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Nature and Structure of Once-Folded Nylon 6 Monodisperse Oligoamides in Lamellar Crystals

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ABSTRACT: Lamellar crystals of the monodisperse 10-amide nylon 6 oligomer were prepared from solution. The crystal structure and morphology were studied using electron microscopy (diffraction and imaging) from individual lamella and X-ray diffraction data from sedimented oriented mats. The lamellar stacking periodicity (LSP) was found to be 4.77 nm, approximately half the length of the all-trans conformation (8.9 nm) for the 10-amide molecule. Under the rapid crystallization conditions used, the molecules fold at the midpoint to form a symmetric hairpin conformation. The straight stems are aligned orthogonal to the lamellar surface and crystallize in the nylon 6 polymeric α-structure, i.e., hydrogen-bonded sheets stacking via van der Waals interactions. A tight fold occurs in the central alkane segment, and the five amide units in each of the straight stems form intramolecular hydrogen bonds. The once-folded conformation and lamellar morphology of the 10-amide molecules are compared with the structure reported for once-folded 9-amide nylon 6 molecules, crystallized under the same conditions; these molecules fold via the central amide unit to form a symmetric hairpin conformation. Thus, the combined results, from both the once-folded 10-amide and 9-amide crystals, suggest that the requirement for all the amide units in the straight-stem pair to form intramolecular hydrogen bonds, together with fully saturated intermolecular hydrogen bonding in the crystalline straight stems, results in symmetric hairpin conformations; the nature of the fold, alkane or amide, is coupled to the conformation of the once-folded molecules. There are two possible alkane fold types (1 and 2) for the 10-amide molecule. Crystalline lamellae with mixed fold types have thicknesses at least 4% greater than the measured mean LSP value. Type 1 folded molecules are favored for energetic reasons and can only juxtaposition side by side; thus, within the apolar lamellae the hydrogen-bonded sheets are polar. The implications of this feature are discussed in terms of chain-folding in the nylon 6 polymer. The evidence shows that the nylon 6 molecule can form tight, adjacent re-entry folds via amide units or via alkane segments on crystallization.

Introduction

We have recently described and discussed the crystalline structures of particular nylon 6 monodisperse oligoamides.[1−3] These molecules were crystallized from solution, and their structures were determined using X-ray diffraction and electron microscopic imaging and diffraction. This work is part of a collaborative venture[4] with Dr. G. Brooke and his research group at the Chemistry Department, University of Durham, who have synthesized a series of precisely defined monodisperse oligoamides.[5−7] The molecules are terminated with short alkane segments[1,2,5−7] ($-C_2H_5$ at the carbonyl end and $-C_3H_7$ at the amine end) to minimize the disturbance to the crystalline lattice. The first four nylon 6 monodisperse oligoamides investigated contained 3, 5, 9, and 17 amide units with a length range of 3−15 nm. It was found that the 3-amide and 5-amide oligomers were too short to fold and crystallized in straight-stem conformations.[1,2] The next member in our series, the 9-amide oligomer (∼8 nm long), was found to crystallize in either a straight-stem conformation or a once-folded conformation depending on the crystallization rate.[2] Under relatively rapid crystallization conditions, the onset of folding was observed with the 9-amide oligomer taking up a once-folded conformation and crystallizing, in the form of thin lamellae (∼4 nm thick), in the classical nylon 6 α-structure.[8] The longer 17-amide oligomer crystallized in a twice-folded conformation.

Analysis of the X-ray and electron diffraction patterns from the once-folded 9-amide nylon 6 oligomer lamellar crystals showed that the molecules adopted a symmetric hairpin conformation with an amide unit at the apex of the fold,[2] as illustrated in Figure 1a. If the molecule were to fold via an alkane segment, then the hairpin conformation would be noticeably asymmetric as shown in Figure 1b, and this was ruled out by the experimental results.[2] These findings raise the following question: Does the 9-amide molecule place the central amide unit in the fold to keep the hairpin conformation symmetric and satisfy the straight-stem hydrogen bonding,[9] or is an amide fold the preferred method of folding in nylon 6? We might add that structural analysis of the twice-folded crystals of the 17-amide nylon 6 oligomer also favored amide folds, but only marginally so.[2] We know with certainty that chain-folded crystals of nylon 4,[10] nylon 4 6[11] and nylon 6 8[12] have amide folds. Thus, the occurrence of amide folds might suggest that alkane folds, via the 5-methylene segments, would be strained in chain-folded nylon 6 crystals. To our knowledge, the nature of the folds in chain-folded polymeric nylon 6 has yet to be established.

To investigate the folding dilemma highlighted by the once-folded 9-amide nylon 6 oligomer further, we have undertaken structural studies on the once-folded 10-amide nylon 6 oligomer crystallized under the same conditions as those of the once-folded 9-amide oligomer.[2] The midpoint of the 10-amide molecule will be an alkane segment, and it will be of interest to see how this particular oligomer behaves under the same crystallization conditions.

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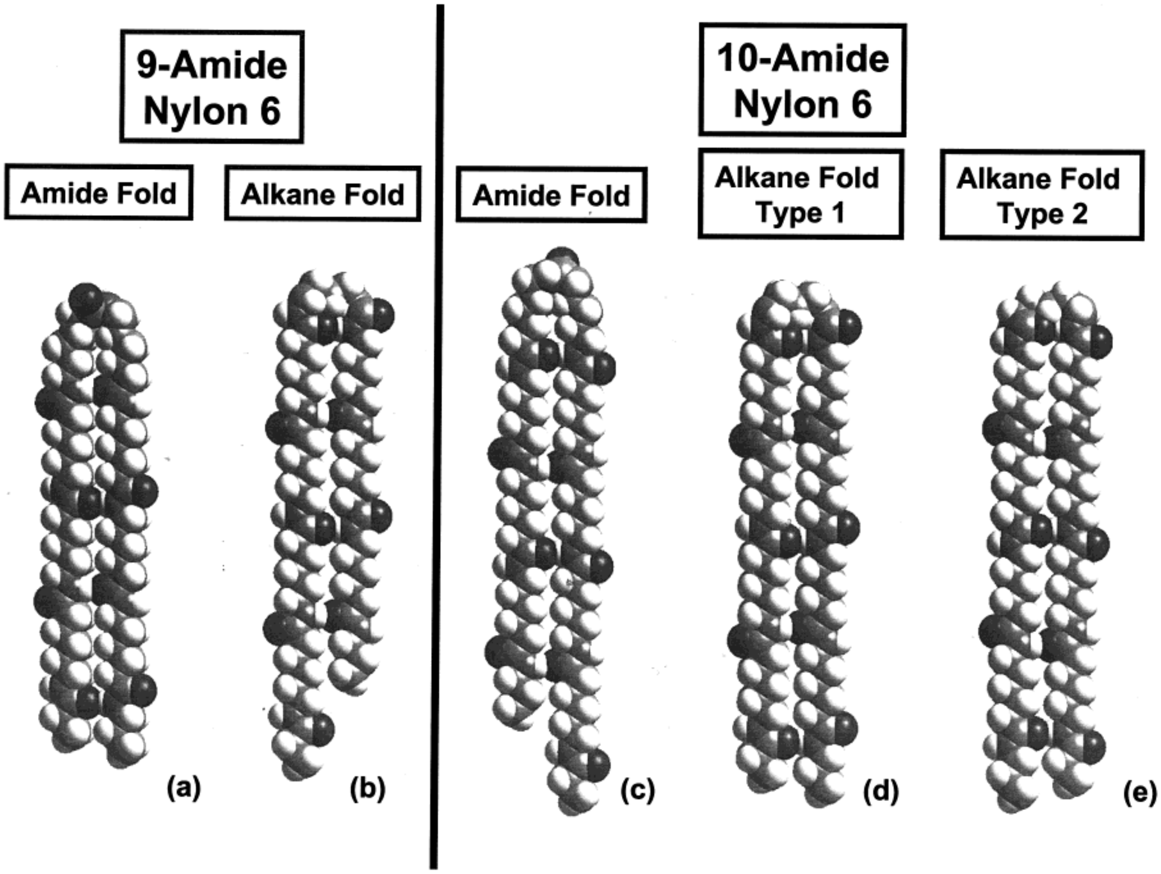

Figure 1. Computer-generated space-filling models of the once-folded nylon 6 oligomers. Models of once-folded 9-amide oligomer: (a) amide fold and (b) alkane fold. Models of once-folded 10-amide oligomer: (c) amide fold, (d) type 1 alkane fold (loose fold), and (e) type 2 alkane fold (tight fold). The straight-stem lengths of the alkane fold 9-amide oligomer (b) and amide fold 10-amide oligomer (c) are noticeably unequal, making the molecule too long in each case to form a lamellar structure commensurate with the experimentally determined LSP. Color code: carbon, gray; nitrogen, dark gray; oxygen, black; hydrogen, white.

The crystalline core of all the chain-folded lamellar structures in this investigation conform to the nylon 6 α-structure. To describe our crystallographic results efficiently, we judge that a summary of the essential features of the α-structure is usefully inserted at this point.

Nylon 6 α-Structure. The monoclinic α-structure, determined originally by Holmes et al.[8] from X-ray fiber diffraction patterns, is the most usual crystalline phase for nylon 6. The unit cell parameters are $a = 0.956$ nm, $b = 0.801$ nm, c (chain axis) = 1.724 nm, $\alpha = \beta = 90°$, and $\gamma = 112.5°$. The salient features are illustrated in Figure 2. Linear hydrogen bonds form between directionally opposite (antiparallel) chains to create hydrogen-bond sheets in the *ac*-plane (Figure 2a). These sheets stack, via van der Waals interactions, with alternating shear parallel to the *c*-axis[13] (Figure 2b) and progressive shear parallel to the *a*-axis (Figure 2c). Two prominent *hk*0 wide-angle diffraction signals help characterize the nylon 6 α-structure: the 200 signal at 0.44 nm (projected interchain/intrasheet spacing) and the 020 signal at 0.37 nm (intersheet spacing), respectively.

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 detailed characterization of this monodisperse oligoamide have already been reported by Brooke et al.,[7] but a brief summary is given in Table 1.

Crystal Preparation of the 10-amide Nylon 6 Oligomer. We used the fast crystallization procedure described previously[2] for preparing the once-folded 9-amide nylon 6 oligomer lamellar crystals. It was important to keep the conditions of crystallization as close as possible to those used[2] for the 9-amide nylon 6 oligomer crystals to answer the question posed in the Introduction. A solution of the 10-amide oligomer in trifluoroethanol (~1 mg/mL) was prepared, and lamellar crystals precipitated at room temperature by adding excess (volume ratio 10:1) of the miscible nonsolvent 1,4-dioxane.

Transmission Electron Microscopy. Drops of the crystal suspension were placed on carbon-coated transmission electron microscopy (TEM) grids, and the solvent was allowed to evaporate in a vacuum oven at room temperature. Some TEM samples were annealed at 140 °C. 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.

X-ray Diffraction. Oriented crystal mats suitable for X-ray diffraction were prepared by draining the crystal suspension through a 0.2 μm filter. As with the TEM samples, some of the mats were annealed at 140 °C. The wide-angle X-ray diffraction patterns were obtained at room temperature using nickel-filtered Cu Kα radiation of wavelength 0.1542 nm, from a Phillips sealed beam 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. Small-angle X-ray diffraction patterns were obtained using a point collimated, evacuated Rigaku-Denki film camera, on an Elliot GX-21 rotating anode generator operating at 40 kV and 40 mA. The beam was directed

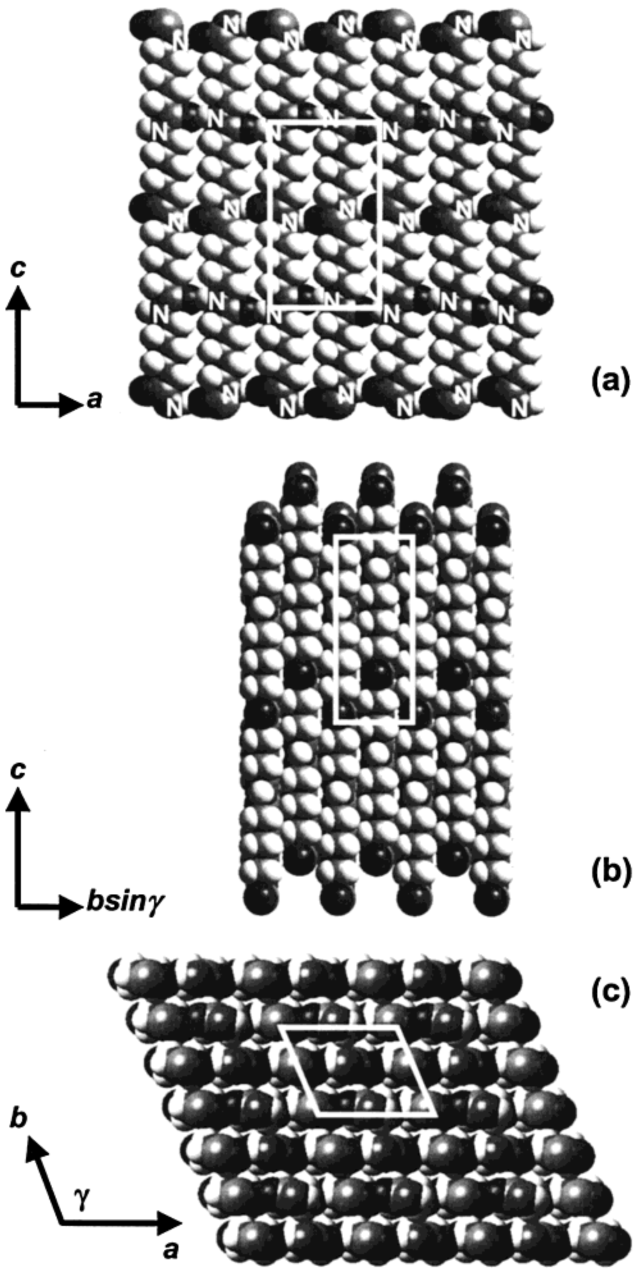

Figure 2. Three views of a space-filling model of the α-structure nylon 6,[8] with the projected monoclinic unit cell illustrated as a white box. (a) Projection of the hydrogen-bonded sheet, orthogonal to the sheet surface; note the alternating *c*-axis shear of the hydrogen-bonded amide units. (b) View parallel to the hydrogen-bonded sheet shown in (a); note the alternating *c*-axis shear between successive sheets which weakens the 00*l* diffraction signals. The sheets also progressively shear parallel to the *a*-axis. (c) View parallel to the chain (*c*) axis. The color code is the same as for Figure 1, and the nitrogen atoms are labeled N.

parallel to the surface of the mat, and the mat normal was vertical.

Model Building and Analyses of Structure. The software package Cerius2, version 3.5 (MSI), was used in the structural modeling. Molecular dynamics (MD) and energy minimization (EMin) simulations were performed utilizing the CVFF force field. In the computer-simulated X-ray diffraction patterns, the degree of arcing and intensity were chosen to match the experimental X-ray diffraction patterns as closely as possible. It will become evident later that the different fold geometries for the once-folded 10-amide molecule will have an important role to play in the structure of the crystalline lamellae. Thus, the stereochemistry of the fold needs to be examined in detail.

Modeling the Folds. In the first instance, the nylon 6 α-structure[8] (see Figure 2) was generated. Chain-folded hairpin models[14] of the 10-amide nylon 6 oligomer were then constructed using all possible alkane fold types on the basis of the straight-stem pair and hydrogen bonding in a manner similar to that of the hydrogen-bonded sheets shown in Figure 2a. To check how the folding affects the straight-stem conformation in the vicinity of the fold, two types of molecular dynamic simulations were performed. First, the whole straight-stem pair was constrained and the fold energy minimized. The atoms that were allowed to move are enclosed by the boxes shown in Figure 3a,b. The rationale was to find the lowest energy conformation for the alkane fold, assuming that all the intrachain hydrogen bonds in the straight-stem pair were fully saturated. In an attempt to ensure that the global minimum is found in the MD simulations, the simulation temperature was raised to 1000 °C in the first instance; this step was followed by extensive MD runs performed at 500 °C and finally at 20 °C. At this stage the fold energy was minimized. In the next step, the effects of the strains in the different types of folds on the straight-stem pair were examined by allowing a greater part (atoms within the boxes shown in Figure 3c,d) of the folded molecule to relax in the simulation. MD and EMin simulations were performed in a manner similar to that already described above.

Results and Discussion

Electron Microscopy. The transmission electron micrographs, shown in Figure 4a,b, reveal that 10-amide and 9-amide nylon 6 oligomers form ribbonlike lamellae, although the 9-amide lamellae are broader. The overall morphology is reminiscent of that of the chain-folded nylon 6 polymer α-structure lamellae (Figure 4c) where the hydrogen bonding occurs in the [100] direction, i.e., parallel to the length of the ribbonlike crystals.

The electron diffraction pattern from lamellae of the 10-amide oligomer, obtained with the electron beam orthogonal to a lamellar surface, is shown in Figure 4d. The interplanar spacings are tabulated in Table 2a and index as *hk*0 diffraction signals (see Table 2b for unit cell parameters). Thus, the straight-stem chain segments are orthogonal to the lamellar surface. There is twinning about the *b**-axis (intersheet direction), a feature commonly observed in even nylon α-structure lamellae. The twinning has the advantage of allowing the relative azimuthal orientation of the lamella to be directly coupled to the *a***b** reciprocal net.

X-ray Diffraction. The wide-angle X-ray diffraction pattern from a mat of sedimented lamellae, taken with the X-ray beam parallel to the mat surface and with the mat normal vertical, is shown in Figure 5, and the interplanar spacings are given in Table 2a. The diffraction signals index on a monoclinic unit cell with parameters $a = 0.968$ nm, $b = 0.826$ nm, c (chain axis) $= 4.77$ nm, $\alpha = \beta = 90°$, and $\gamma = 114.0°$ (Table 2b). These values differ by up to a few percent[17] from the values reported by Holmes et al.[8] for the nylon 6 α-structure in crystalline fibers (see Table 2b). The structural repeat (sublattice *c*-value) along the all-trans chain is 1.724 nm, the same as that of Holmes et al.;[8] however, in the 10-amide nylon 6 structure, the sampling in the *c*-direction is different.[18] The occurrence of the 0.44 nm (200) and 0.37 nm (020/$\bar{2}20$) arcs on the equator confirms that the lamellae have crystallized in the nylon 6 α-structure and that the straight stems are normal to the lamellar surface. The small-angle X-ray diffraction pattern is shown as an inset in Figure 5. A strong meridional arc

Table 1. Characterization Information for the 9-Amide and 10-Amide Nylon 6 Oligomers

chemical analysis[5−7]	9-amide nylon 6 oligomer, $C_{54}H_{101}N_9O_9$		10-amide nylon 6 oligomer, $C_{60}H_{112}N_{10}O_{10}$	
	found (%)	required (%)	found (%)	required (%)
carbon	63.43	63.56	63.37	63.57
hydrogen	10.15	9.98	10.11	9.96
nitrogen	12.45	12.35	12.32	12.36
melting temperature[a] of crystalline mats (°C)	210.3		212.8	

[a] This work, as measured using differential scanning calorimetry.

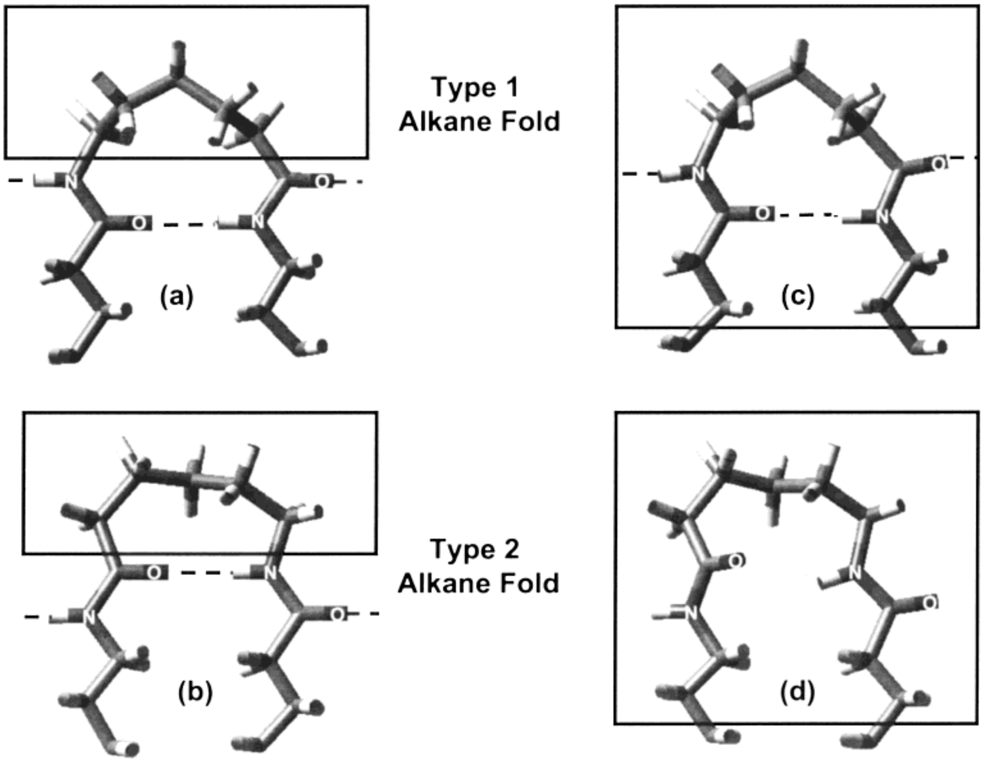

Figure 3. Energy-minimized nylon 6 alkane folds for the segments within the box for each model. Left-hand side: fold minimized with the straight stems constrained. (a) Type 1 alkane fold. (b) Type 2 alkane fold. The hydrogen bond adjacent to a type 1 fold (a) is between different molecules (intermolecular hydrogen bond), whereas the hydrogen bond adjacent to a type 2 fold is between an N—H group and a C═O group within the same molecule (intramolecular hydrogen bond). Right-hand side: alkane fold minimized with the fold, adjacent amide units, and alkane segments unconstrained. (c) Type 1 alkane fold. (d) Type 2 alkane fold. Type 1 fold minimization resulted in relatively unstrained chain folds and hydrogen bonds. Conversely type 2 alkane fold minimization resulted in either a strained fold (b) or a broken hydrogen bond (d). Color code as in Figure 1; hydrogen bonds are indicated by dashed lines.

is observed at a spacing of 4.77 nm, together with its second order (the latter can be seen close to the beam stop in the wide-angle X-ray diffraction pattern; Figure 5). The value of 4.77 ± 0.05 nm for the lamellar stacking periodicity (LSP) confirms that the 10-amide oligomer is once-folded, since the length of the molecule in the all-trans conformation is 8.9 nm.

Structural Modeling of the Once-Folded 10-Amide Oligomer. Figures 1c−e display three stereochemically possible once-folded conformations for the 10-amide oligomer. In Figure 1c the molecule is folded asymmetrically, i.e., with an amide fold. The outer-limit length is 4.94 nm, and if allowance is made for the estimated 0.2 nm *c*-axis intersheet shift[13] on forming crystals (see Figure 2b), the lamellar outer-limit thickness increases to 5.14 nm; both these values are in excess of the measured LSP value of 4.77 ±0.05 nm. The tail on the right-hand side of the asymmetric amide-fold conformation (Figure 1c) could, of course, be bent around, as long as it is confined within the *ac*-sheet. However, the outer-limit thickness would still exceed the measured LSP value, and so we can rule out this asymmetric amide-fold conformation in these lamellar crystals. Furthermore, the asymmetric, amide-fold conformation would not be able to saturate all its straight-stem hydrogen bonds. Thus, we are left with only symmetrically folded molecules, with alkane folds, to consider seriously for the 10-amide oligomer. There are two conformations to consider, with different fold geometries as shown in Figure 1d,e. In each case, the outer-limit length is 4.54 nm; this rises to 4.74 nm if allowance is made for the estimated 0.2 nm *c*-axis intersheet shift[13] and matches the measured LSP of 4.77 ± 0.05 nm.

Detailed Consideration of the Alkane Folds. The two possible alkane folds to consider for the 10-amide oligomer, when the folded molecules are embedded in the nylon 6 α-structure hydrogen-bonded sheets, are shown in Figures 1d,e and 3a,b.

(1) Type 1 Alkane Folds. In these folds the interchain hydrogen bonds closest to the fold surface are *intermolecular* hydrogen bonds, i.e., between neighboring 10-amide nylon 6 molecules (Figures 1d and 3a).

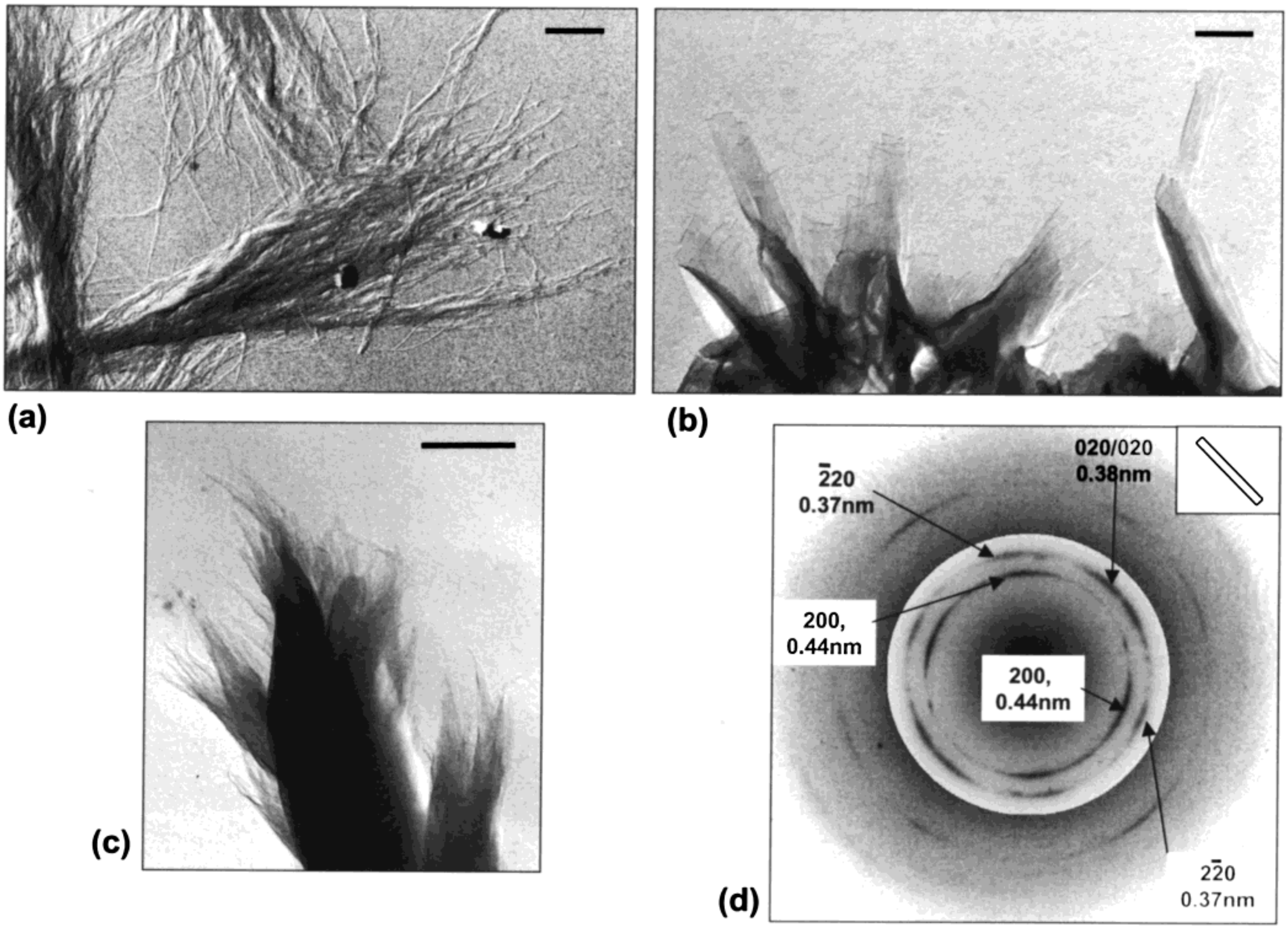

Figure 4. Transmission electron micrographs (scale bars 1 μm) of nylon 6 lamellar crystals, shadowed with Pt/Pd, of (a) a 10-amide oligomer and (b) a 9-amide oligomer, both obtained by rapid crystallization from solution in trifluoroethanol by the addition of dioxane.[2] (c) Chain-folded nylon 6 polymer α-structure lamellar crystals obtained by thermal crystallization at 115 °C from a 0.003% solution of 1,4-butanediol (seeding temperature 190 °C).[15,2] (d) Electron diffraction pattern obtained from a lamellar crystal of the 10-amide oligomer with the electron beam orthogonal to the lamellar surface. The diffraction pattern is characteristic of twinned nylon 6 crystals.[16] The diffraction signals derive from two separate lamellae, differentiated by the color of the spacing and index labels (gray or black). Single-crystal diffraction patterns were never observed. The schematic lamella shown in the inset is oriented with the diffraction pattern, allowing us to assign the diffraction signals perpendicular to this lamella as the 020 intersheet diffraction signals of both twinned lamellae. The observed electron diffraction spacings are listed in Table 2a.

Table 2. (a) Measured and Calculated Diffraction Spacings for 10-Amide Nylon 6 Lamellae

index	electron diffraction (nm)	X-ray diffraction (nm)	calcd (nm)
200	0.442 ± 0.005	0.444 ± 0.005	0.442
020	0.376 ± 0.005	0.376 ± 0.005	0.377
040	0.189 ± 0.005		0.189
$\bar{2}20$	0.371 ± 0.005	0.376 ± 0.005	0.371
$4\bar{2}0$	0.239 ± 0.005		0.237
220	0.243 ± 0.005		0.242
LSP 001		4.77 ± 0.05	4.770
LSP 002		2.38 ± 0.02	2.385

(b) Unit Cell Parameters for 10-Amide Nylon 6 Lamellae and Comparison with Previously Published Values Obtained from Crystalline Fibers[8]

nylon 6	*a* (±0.005) (nm)	*b* (±0.005) (nm)	*c* (±0.005) (nm)	α (±0.5) (deg)	*β* (±0.5) (deg)	*γ* (±0.5) (deg)
10-amide	0.968	0.826	4.77[a] ± 0.05	90	90	114.0
fibers[8]	0.956	0.801	1.724	90	90	112.5

[a] The *c*-sublattice repeat distance for the 10-amide nylon 6 is 1.724 nm.

(2) Type 2 Alkane Folds. In this case the hydrogen bonds closest to the fold surface are *intramolecular* hydrogen bonds, i.e., between C═O and N─H groups within the same 10-amide nylon 6 molecule (Figures 1e and 3b).

The fold conformations were studied using the molecular modeling techniques already described. The final predicted conformations for type 1 and 2 alkane folds are shown in Figure 3. Folds optimized with the whole of the straight stems constrained are shown in Figure 3a,b. Fold conformations where the adjacent amide units and a portion of the alkane segments adjacent to the fold were also optimized are shown in Figure 3c,d. In type 2 alkane folds, the constraint of the amide units

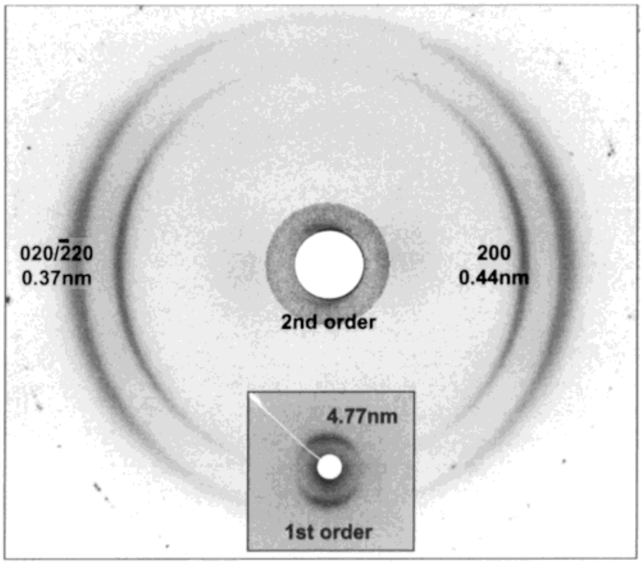

Figure 5. Wide-angle and small-angle (inset) X-ray diffraction patterns obtained from sedimented oriented mats of 10-amide nylon 6. The mat normal is vertical, and the X-ray beam is directed parallel to the mat surface. In the small-angle pattern there is a single meridional diffraction signal of spacing 4.77 ± 0.05 nm (plus second order), corresponding to the LSP. In the wide-angle pattern there are two prominent interchain diffraction signals: an inner equatorial diffraction signal at spacing 0.444 nm (200) and an outer, broader, equatorial diffraction signal at spacing 0.376 nm (combined 020 and $\bar{2}$20). These equatorial diffraction signals are characteristic of the nylon 6 α-structure. In addition, the second-order small-angle meridional arcs of the LSP (2.38 nm spacing) are also visible on either side of the beam stop. We observe an off-meridional diffraction signal at spacing 0.62 nm which emanates from the 1/4.77 nm^{-1} periodic *c*-direction sampling. The detailed nature of this diffraction feature will be published in another paper from this laboratory concerning the nylon 6 polymer and oligomers.

prior to minimization leads to bond angle and torsion angle values within the fold displaced from equilibrium. Conversely, type 1 alkane folds, minimized with the straight stems constrained, are close to equilibrium values. These models were further examined by performing optimization on the fold and part of the straight stems as illustrated by the boxed regions in Figure 3c,d. Relaxing these constraints should lower the conformational energy, but amide unit motion might result in the loss of hydrogen bonds. For type 1 alkane folds, only small changes in the positions of amide units occurred (compare Figure 3a,c) and all hydrogen bonds were preserved. For type 2 alkane folds, the large conformational energy of the fold, when optimized without constraining the adjacent amide units and associated alkane segments (compare Figure 3b,d), is now transferred into significant rotation of the amide units. As a consequence, hydrogen bonds close to the fold are broken. The total energy for type 1 folds, including the conformational components, van der Waals and Coulombic interactions, and hydrogen bonding is 54 kJ/mol less than that for type 2 folds; thus, type 1 alkane folds are preferred. For type 2 alkane folds, the 5-methylene alkane segment is too short to form an unstrained fold.

Arrangement of the Once-Folded 10-Amide Molecules in the Nylon 6 Hydrogen-Bonded Sheets. It turns out that there are severe restrictions on how these symmetric hairpin alkane-fold molecules can juxtaposition within the nylon 6 α-structure hydrogen-bonded sheets. Type 1 alkane folded molecules can only form the appropriate hydrogen-bonded sheet arrangement if they associate in a straightforward side by side repetitive manner; up and down associations and/or *c*-axis π-rotations between adjacent molecules are not possible if the hydrogen-bonded sheet structure is to be maintained.[19] Thus, for type 1 folded molecules the sheets are polar, with *all* the alkane folds at one edge only. The same feature is true for type 2 alkane folded molecules. The only way we are able to construct a hydrogen-bonded sheet with folds on both edges and with a thickness commensurate with the diffraction data is to have mixed alkane-fold geometries, i.e., both type 1 and type 2 alkane folded molecules within a sheet, as illustrated in Figure 6. It transpires that molecules with different alkane-fold types can only associate in the nylon 6 hydrogen-bonded sheet scheme if they are aligned antiparallel, e.g., the extreme two molecules on the left-hand side in Figure 6. Molecules with similar alkane-fold types can only associate in the nylon 6 hydrogen-bonded sheet scheme if they are aligned parallel, e.g., either the second or third pair of molecules, from both left-hand and right-hand sides, in Figure 6. It should be noted that the sheet still has a degree of polarity since the 10-amide molecules are arranged, alternating or random, with one sheet edge wholly decorated with type 1 alkane folds and the other with type 2. Furthermore, should one of these two alkane-fold types be stereochemically unfavorable, then the sheet will be decorated with folds on one edge only, as already discussed. Of course, when the sheets stack to form a crystalline lamella (see Figure 2b), there is no a priori condition regarding their relative polarity with respect to the lamellar normal.

Molecular Arrangement within a Crystalline Lamella and Consequences for Lamellar Stacking. Consideration is now given to the stacking of the three different hydrogen-bonded sheet structures to see which, if any, is the most favorable, or indeed, if it is possible to rule out any models. We have undertaken this comparison in three steps.

(1) Sheets with Mixed Type 1 and Type 2 Alkane Folds (Figure 6). The outer-limit sheet width is 4.75 nm, which rises to 4.95 nm if allowance is made for the estimated (minimum) 0.2 nm *c*-axis intersheet shift.[13] This value is in excess of the measured LSP value of 4.77 ± 0.05 nm and is therefore not favored. In addition, the concept of mixed energy folds is not particularly appealing.

(2) Delineation between Sheets Incorporating Molecules with Either Type 1 or Type 2 Alkane Folds. Lamellar structures composed of either of these sheets, irrespective of the sheet stacking mode (polar or apolar), have thicknesses commensurate with the measured LSP of 4.77 nm. We can only delineate between the two models on the basis of fold energy calculations. On these comparative energy criteria, sheets with the lower energy type 1 folds are preferred.

(3) Polar or Apolar (Alternating or Random) Stacking of the Sheets? Within the experimental limits of the measured LSP, we cannot categorically rule out any of these three models. If polar stacking occurred, the lamellae would also be polar and there is the likelihood that a proportion, if not all, of the lamellae would stack with like faces together to generate bilamellar structures. Such bilamellar models would demand LSP values in the range 9−10 nm and can be ruled out since we know that the 4.77 nm spacing is

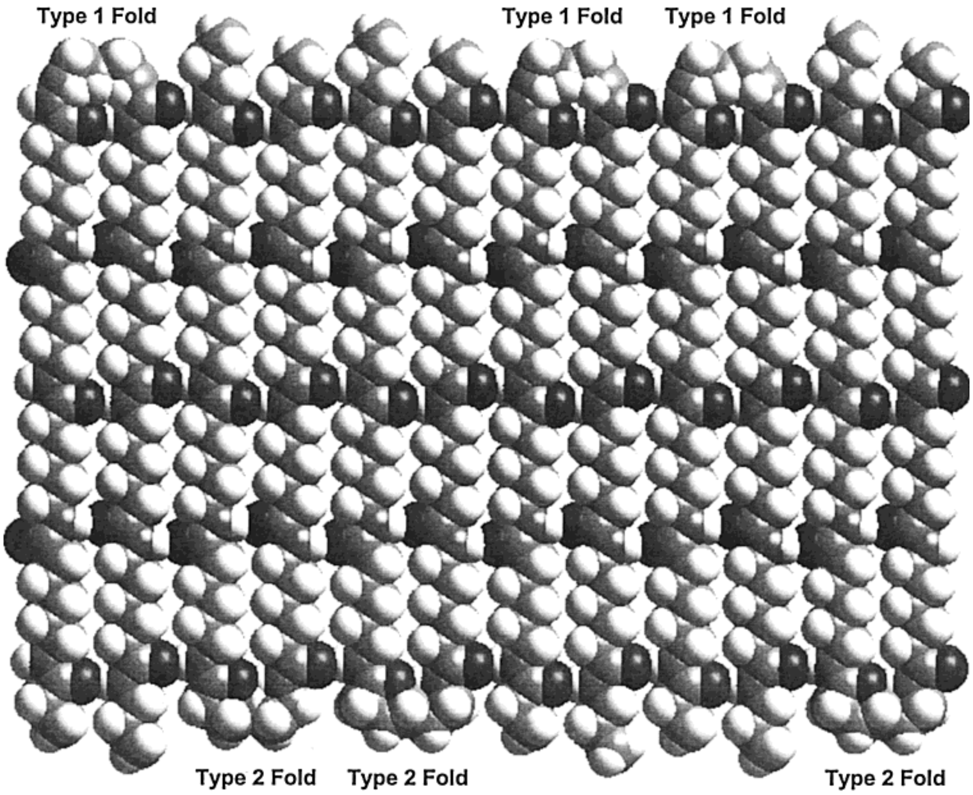

Figure 6. View (*ac*-plane) of a chain-folded hydrogen-bonded sheet for 10-amide nylon 6 molecules with alkane folds; color code as in Figure 1. To saturate all available straight-stem hydrogen bonds, the alkane folds must segregate into the top (type 1) and bottom (type 2) fold edges, i.e., generating a polar sheet.

the first order of the LSP. The apolar (alternating) sheet stacking gives rise to the thinnest lamellar crystals, with the lowest surface energy, and the closest match to the measured LSP value; the lamellae stack together comfortably, with an interlamellar spacing marginally less than LSP, as shown in Figure 7. There are other reasons for favoring this structure,[20] and some of these will be outlined in the following sections.

General Discussion

Comparison with the Once-Folded 9-Amide Nylon 6 Oligomer. The specific reason for studying the 10-amide nylon 6 oligomer in a once-folded conformation was to compare it with the behavior of the related 9-amide nylon 6 oligomer, which crystallized in a symmetric hairpin conformation with the central amide unit in the tight fold.[2] This raised the following question: Is it the symmetry of the hairpin conformation, or is it the stereochemistry of the fold, that dominates in the folding behavior of these molecules?

Structure analysis of the once-folded, 10-amide oligomer lamellar crystals shows that the molecules adopt a symmetric hairpin conformation by folding at the midpoint. Because of the even number of amide units in this molecule, the fold has to be via an alkane segment (alkane type 1 fold preferred; see Figure 1d). It is of interest to compare this conformation to the once-folded 9-amide nylon 6 oligomer, which also adopted a symmetric hairpin conformation by folding at the midpoint.[2] The fold in this 9-amide case is, of course, an amide fold, as a consequence of the odd number of amide units in the molecule. The new results on the 10-amide molecule support the contention that the symmetry of the hairpin conformation is the dominant factor in the crystallization of these molecules. Indeed, the choice of the 10-amide nylon 6 oligomer was part of our strategy to test this very feature.

It is perhaps worth remembering that the crystallization conditions chosen (low concentration and relatively fast crystallization)[21] will encourage intramolecular hydrogen bonding in the first instance since the entropic penalty for an individual molecule of this length (~9 nm) to remain straight in solution is substantial. Thus, once intramolecular hydrogen bonds form, as a consequence of the deterioration in solution solubility (addition of a miscible poor solvent), they can only be maximized if all the straight-stem amide units form linear hydrogen bonds. For the nylon 6 α-structure the hydrogen bonding is between antiparallel chains only, and the straight-stem pairs in these once-folded oligomers conform to this exacting condition. We conclude that the nature and geometry of the fold in both these once-folded nylon 6 molecules are wholly subservient to the intramolecular straight-stem interactions.

Implications for Chain-Folding in Nylon 6 Polymer. The results and discussions so far suggest that both amide and alkane folds would be possible in chain-folded nylon 6 polymer crystals. Considering all of the above, we are able to make some further inferences concerning the alkane folds in chain-folded nylon 6 polymer crystals. It is known from studies on nylon 6 6 chain-folded crystals, for example,[22] that the lamellar thickness can be changed in quantized steps by altering the crystallization conditions. Thus, in nylon 6, should the crystallization conditions require an even number of amide units per straight stem segment, then, for alkane folding to be maintained, both type 1 and type 2 alkane folds will be required.[23] If type 2 alkane folds are unfavorable for nylon 6, then crystallization may only proceed by replacing any type 2 alkane folds with

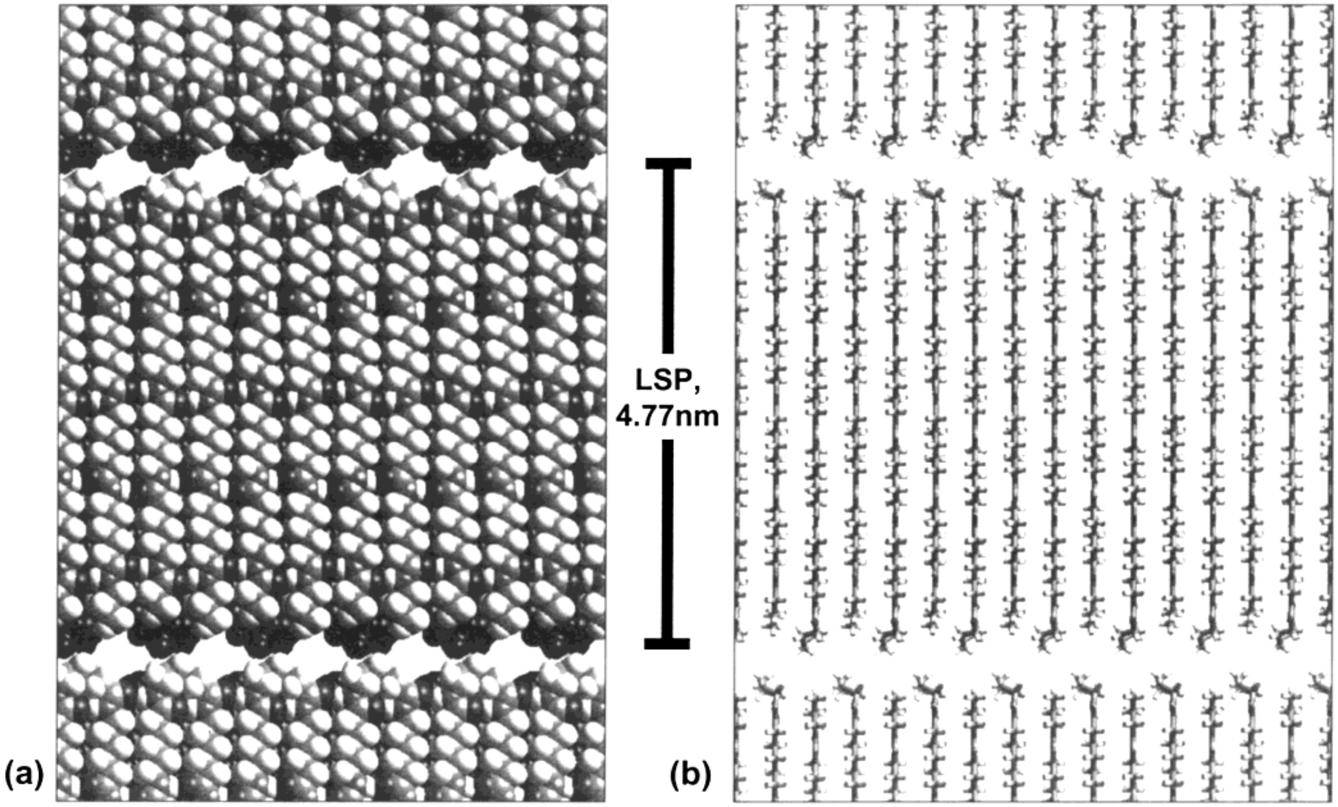

Figure 7. Views of the preferred lamellar structure for a once-folded 10-amide oligomer in the nylon 6 α-structure: (a) orthogonal to the *ac*-plane (*c*-axis vertical) with space-filling modeling; (b) parallel to the *a*-axis (*c*-axis vertical) with stick modeling. Each polar sheet contains the energetically favorable type 1 alkane folds only with five amide units per straight-stem segment. The sheets stack with alternating polarity so that the alkane folds decorate each lamellar surface equally, resulting in an apolar crystalline lamellar structure. The lamellae stack with random azimuthal orientation about the *c*-axis to generate the observed 4.77 nm LSP. Color code as in Figure 1.

amide folds. Conversely, should an odd number of amide units per straight-stem segment be required, then type 1 alkane folding may occur on either edge of a chain-folded sheet.

Conclusions

Under the crystallization conditions used, monodisperse 10-amide nylon 6 oligomers crystallize in the nylon 6 polymeric α-structure, i.e., hydrogen-bonded sheets stacking via van der Waals interactions. It has been established, using a combination of X-ray diffraction on sedimented oriented mats and electron microscopy (diffraction and imaging) on individual lamella, that the lamellar thickness is approximately half the length of the molecules. The evidence shows that the molecular conformation is a once-folded symmetric hairpin with the straight stems aligned orthogonal to the lamellar surface. A tight fold occurs in the central alkane segment, and the five amide units in each of the straight stems form intramolecular hydrogen bonds. Thus, it would appear, from the combined results of the once-folded 10- and 9-amide crystals, that the symmetry of the hairpin is paramount; i.e., the requirement that all the amide units in the straight-stem pair form intramolecular hydrogen bonds and, further, the requirement that hydrogen bonds in the sheets be fully saturated dictate the final conformation in these nylon 6 oligomers. The nature of the fold, amide or alkane, appears to be a consequence of these requirements. However, the results do show that nylon 6 can fold with either amide units in the fold, like the polypeptides, or with alkane segments in the fold, like polyethylene.

There are two possible types of alkane folds (1 and 2) for the 10-amide nylon 6 oligomer, and the one with lower energy (type 1) is favored. It is found that there are severe restrictions on the ways in which the 10-amide nylon 6 hairpin molecules can hydrogen bond into nylon 6 α-structure sheets, and for these sheets to stack together. For example, type 1 folded molecules can only hydrogen bond together by jutapositioning side by side to form a polar sheet, i.e., with all the folds on one edge of the sheet. The experimental data place limits on the lamellar thickness, and these, together with stereochemical restrictions, support a structure (Figure 7) with polar sheets stacking with alternating polarity to create apolar lamellae with surfaces equally decorated with type 1 folds.

This work highlights the importance of studying monodisperse nylon molecules if we wish to understand, and accurately predict, the behavior of more complex polydisperse nylon polymers, particularly with regard to folding and its consequences on crystallization and crystal structure and properties.

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(4) The chemical synthesis of these high-pedigree monodisperse oligoamides by Dr. G. Brooke and his colleagues at the Chemistry Department, University of Durham, Durham, U.K., was in response to a request by Professor E. Atkins, at the Physics Department, University of Bristol, for high-fidelity oligo- and polyamides, which were considered essential in the study of fundamental aspects of polymer physics, in this case the subtle interplay among van der Waals interactions, hydrogen bonding, chain-folding, and crystallization. We appreciate the foresight of the Engineering and Physical Sciences Research Council, U.K., in supporting this collaborative venture.

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(9) In relation to the once-folded 9-amide oligomer. If the amide unit is not in the fold (see Figure 1b and ref 2), then, because of the unequal lengths of the straight-stem pair, one amide unit is not utilized, not even when these once-folded molecules crystallize into lamellae. Therefore, only eight amide units form intramolecular hydrogen bonds. The lamellae would also have a larger surface energy than if the amide units were in the folds. With the amide unit in the fold (see Figure 1a and ref 2), all eight amide units in the straight-stem pair form intramolecular hydrogen bonds. Furthermore, they also form intermolecular hydrogen bonds on crystallization and create lamellae with lower surface energy. Thus, having amide units in the folds does not reduce stabilization of the crystalline lamellae.

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(13) The relative c-axis shift (in the ac-plane) of the central sheet of the nylon 6 α-structure[8] suppresses the intensities of the $00l$ diffraction signals, and usually only a relatively weak 002 signal is seen. Holmes et al.[8] chose a value of $3c/14$ ($=0.37$ nm) for this relative c-axis shift on the basis of the value reported for nylon 6 6 (Bunn, C. W.; Garner, E. V. *Proc. R. Soc. A* **1947**, *189*, 39). Since the hydrogen-bonded sheet structures in nylons 6 6 and 6 are different, this c-axis shift value should be treated with caution. Reasons based on stereochemistry were given by Holmes et al.[8] for this shift not to exceed $3c/14$, but none for it to be less than $3c/14$. Indeed, Holmes et al.[8] also reported on a crystalline polymorph with zero c-axis shift of the central sheet, which they called the β-structure (although they also changed the hydrogen-bonded sheet structure[8]). The shift was crudely estimated from the relative intensity of the 002 diffraction signal. There is no doubt that in the 10-amide nylon 6 lamellar structure there is some central sheet c-axis shift, but not as much as 0.37 nm. We have calculated the relative intensities as a function of c-axis shift and find that a range between 0.2 and 0.3 nm is consistent with the experimental results. We have chosen the value of 0.2 nm as the value that gives the best match with the measured 4.77 nm LSP value (see the end of note 18 also). All structures modeled on a 0.2 nm c-axis shift with minimum LSP greater than 4.77 nm would be even less satisfactory if the c-axis shift were greater.

(14) The asymmetrically folded 10-amide oligomer (Figure 1c), with an amide fold, was found to be too long to fit into the lamellar crystal (see the structural modeling section in the Results and Discussion), and so detailed modeling of the fold was not necessary.

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(17) Compared with those of Holmes et al.,[8] the a and γ values of the 10-amide nylon 6 unit cell differ by ~1% and are closer to those reported for the once-folded 9-amide and twice-folded 17-amide oligomer crystalline structures.[2] The 10-amide nylon 6 b value is ~3% greater than that reported for fibers.[8] This is not surprising when the effect of folding is considered (see, for example, Figure 7b). These variations in parameters are all within the perceived definition of a nylon 6 α-structure as determined by Salem, D. R.; Weigmann. H. D. *Polym. Commun.* **1989**, *30*, 336.

(18) The 10-amide nylon 6 lamellar crystals stack with a c-axis (normal to the lamellar surface) periodicity of 4.77 nm and therefore only contain two whole stereochemical repeats within each lamella. Thus, the c-direction sampling is not the same as in fibers; in this case the coherent length is large in the chain direction (c-axis). The salient features of this phenomenon where given by Atkins, E. D. T.; Keller, A.; Sadler, D. M. *J. Polym. Sci., Part A: Polym. Chem.* **1972,** *2*, 863 when studying chain-folded crystals of nylon 6 6. A paper focusing on the detailed comparisons of the X-ray diffraction patterns from the 10-amide and other oligomers of nylon 6 with the α-structure[8] deduced from nylon fibers will be submitted separately.

(19) Up and down association between molecules is possible if large c-axis relative displacements between molecules are considered. However, the outer-limit lamellar thickness of these structures is in excess of 5.5 nm, and therefore such models can be dismissed.

(20) It is also possible for the polar hydrogen-bonded sheets to stack with alternating polarity but with the chain folds embedded within a lamella. Such a structure is not favored since the calculated LSP value exceeds the measured value. Furthermore, the buried fold creates stereochemical clashes in the direction orthogonal to the ac-planes.

(21) If the crystallization rates are slower, there is a tendency for nylon 6 oligomers of this size to crystallize in a nonfolded conformation as reported, for example, for the 9-amide nylon 6 oligomer.[2]

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(23) Since the fold distribution is different between hydrogen-bonded sheets of the once-folded nylon 6 oligomers and nylon 6 polymer, the requirements for type 1 folding on both sheet edges also change.

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