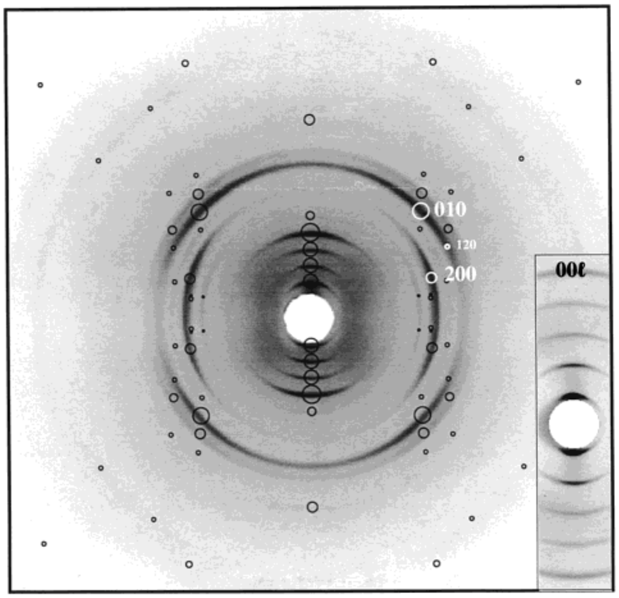

Figure 4. Wide-angle X-ray diffraction pattern obtained from sedimented crystals of 5-amide nylon 6 isothermally crystallized from DMF at 95 °C. The crystal mat normal is vertical, and the X-ray beam is directed parallel to the mat surface. This is effectively a single-crystal rotation (c^*-axis) photograph. Note the azimuthal splitting with respect to the equator of the 010 (±43.4°), at a spacing of 0.370 nm, and the 200 (±16.8°) diffraction signals, at a spacing of 4.37 nm. The 002, at spacing 1.659 nm, and additional orders appear on the meridian. The low-angle X-ray diffraction pattern (inset) shows the 001 and next four (00l) orders in more detail. The spacings, indexing, and estimated relative intensities are given in Table 1a. The calculated intensities and positions of the diffraction signals are overlaid as circles (area proportional to the calculated intensity) on the experimental diffraction pattern.

measurement of the 010 azimuthal angle, since the arcing of the weaker 210 angle, at almost the same spacing but at a different azimuthal angle, partially overlaps (see Figure 4) the stronger 010 diffraction arc. In the nylon 6 α-structure this diffraction signal is sited on the equator.[1,2,15] This feature is reminiscent of lamellar crystals of nylon 6 6[27] and points to substantial and *progressive*, rather than *recuperative*, c axis intersheet shear of the hydrogen-bonded sheets. Other noticeable features are the off-equatorial azimuthal splitting (±16.8° [90° − β^*]) of the 200 nylon 6 diffraction signal at a spacing of 0.437 nm (see caption to Figure 4) and the series of meridional (c^*-axis) diffraction signals, having orders of the lamellar stacking periodicity (LSP) of 3.31 nm. The overall features of the diffraction fingerprint bear a similarity to the diffraction pattern observed almost 30 years ago in the case of the triclinic nylon 6 6 lamellar crystals.[27,32] Thus, before we consider the electron microscopic evidence, the electron diffraction data in particular, we know a priori that the lamellar stacking direction is c^* and that the molecular (chain) c-axis lies at an angle given by $c \wedge c^* = 43.5°$. It is worth noting, that the outer limit lamellar thickness[33] is 3.41 nm (4.70 cos(43.5°) nm) is slightly greater than the LSP value of 3.31 nm. Thus, slight interdigitation (by 0.1 nm) of the crystals occurs, as shown in Figure 2b. Figure 5 (lower) shows the powder X-ray diffraction photograph obtained from 5-amide nylon 6. The derived experimental intensity distribution (Figure 5; upper) is plotted as a function of 2θ° for straightforward comparison with the calculated intensity profile derived from the proposed model to be discussed later.

Table 1. Comparison of Observed and Calculated Diffraction Spacings from 5-amide Nylon 6 Isothermally crystallized from DMF[a]

hkl	d_{obs} (nm)	d_{calc} (nm)	Int$_{obs}$[b]	hkl	d_{obs} (nm)	d_{calc} (nm)	Int$_{obs}$[b]
(a) X-ray Diffraction Spacings and Estimated Relative Intensities							
001	3.315	3.311	vs	010	0.370	0.372	vs
002	1.659	1.656	s	210	0.369	0.371	m
003	1.104	1.104	s	$21\bar{1}$	0.349	0.352	s
004	0.830	0.828	s	$01\bar{1}$	0.349	0.344	s
005	0.662	0.662	vs	$01\bar{2}$	0.315	0.319	w
006	0.552	0.552	w	$21\bar{3}$	0.315	0.312	w
015	0.502	0.504	w	00 11	0.301	0.301	w
$20\bar{3}$	0.455	0.455	vw	$1\bar{1}\,\overline{18}$	0.241	0.243	w
$20\bar{1}$	0.455	0.452	vw	$2\bar{1}0$	0.241	0.238	w
200	0.437	0.439	s	11 18	0.225	0.230	m
011	0.402	0.401	w	$1\bar{2}\,\overline{18}$	0.218	0.217	wv
212	0.402	0.401	w	$22\bar{1}$	0.197	0.200	wv
(b) Electron Diffraction Spacings and Estimated Relative Intensities from the [001] Zone							
200	0.435	0.439	vs	220	0.204	0.205	m
010	0.375	0.372	vs	020	0.188	0.186	m
210	0.367	0.371	vs	420	0.184	0.185	m
410	0.237	0.238	m	430	0.135	0.135	w
$2\bar{1}0$	0.237	0.238	w	230	0.135	0.135	w
400	0.218	0.219	w	030	0.125	0.124	w

[a] Unit cell parameters: $a = 0.967 \pm 0.002$ nm, $b = 0.540 \pm 0.002$ nm, $c = 4.56 \pm 0.02$ nm, $\alpha = 49.3 \pm 0.5°$, $\beta = 90°$, $\gamma = 71.4 \pm 0.5°$. Reciprocal unit cell parameters: $a^* = 1.139 \pm 0.002$ nm^{-1}, $b^* = 2.691 \pm 0.002$ nm^{-1}, $c^* = 0.302 \pm 0.02$ nm^{-1}; $a^* = 133.4°$, $b^* = 73.2°$, $g^* = 114.8°$. The angle β is fixed at 90° by the nature of the nylon 6 hydrogen-bonded sheets. [b] Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

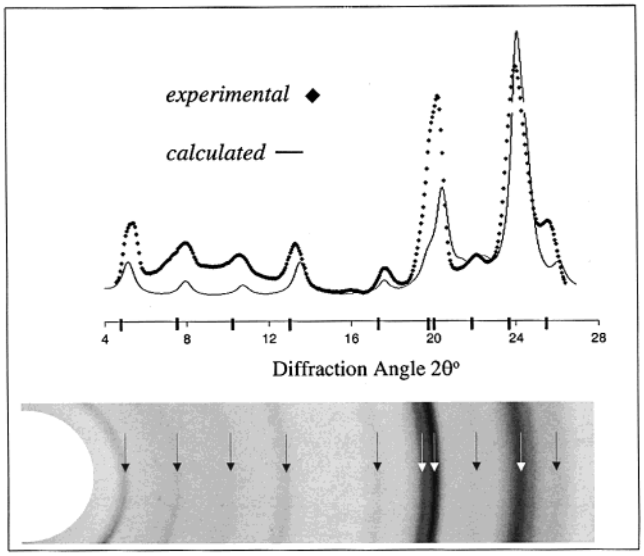

Figure 5. Powder X-ray diffraction pattern obtained from the 5-amide nylon 6 crystals isothermally crystallized from DMF. The actual photograph is shown at the bottom with the prominent diffraction signals marked with white arrows. The experimental and calculated traces are compared in the upper part of the figure; the vertical bars on the abscissa represent the positions of the observed (arrowed) diffraction signals.

Electron Microscopy. (a) Real Space Imaging. Figure 6 shows the prismatic-like crystals obtained from 5-amide nylon 6 isothermally crystallized from DMF. X-ray diffraction, supplemented with selected area electron diffraction results (see next section), show that the crystals lie on their (001) surface (ab-plane) and with the a-axis (hydrogen bond direction) parallel to the long axis of the crystals. There is noticeable terracing (lon-

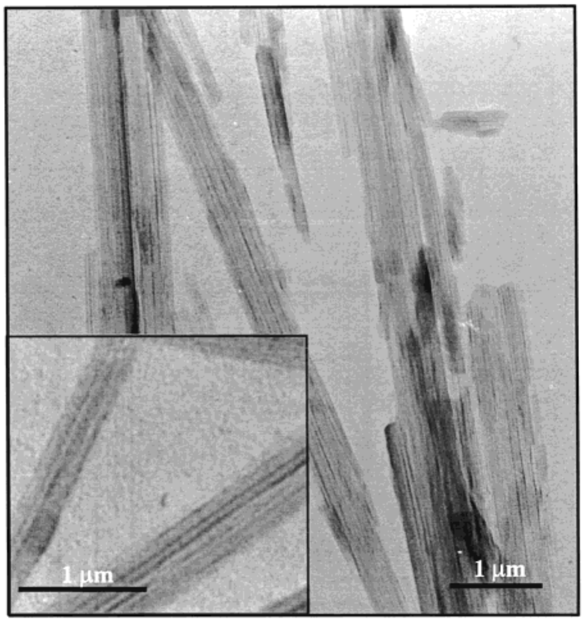

Figure 6. Transmission electron micrograph of the prismatic 5-amide nylon 6 crystals, prepared by isothermal crystallizing in DMF at 95 °C and shadowed with Pt/Pd to enhance the contrast. Note the longitudinal terracing of the crystals, highlighted in the lower, left inset.

gitudonal lines) within the crystals, as seen more clearly in the inset (Figure 6).

(b) Electron Diffraction. We know, a priori, that the crystals are expected to lie with the c^*-axis parallel to the substrate normal; thus, the c-axis will be tilted from the beam by 43.5° and in a precisely defined direction with respect to the crystallographic axes. Therefore, to obtain the [001] zone electron diffraction pattern, the sample has to be tilted by a large angle in a specific direction, and such a procedure is technically demanding. However, we did manage to achieve it experimentally (Figure 7a) and record the a^*b^*-reciprocal net, including intensities, and directly measure[34] the reciprocal parameters $a^* = 1.139 \pm 0.002$ nm^{-1}, $b^* = 2.691 \pm 0.002$ nm^{-1}, and $\alpha^* = 115 \pm 1°$. Thus, from $\beta = 90°$ and the value of c^* (from X-ray diffraction data), all the unit cell parameters of the triclinic unit cell could be determined with confidence. A projection of the structure parallel to the c-axis ([001] zone) can be seen in Figure 1b if one imagines that successive hydrogen-bonded sheets are progressively sheared out of the plane of the paper by the appropriate value of Δc; the black box represents a projection of the two-chain triclinic unit cell on a plane (a^*b^*-plane) orthogonal to the c-axis (indeed the obtuse angle is equivalent to γ^*). The electron diffraction pattern with the incident beam orthogonal to the crystal, i.e., parallel to c^*, (close to [0$\bar{5}$1] zone) does not provide particularly useful information, although the prominent $h00$, for even h, diffraction signals are evident.

Structure. In summary, all the evidence favors a structure consisting of the nylon 6 hydrogen-bonded sheets, as shown in Figure 1a, progressively c-axis sheared as illustrated in Figure 8. The chain axis direction makes an angle of 43.5° with the lamellar surface normal and the triclinic unit cell contains two antiparallel molecules in the ac-plane. The calculated density is 1.15 g cm^{-3}; a value 4.5% greater than that calculated for the 5-amide nylon 6 α-structure. A structure refinement was undertaken and it was found that the lamellae stack to form a three-dimensional crystal by interdigitating gently (see Figure 2b inset). The intensities and positions of the refined model structure are overlaid as circles in Figure 4 to illustrate the goodness of fit (area is proportional to relative intensity) and this information, together with indexing, is listed in Table 1a. The intensity profile of the powder diffraction pattern of the refined structure is also compared with the experimental pattern in Figure 5. During the refinement process, due regard was taken of the relative intensities provided by the useful electron diffraction $hk0$ reciprocal net (see Figure 7a) since the intensity of these diffraction signals are sensitive to the setting angles of the chains within the [001] zone. The calculated weighted $hk0$ reciprocal net of the refined model is shown in Figure 7b; the relative intensities are proportional to the area of the filled circles (see also Table 1b).

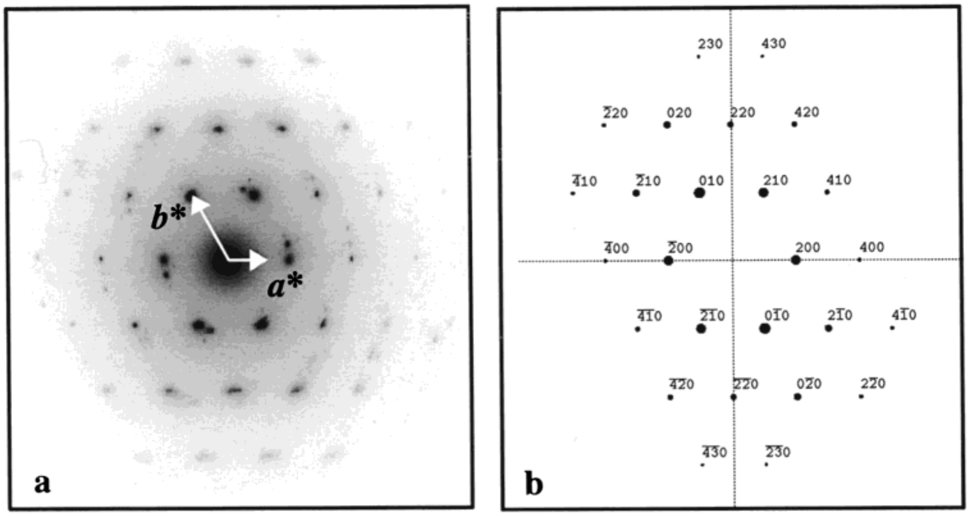

Figure 7. (a) Electron diffraction pattern obtained with the incident beam along the [001] zone axis. The spacings, indexing, and estimated relative intensities are given in Table 1b. This zone pattern has to be achieved by dramatic (43.5°) tilting of the specimen in the electron microscope and so it is difficult to get a perfect single zone without any satellite diffraction spots. Fortunately the weaker satellite spots to not interfere with the data for the [001] zone. (b) Computer-simulated [001] weighted reciprocal net. The circular spot diameter is proportional to the relative intensity.

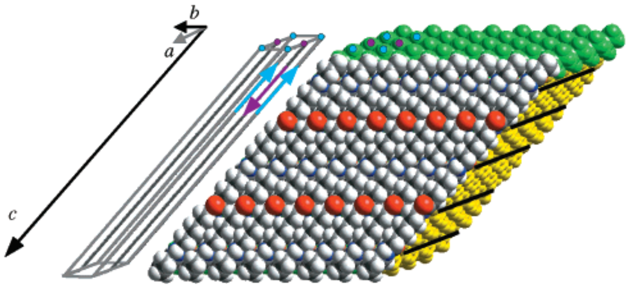

Figure 8. Oblique view in space-filling mode of an individual lamella of 5-amide nylon 6 monodisperse oligomers in the -structure. The chain direction is 43.5° to the lamellar normal (vertical). The two-molecule triclinic unit cell is shown to the left with arrows indicating the direction of individual molecules. The open and filled circles in the space-filling model highlight the antiparallel nature of the molecules in the hydrogen-bonded sheets (*ac*-planes). The five black lines show the positions of the amide layers that exist in the structure. The color code is the same as in Figure 1.

In this particular structure refinement there are few realistic variables. We have placed the chains in the all-trans conformation and hydrogen-bonded two molecules together in an antiparallel fashion to form the usual nylon 6 sheet. The resolution of the X-ray data ($\leq 1/0.2$ nm^{-1}) and error limits in the intensity measurements mean that the experimental data are insensitive to small variations in this basic two-molecule motif. The setting angle in the triclinic unit cell is determined by the [001] zone electron diffraction (Figure 7) data and the unit cell parameters have been optimized by comparison with both electron diffraction and X-ray diffraction data (Figures 7a and 4, respectively). Energy minimization procedures on the packed structure had little effect and the structure was confirmed to be stereochemically sound. In this triclinic structure there are no other degrees of freedom to consider.

General Discussion

Monodisperse 5-Amide Nylon 6. Our experiments concerned with the crystallization of monodisperse 5-amide nylon 6 oligomers from solution show that the individual molecules associate to form the usual nylon 6 hydrogen-bonded sheets (Figure 1a).[1,2] However, we have discovered that the type of *c*-axis intersheet shear, *recuperative* or *progressive,* for 5-amide nylon 6 oligomers can be influenced by the conditions of crystallization.[15,16] When the 5-amide oligomers were dissolved in trifluoroethanol and crystals prepared by adding the miscible nonsolvent 1,4-dioxane, the *c*-axis intersheet shear was recuperative,[15] producing smectic A-like layers with a periodicity of 4.79 nm (Figure 2a). Such a structure is similar to the α-structure[1,2] of nylon 6 polymer, although the actual value of the shear has been recently revised.[6] This method of crystallization is of course relatively crude, since control and reproducibility of crystallization rates is not straightforward. Since the intersheet shear is mainly controlled by van der Waals interactions[35] it is not surprising to discover other modes of orchestrated *c*-axis intershear, especially if more sophisticated control of the crystallization process is achieved. Thus, when the 5-amide oligomers are crystallized slowly (14 h) and isothermally from DMF solution at elevated temperature, 95 °C in this particular case, the crystals have pronounced progressive *c*-axis intersheet shear (≈ 49°), i.e., smectic C-like layers with a periodicity of 3.31 nm (Figure 2b). Recently, we have called this progressive intersheet form the λ-structure.[18]

Relationship with Polymeric Even Nylon α*-Structure. To our knowledge, a detailed structure for progressive *c*-axis intersheet in even nylons[36] was first described by Cojazzi et al. in 1985.[30] An oriented diffraction pattern was obtained from flakes prepared by allowing a solution of nylon 10 in formic acid to dry out and with the incident beam orthogonal to the flake surface normal (meridian). The spacing of the meridional 002 diffraction signal was found to be 22% less than the expected all-trans backbone value, suggesting that the chains were tilted by 39° to the flake normal. The diffraction data were indexed on a triclinic unit cell, and a detailed structure, called the α*-structure, with progressive *c*-axis shear was proposed.[30] However, in a subsequent paper[37] 2 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 *c*-axis intersheet shear (Δc) values occurring with particular probabilities and also with paracrystalline disorder in the stacking of the hydrogen-bonded sheets. Thus, it would appear[37] that the nylon 10 α*-structure is no longer so precisely defined in terms of progessive *c*-axis intersheet shear; it might be deemed to be a mixed crystalline phase. As far as we are concerned, the original nylon 10 α*-structure[30] and our proposed 5-amide nylon 6 λ-structure are conceptually the same.

Cojazzi et al.[38,30] also proposed that the α*-structure existed in crystals of nylons 8 and 12 prepared from formic acid solution, based on the presence in respective X-ray powder diffraction patterns of a 002 diffraction ring with reduced spacing (from expected all-trans value). In addition, an irreversible $\alpha^* \rightarrow \gamma$ phase transformation was found to occur on heating in nylons 8, 10, and 12.[38]

Nylon 6 λ-Structure. Although, to our knowledge, the nylon 6 λ-structure was first noticed in studies of 5-amide oligoamide crystals in our laboratory,[15] we have since discovered that it occurs in nylon 8[25] and nylon 6[26] chain-folded polymer crystals grown under isothermal conditions at elevated temperature from solution. Thus, the nylon λ-phase should not be considered to be an esoteric structure, occurring only in monodisperse oligoamides. Indeed, in a recent study,[6] where the sheet interaction energy was calculated as a function of *c*-axis intersheet shear for nylon 6, two energy minima were found, one of which correlated with the progressively sheared λ-structure. In unoriented X-ray diffraction patterns it is more difficult to delineate between the α- and λ-structures. Usually, the only clue is the occurrence of 00*l* diffraction signals, for example,[30,38] with spacings noticeably less than those expected from an all-trans conformation. Thus, in the past the λ-structure might not have been recognized if mixed crystalline phases were present.

The recent discovery of the λ-structure in both nylon 8[25] and nylon 6[26] chain-folded lamellae, coupled with the pioneering discoveries of Cojazzi and colleagues[30,37,38] would suggest that the crystallization of even nylons from the melt, or melt spun fibers, should be re-visited. For example, spinning or stretching under different conditions, or controlled annealing, perhaps with plasticizer present, might also reveal a nylon 6 λ-structure.

Conclusions

Crystals from monodisperse 5-amide nylon 6 oligomers have been solution-grown by isothermal crystallization at 95 °C in *N*,*N*-dimethylformamide and the crystalline structure determined. The collection of [001] zone axis data using electron diffraction together with X-ray diffraction data obtained has enabled a structure refinement to be undertaken. The diffraction signals index on a two-molecule triclinic unit cell with a *c*-dimension commensurate with the length of the molecules (4.60 nm). The 5-amide oligomers associated in an antiparallel fashion to form the usual nylon 6 hydrogen-bonded sheets (*ac*-plane) that stack with progressive shear in both *a*- and *c*-directions. These molecular layers stack with crystallographic register to generate a truly three-dimensional crystal with triclinic symmetry. This type of nylon 6 structure has been called the λ-structure to delineate it from the traditional nylon 6 monoclinic α-structure where hydrogen-bonded sheets stack with recuperative *c*-direction intersheet shear. Thus, the 5-amide nylon 6 λ-structure is not an esoteric structure found in monodisperse oligomer crystals; it has also been found in solution-grown, chain-folded crystals of nylon 6 and nylon 8 polymers and possibly in crystals of nylons 10 and 12. In some respects the nylon 6 triclinic λ-structure may be described as an architectural analogue to the nylon 6 6 triclinic α-structure, since the latter also exhibits progressive *c*-axis intersheet shear.

Acknowledgment. We are grateful to Drs. G. Brooke, S. Mohammed, and H. MacBride for synthesizing pure, monodisperse nylon 6 oligoamide samples, which made this research investigation possible, and to Mr. A. Winkel for his valuable help in obtaining the AFM pictures. We thank the Engineering and Physical Sciences Research Council, U.K., and The University of Bristol and the Overseas Research Council for a Ph.D. scholarship to P.S. We wish to record our thanks to (the late) Professor A. Keller and Professor H. Zahn (who pioneered the first synthesis of monodisperse nylon 6 oligoamides over 40 years ago) for their constant encouragement.

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(31) The *c*-value is less than the molecular length since the stacked lamellar layers interdigitate slightly, as shown in Figure 2b.

(32) In the case of the nylon 6 6 lamellar crystals[27] the 00*l* meridional diffraction signals emanated from the *c*-value of the sub-lattice, i.e., the crystallographic repeat within a lamella, since the stacked lamellae were not three-dimensional crystals.

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MA010305D