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Chain-folding and structures in nylon 6 oligoamide lamellar crystals

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A series of carefully selected monodisperse nylon 6 oligomers, terminated with short alkane segments, have been crystallised from solution. This contribution contains an overview of the folding and structures in nylon oligomer crystals, recorded at room temperature, using transmission electron microscopy and X-ray diffraction (both wide- and small-angle); together with important conclusions drawn from studies of these molecules. The work is set in the context of much earlier studies by Professors Zahn and Keller and their co-workers. The oligomers contained 2, 3, 5, 9, 10 and 17 amide units, with a length range of 2 nm to 15 nm. The shorter oligomers (with 2, 3 and 5 amide units) crystallised with non-folded chains; the longer 9- and 10-amide oligomers were once-folded, following rapid crystallisation; whilst the 17-amide oligomer was found to fold twice. Thus chain folding sets in on rapid crystallisation, with the 9-amide molecule (length ∼8 nm). Studies of the once folded 9- and 10-amide oligomers show that both amide unit and alkane segment folds occur, in this instant the symmetry of the hairpin and the requirement for saturated hydrogen bonds between straight stems are the controlling factors; the nature of the fold is subservient. This shows that nylon 6 chains can stereochemically accommodate either alkane or amide folds. All the folded molecules were observed in the nylon 6 α-structure, where chains are antiparallel within the hydrogen-bonded sheets, which have alternating chain (c)-axis shear alternately. In the shorter oligoamides (2-, 3- and 5-amide), where the molecules do not fold, the crystallisation is less restricted (e.g. the chains can form a parallel array) and two new crystal structures have been identified. In the 2- and 3-amide crystals, hydrogen bonds can occur in two directions between parallel chains and orthogonal to the molecular axis (c-axis), which is inclined at a substantial angle to the lamellar surface (the κ-structure). The 5-amide oligomer also does not fold. In this case, the hydrogen bonds are made between antiparallel chains, as in the nylon 6 α-structure; however, these sheets progressively c-axis shear to give a new structure (the λ-structure). Chain-folded molecules can crystallise in the λ-structure although not in the κ-structure because it requires parallel chains. © *2000 Kluwer Academic Publishers*

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1. Introduction and background

An important and enduring legacy that polymer science has inherited from the sustained efforts of Professor Andrew Keller is the cognisance, substantiated by unshakable and convincing experimental proof, that long flexible chain molecules are able, indeed often prefer, to settle in a free energy minimum that expresses itself in the form of regular chain-folded lamellar-like crystals. The delightful elegance of these nanometer-thin, wafer-like crystals, with their large surfaces decorated with two-dimensional, repetitive folds, was first visualised for the chemically unpretentious polyethylene molecule when crystallised isothermally from solution [1]. Electron microscopy and electron diffraction from individual lamellar crystals together with X-ray diffraction from sedimented lamellae (mats), oriented by uniaxial compression, were the basic methods used for establishing the structures and morphologies [1–5]. Although much of the pioneering polymer physics, at least at Bristol under the overall guidance of Professor Sir Charles Frank, were focussed on polyethylene, e.g. its crystal habits, growth and development into spherulites, lamellar thickening, unfolding, etc., it was also recognised that, at least, two further ingredients would be useful, indeed some would say essential, if the polymeric chain-folded crystalline state was to gain universal acceptance in the synthetic polymeric field.[†] Firstly, it was necessary to show that the phenomenon occurred using other long chain molecules with other types of interchain interactions, e.g. the polyesters with their dipole-dipole

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[†] The concept and discovery of adjacent re-entry chain folding in apβ-sheet proteins was also developing in parallel [6–8].

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interactions, or the additional hydrogen-bonding interactions in the polyamides. Secondly, if the fundamental and underlying polymer physics was to be understood, and the precise interplay between the folds and straight-stems ascertained, then molecules of fixed lengths, i.e. monodisperse oligomers, would be a necessary part of the study.

It would appear that the first opportunity for studies using monodisperse oligomers occurred when Zahn [9], synthesised nylon 6 oligoamides with the generalised formula: $C_6H_5CH_2OOC[NH(CH_2)_5CO]_nOH$, with integer n in the range 1 to 12. Using low-angle X-ray diffraction, Zahn [9] and Zahn and Pieper [10] measured the lamellar stacking periodicity (LSP) from oriented mats of lamellae, crystallised from solution, and found a linear correlation with increasing chain length until the octomer (length $\approx$8 nm), beyond which the LSP value remained constant. The bulky aromatic unit at one end of the molecules and a carboxyl group at the other end were, of course, irritants in the crystallisation process, the final quality of the crystals and, in particular, the diffraction analyses. Work on these monodisperse samples started in the H. H. Wills Physics Laboratory at the University of Bristol in 1960 when Professor Zahn sent samples from Germany to Professor Keller, who, together with his Ph.D research student Francisco Balta Calleja, undertook both low- and wide-angle X-ray diffraction experiments [11, 12]. The investigation was also extended to include electron microscopy, both imaging and diffraction, from individual lamellar crystals. Although the interpretation of the results was clouded by concerns of chain obliquity to the lamellar normal, especially for the longer oligomers, it was concluded that the chains remained non-folded up to $\approx$8 nm, beyond which chain-folding offered the most probable explanation [12].

Unfortunately, work on monodisperse oligoamides remained dormant until the Engineering & Physical Sciences Research Council were first encouraged, and finally persuaded, to support a new chemical synthesis and structural study in a joint venture between the Chemistry Department, University of Durham and our own laboratory at Bristol. Dr. Gerald Brooke and his colleagues [13–15] at Durham have synthesised a series of precisely defined monodisperse oligoamides. The molecules are terminated with short alkane segments [13–18] (see Fig. 1) in order to minimise the disturbance in the crystalline lattice. We have recently studied the nylon 6 series [16–20] containing 2, 3, 5, 9, 10 and 17 amide units with a length range of 2 nm to 15 nm, as illustrated in Fig. 1.

Using these new high-fidelity oligoamides we have been able to study the onset of folding as a function of increasing chain length in nylon 6 [17]. We have also been able to consider different folding geometries and the chemical nature of the fold, i.e. alkane segment folds or amide unit folds [18]. In addition, we have identified and established entirely new crystal structures for the short non-folded nylon 6 oligomers [16, 19–20]. In this paper we present an overview of our recent findings, highlighting specific features regarding folding and its consequences which, we judge, would have been a delight to Professor Andrew Keller.

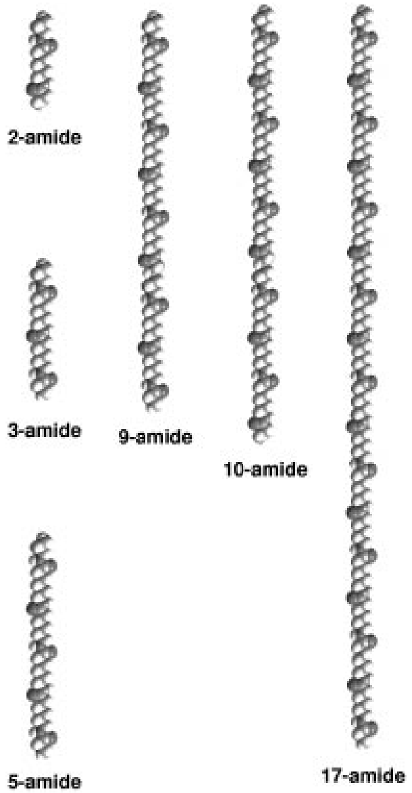

Figure 1 Computer models of all the nylon 6 oligomers discussed. Note that all these oligomers are terminated by C_2H_5 (carbonyl end) and C_3H_7 (amine end) groups. Colour code: carbon, grey; nitrogen, dark grey; oxygen, black; hydrogen, white.

1.1. Solution-grown nylon 6 crystals

The crystallisation of nylon 6 is, as it is for other even and even-even nylons, dominated by the need to maximise the number of interchain (linear) hydrogen bonds, compatible with the overall stereochemistry and crystallinity. In the regularly chain-folded nylon 6 α-structure, the folded, and therefore antiparallel chains, hydrogen bond together to form sheets (ac-plane) with the chain axes (c-axis) orthogonal to the horizontal sheet edge, as illustrated in Fig. 2a. The sheets stack together via van der Waals interactions, with alternating c-axis shear (Fig. 2b) [21] and progressive a-axis shear (see Fig. 2c) in the ac-plane. The nylon 6 sheet structure differs from that of nylon 6 6, and those of many other even-even nylons; in these latter cases, the chains need to progressively c-axis shear by 13° within the sheets in order to form linear interchain, intrasheet hydrogen bonds. Usually, these sheets are found to stack progressively [22]. In all cases two strong diffraction signals are evident at spacings 0.44 nm, corresponding to the projected interchain, intrasheet spacing, and 0.37 mn, corresponding directly to the intersheet spacing. This straightforward diffraction fingerprint is characteristic of the room temperature nylon α-structures [23].

Two other crystalline polymorphs have been proposed for nylon 6. (i) The well-documented γ-structure, where the amide units twist out of the all-trans chain conformation and hydrogen bonds form between parallel chains [24, 25]. The characteristic diffraction fingerprints of the γ-structure are a pair of strong interchain diffraction signals, now at spacings of 0.42 nm and

0.41 nm, about a 5% reduction in the c-repeat as a consequence of the twisted backbone conformation, and a crystallographic γ value $\geq 120^\circ$ [23]. (ii) An unstable β-structure, where the c-direction shear is zero and, possibly, the hydrogen-bonded sheets consist of parallel chains and non-linear hydrogen bonds [21].

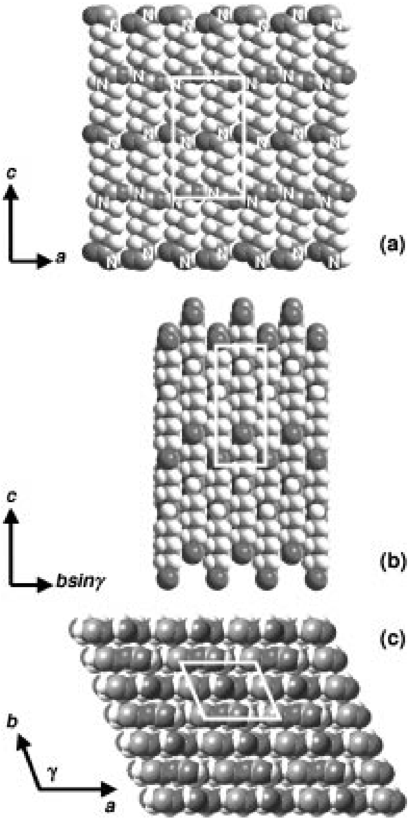

Figure 2 Three views of a space-filling model of the nylon 6 α-structure [21], with the projected monoclinic unit cell illustrated as a white box. (a) Projection of the hydrogen-bonded sheet, orthogonal to the sheet surface; note the alternating c-axis shear of the hydrogen bonding. The nitrogen atoms are labelled N; (b) View along the a-axis, parallel to the hydrogen-bonded sheet shown in (a); note the alternating c-axis shear between successive sheets. The sheets also progressively shear parallel to the a-axis, as can be seen in (c); a view along the chain (c) axis. The colour code is the same as for Fig. 1.

Although, in chain-folded lamellae, the nylon 6 6 chains must fold via alkane segments in order to maintain a fully saturated and orchestrated inter-sheet hydrogen-bonding scheme, there is no such requirement for nylon 6. Chain-folded, hydrogen-bonded sheets can be constructed with either alkane or amide folds, as illustrated in Fig. 3 [18]. Although, the amide-in-fold model would appear to have the disadvantage that one amide unit per fold would be lost to straight-stem hydrogen bonding, it has the advantage that a greater length of chain would be available for folding. We know from studies on the even-even nylons 4 6, [26] 6 8, [27] 8 10 and 10 12 [28] that the length of alkane segment in nylon 6 maybe too short for unstrained alkane folds.

2. Important questions to be addressed by experiments on Nylon 6 oligomers

Using solution-grown lamellae of the nylon 6 oligomers we planned to address a number of issues:

The onset of folding. At the outset of the work we expected that the shorter oligomers would form crystals that were not chain-folded and that the longer oligomers would fold; at what chain length would folding set in?

The nature of the fold. It was anticipated that by comparing crystals of oligomers with odd and even numbers of amide units, specifically the 9- and 10-amide oligomers, we would obtain insight into the nature of folding in nylon 6.

Crystal structures. Would all the oligomers crystallise in the nylon 6 α–structure? This was not a foregone conclusion where folding did not occur; indeed, it turns out that a number of new structures are observed for crystals the chains are not folded.

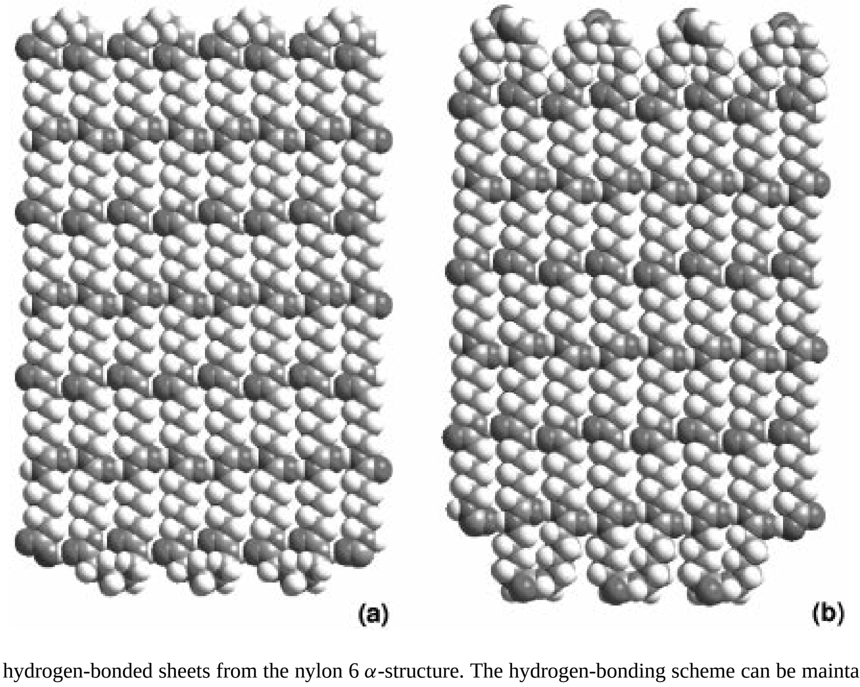

Figure 3 Chain-folded, hydrogen-bonded sheets from the nylon 6 α-structure. The hydrogen-bonding scheme can be maintained with either alkane folds (a), or amide folds (b). Colour code as in Fig. 1.

In the event, we obtained valuable insights on all these points.

3. Experimental

The starting materials, in the form of purified powders, were generously provided by Dr. G. Brooke, University of Durham, Durham, U.K. Brooke *et al.* [13–15] have already reported the chemical syntheses and detailed characterisations of these monodisperse oligoamides.

The detailed methods for lamellar crystal preparation, both solvent/non-solvent precipitation and thermal crystallisation, are given in references [16–19]. Rapid crystallisation was achieved by adding excess miscible nonsolvent to the oligoamide solution. Alternatively, slower crystallisation was accomplished by allowing the more volatile solvent to evaporate from a mixed solvent/nonsolvent solution. Thermal crystallisation at elevated temperatures allowed better control of the crystallisation process. Individual lamellar crystals were studied using transmission electron microscopy (both imaging and diffraction) and both wide- and low-angle X-ray diffraction was undertaken on oriented mats [4]. Computing methods were used for model building, structural analyses and modelling the folds [16–18].

4. Results and discussion

4.1. Onset of folding

X-ray diffraction evidence showed, unambiguously, that the shorter oligoamides (2-, 3- and 5-amide) were not folded [16, 17, 19, 20]. On slow precipitation the 9-amide oligomer does not fold and crystallises in the nylon 6 γ-structure [17]. However, on rapid crystallisation both the 9- and the 10-amide oligomers form once-folded conformations and crystallise in the α-structure. [17, 18] The 17-amide oligomers fold twice to give α–structure crystals with a similar morphology to those of the α–structure nylon 6 polymer [17].

Wide-angle X-ray diffraction data from oriented mats enabled the angle of inclination between the chains and the lamellar normal to be determined unequivocally. The lamellar stacking periodicity (LSP), measured by low-angle X-ray diffraction, was then compared with the known length of the non-folded oligomer. For each crystal preparation with chains orthogonal to the lamellar surface (the α- and γ-structures[‡]) it was straightforward to establish if the chains were non-folded (LSP equal to the oligomer length); once-folded (LSP value a little more than half oligomer length) or folded more frequently, e.g., the twice-folded 17-amide oligomer. For non-folded molecules the lamellae stack with crystallographic precision and many LSP orders are observed. In the case of the chain-folded lamellae, the stacking is not so perfect, and typically only the first or first and second orders appear. In these cases the LSP values are greater that the outer limit length of the folded molecules; [4, 17] thus, appropriate allowance needs to be made for stacking imperfections.

It also turns out that there are only certain ways in which the molecules, for instance the once-folded hairpins, can hydrogen bond together to generate sheets incorporating the appropriate hydrogen-bonding scheme [17, 18]. All these considerations will contribute to an LSP that is greater than the integer fraction of the oligomer chain length. In Table I, only crystals in the nylon 6 α–structure are listed. In this structure the chains must run normal to the lamellar surfaces; there is no chain tilt and the number of folds per molecule can be determined by direct comparison of the chain length with the measured LSP value. It is apparent from Table I that there is no doubt as to the exact number of folds in each crystal type studied. Table I also shows that, in our particular set of nylon 6 oligoamides, the molecules fold such that the lamellar thickness is ≈5 nm.

TABLE I Characteristics of α–structure nylon 6 crystals, where the chains run normal to the crystal surfaces. Lamellae with other crystal structures will be dealt with below. In all lamellae observed in structures other than the α–structure at room temperature the chains were non-folded

Oligomer	Chain length (nm)	LSP (nm)	Folding status	Reference
5-amide	4.6	4.8	Non-folded	17
9-amide	8.0	4.8	Once-folded	17
10-amide	8.9	4.8	Once-folded	18
17-amide	15	5.4	Twice-folded	17
polymer	long	∼7	Many times folded	29

4.2. The nature of the fold

The nylon 6 polymer can form chain-folded, α-structure hydrogen-bonded sheets incorporating either alkane segment or amide unit folds, as shown in Fig. 3. There are advantages in both fold types, as explained above, and the preferred fold type has not, to our knowledge, been determined for the nylon 6 polymer. Recent crystallisation and structural studies on the 9- and 10-amide nylon 6 oligomers have provided some interesting insights [18, 17].

By crystallising the 9- and 10-amide oligomers under similar conditions into once-folded structures, we found that in both cases the molecules folded in the middle to give symmetric hairpin-like conformations as shown in Fig. 4. All the hydrogen bonds in the straight-stems are saturated. The consequences are that the folds are different in these two structures. The 10-amide hairpin conformation has an alkane segment in the fold, while the 9-amide hairpin has an amide unit in the fold. It would appear, that the symmetry of the hairpin has a controlling influence, i.e. the requirement that all the amide units in the straight-stem pair form intramolecular hydrogen bonds, and the further condition that hydrogen bonds in the sheets, generated from the juxtapositioning of these once-folded molecules, are fully saturated, dictates the final chosen conformation. Thus, the nature of the fold, alkane or amide, is a consequence of these requirements. This evidence suggests that both alkane and amide folds may occur in the nylon 6 polymer.

4.3. New crystal structures

The folded molecules that we have examined all crystallise in the nylon 6 α–structure. In this structure,

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[‡] For the γ-structure, the ≈5% chain contraction must also be considered.

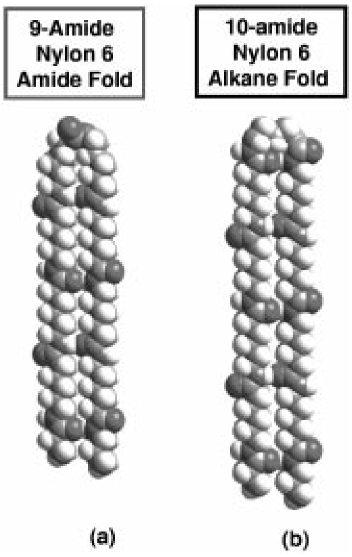

Figure 4 Computer generated space-filling models of once-folded nylon 6 oligomers: (a) 9-amide oligomer with an amide fold and (b) 10-amide oligomer with an alkane fold. The colour code is the same as for Fig. 1.

adjacent polar chains are antiparallel within the hydrogen-bonded sheets and, for the polymer, this has to be the case if, as is observed, there is adjacent re-entry chain folding in the same plane as the hydrogen bonding (*ac*-plane, Fig. 2). All the folded oligomers are observed to have diffraction fingerprints commensurate with the nylon 6 α–structure [23], and therefore have the hydrogen bonding arrangement shown in Fig. 2a. In the α–structure, the chain-folded sheets always stack with alternating c-axis shear. However, when the chains are not folded there is also the possibility of hydrogen bonding between adjacent parallel chains, and this can give rise to other hydrogen-bonding schemes, both the γ-structure [20, 17, 24] and other structures besides [16, 19]. We found two new crystal structures for the shorter non-folded oligoamides, as illustrated in Fig. 5. The experimental evidence for these structures and the detailed analyses are given in elsewhere [16, 19]. The salient features of the structures found for our nylon 6 oligomers are summarised in Table II. Detailed studies of the short nylon 6 oligoamides reveal some interesting

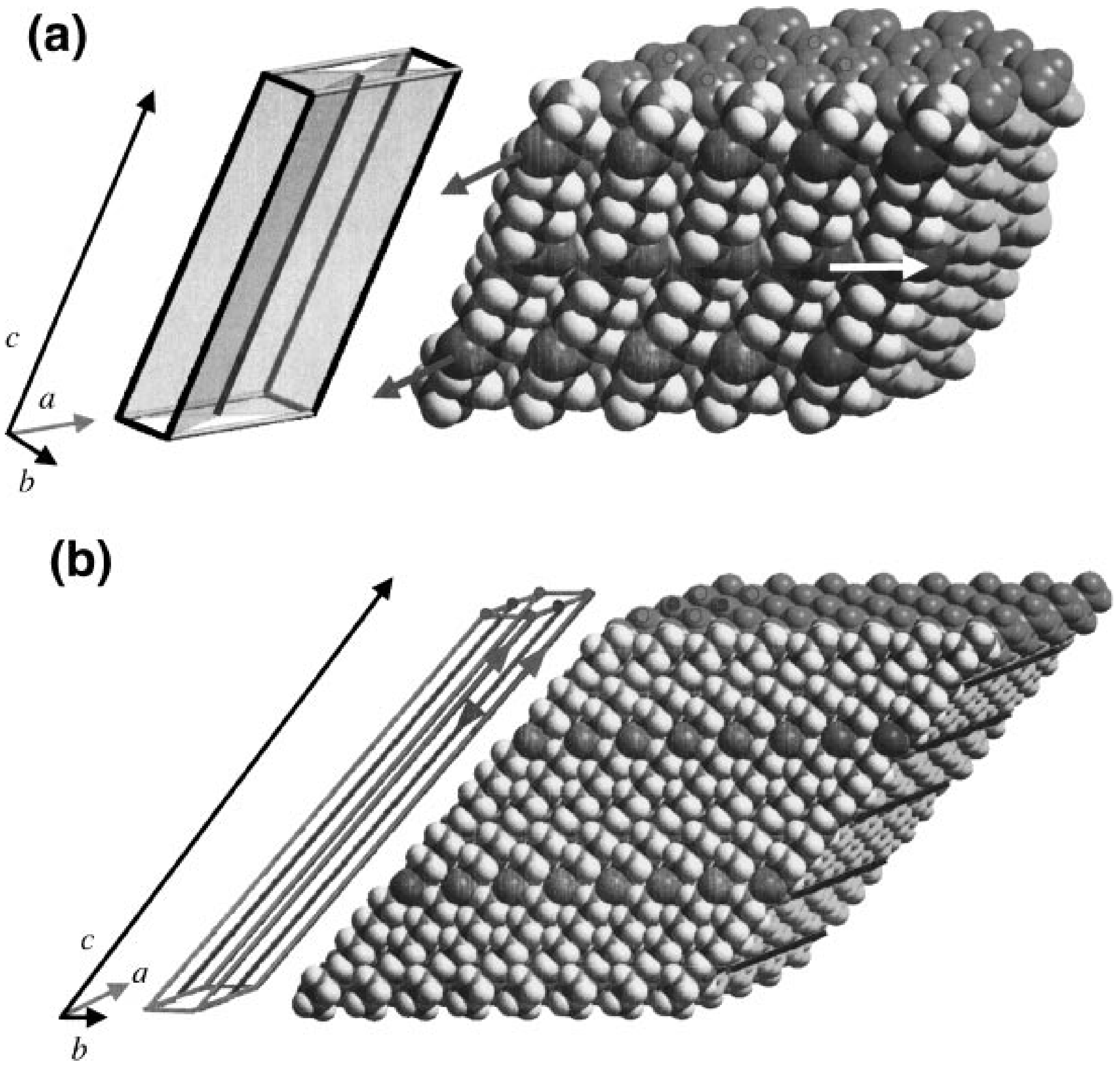

Figure 5 Computer generated models, with unit cells on left, of (a) the new κ-structure observed for the 3-amide oligomer (a similar structure occurs for the 2-amide oligomer). The hydrogen bond directions are indicated by the semi-transparent intersecting planes on the unit cell and by the arrows in the space filling model; (b) The λ-structure observed for 5-amide nylon 6 oligomer. The bars on the side of the real space model represent the five layers of amide units. The colour code is the same as for Fig. 1, with the colours of the atoms on the top and side surfaces changed for clarity. In both models the unit cells have been marked with points, and different colours indicate the different chain directions.

TABLE II The structures that we have obtained for monodisperse nylon 6 oligomers at room temperature

Nylon 6 Oligomer	Reference	Preparation Technique	Structure at Room Temperature	Chain Form at Room Temperature
2-amide	20*	Dodecane	κ-structure	Non-folded
3-amide	16	Trifluoroethanol/Dioxane (rapid crystallisation)	κ-structure	Non-folded
3-amide	28*	Dodecane	λ-structure κ-structure γ-structure	Non-folded Non-folded Non-folded
5-amide	17	Tri-fluorethanol/Dioxane (rapid crystallisation)	α-structure	Non-folded
5-amide	19	Dimethylformamide (23°C)	α-structure	Non-folded
5-amide	19	Dimethylformamide (70°C)	λ-structure	Non-folded
9-amide	17	Tri-fluorethanol/Dioxane (rapid crystallisation)	α-structure	Once-folded Amide fold
9-amide	17	Tri-fluoroethanol/Dioxane (slow crystallisation)	γ-structure	Non-folded
10-amide	18	Tri-fluorethanol/Dioxane (rapid crystallisation)	α-structure	Once-folded Alkane fold
10-amide	*	Cyclohexane	α-structure	Once-folded Alkane fold
17-amide	17	Tri-fluorethanol/Dioxane (rapid crystallisation)	α-structure	Twice-folded Amide fold

Key:
Trifluoroethanol/Dioxane: Solvent/non-solvent crystallisation preparation technique.[16-18]
Slow crystallisation: Crystallisation by evaporation of solvent.
Rapid crystallisation: Crystallisation by addition of excess non-solvent.
Cyclohexane, Dodecane [20] or Dimethylformamide [19]: single solvent thermal crystallisation.
α-structure: Bunn and Holmes nylon 6 α-structure [21] (to within the limits described by Salem and Weighmann) [23].
κ-amide structure: Bi-directional hydrogen bond structure of parallel non-folded molecules, see Fig. 5a [16, 20].
λ-structure: Hydrogen-bonded sheets identical to those of the α-structure, stacked with a progressive shear, see Fig. 5b [19].
γ-structure: Hydrogen-bonded sheets consisting of parallel and aligned chains, stacked with no intersheet shear [17, 20, 24, 25].
*Previously unpublished data.

features. It was possible to assess the effect that folding has on the polymer chain conformation and on the crystalline structures.

When structures of the short 2-amide and 3-amide oligomers were studied, it was discovered that under most crystallisation conditions (including slow isothermal crystallisation) they crystallised into a new structure in which hydrogen bonds are formed between parallel molecules in two directions orthogonal to the molecular axis (Fig. 5a) [16, 20]. We call this structure the nylon 6 κ-structure. A noticeable difference in crystal morphology was observed: the α-structure even nylons form thin ribbons, in which the hydrogen-bonding direction runs along the length of the crystals, whereas the κ-structure crystals have rectangular, plate-like shapes (Fig. 6a), without any obviously preferred direction of growth. In the κ-structure, first discovered for the 3-amide oligomer [16], the crystals consist of layers of all parallel molecules stacking together in crystallographic order to form micron-thick crystals. This structure, not possible for chain-folded nylon 6 molecules, gives substantial improvement in the

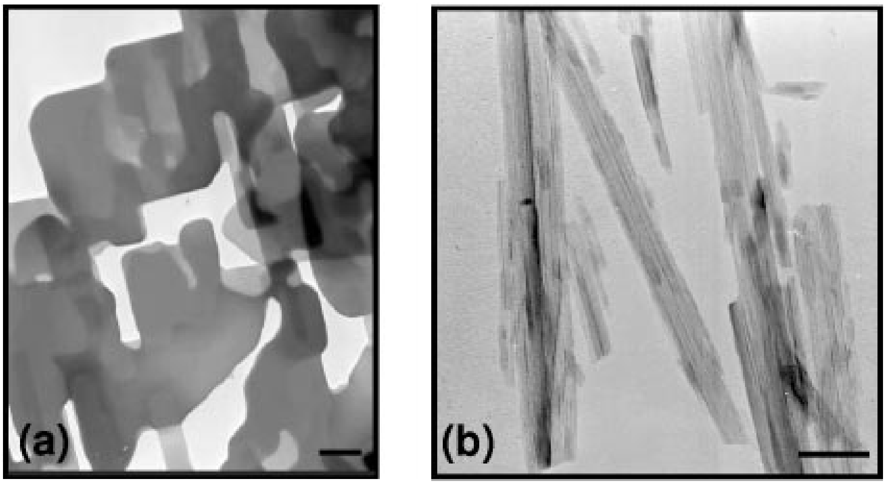

Figure 6 Transmission electron micrographs showing the layered crystal morphologies of 2-amide nylon 6 in the κ-structure [20] and 5-amide nylon 6 in the λ-structure [19]. Scale bars represent 1 μm.

quality of the diffraction data and offers an opportunity to study molecular conformations in these systems in more detail. When the unit cells, crystal structure determination and the schemes of hydrogen bonding were established, it became clear that the chain conformation of the molecule in the κ-structure is different from the chain conformations observed previously in α- and γ-nylon 6 structures. In this new structure both amide torsion angles are equal to $\pm 150^\circ$, compared with $\pm 180^\circ$ in α-structure and $\pm 120^\circ$ in the γ-structure. For the 2- and 3-amide molecules, the nylon 6 α-structure was not observed experimentally.

Bernado *et al.* describe [30] interactions between amide units adjacent to each other; these play a role in stabilising the all-trans chain conformation, and only become significant when a sufficient number of amide units are present in the molecule (polymer chain). For short molecules, or long alkane segment even nylons, such an energy benefit is insignificant, and therefore they are not expected to crystallise in the α-structure, but rather in γ-structure, which allows more efficient packing of the alkane segments. Interestingly, short molecules have a third option: they can form layered crystals, and within each layer all the molecules are parallel (κ-structure). In this structure the amide torsion angles are in their global energy minima, and all hydrogen bonds are saturated.

The experimental observations [17, 19] are different for the 5-amide molecule, which has been found to crystallise in the nylon 6 α-structure, or, when isothermally crystallised at elevated temperatures [19] in a new crystalline form, hereafter referred to as the λ-structure. In this λ-structure, hydrogen-bonded sheets have the same hydrogen-bonding scheme as in the commonly observed α-structure, but the arrangement (stacking) of these sheets is different, see Fig. 5b [19]. X-ray and electron diffraction studies revealed that in this new λ-structure the molecules are tilted at a substantial angle (44°) to the crystal surface, in a similar way to that observed in the nylon 6 6 α-structure [22]. The tilt implies that the sheer between hydrogen-bonded sheets is regular and progressive. The morphology (Fig. 6b) shows long crystals with parallel, well defined edges, having thickness in the range 3.7 nm (one layer) to $\sim 0.1\ \mu$m (30 layers). Unlike the κ-structure, chain-folded molecules can crystallise in the λ-structure, indeed an analagous structure has already been reported for chain-folded nylon 8 polymer [29].

5. Summary

The crystallisation and coupled structural studies on these high-fidelity monodisperse nylon 6 oligoamides are critical ingredients in laying down the basis for a more fundamental understanding of the polymer physics of polyamide macromolecules. There is no doubt in our minds that the work we have outlined in this mini-overview should have been undertaken much earlier. In this respect, the original chemical synthesis by Professor Zahn in Aachen during the late 1950's, and the immediate realisation of the value of such molecules to polymer physics by Professor Andrew Keller in Bristol, were pioneering events of considerable significance. Unfortunately, this synergism physics was not maintained in this area and has only been rekindled recently.

Our conclusions, so far, are as follows:

Onset of folding. Starting with the 2-amide molecule (length 2 nm), and following the crystallisation behaviour as a function of increasing length, the first molecule in our nylon 6 oligoamide series to exhibit folding was the 9-amide oligomer (length 8 nm). Under rapid crystallisation it folds once, in the middle, placing the central amide unit in the fold. The 10-amide oligomer also folds once and the longer (length 15 nm) 17-amide molecule folds twice. Once folding has set in only the nylon 6 α–structure has been observed, so far. Note that Zahn and Keller and their co-workers, who studied oligomers with different (bulkier) terminal groups also observed the onset of folding at a molecular length $\sim$8 nm.

The nature of the fold. Both amide unit and alkane segment folds have been recorded for the once-folded oligomers. It would appear that the symmetry of the hairpin and the requirement for saturated hydrogen bonds are the controlling factors. The nylon 6 chain can stereochemically accommodate either fold type. Since in nylon 6 all the chemical units are the same, the incorporation or not, of an amide unit in the sharp reverse turns does not affect the α–structure intrasheet hydrogen-bonding scheme. In this respect nylon 6 differs from nylon 6 6, with its alternating diamine and diacid segments; nylon 6 6 cannot place a single amide unit in the reverse turn without breaking the orchestrated intrasheet hydrogen-bonding scheme.

Crystal structures. In the shorter oligoamides (2-, 3-, 5-amide) the molecules do not fold and, as a result, the requirement for antiparallel chains within the hydrogen bonded sheets is removed. Two new crystal structures have been identified. In the 2- and 3-amide crystals, hydrogen bonding occurs between parallel chains, in two directions and orthogonal to the molecular axis (c-axis) which is inclined at a substantial angle to the lamellar surface. We have termed this the κ-structure. The 5-amide oligomer does not fold but here the hydrogen bonding is between antiparallel chains, as in the nylon 6 α–structure hydrogen-bonded sheets. However, a new structure has been found where the sheets progressively c-axis shear. We have termed this the λ-structure.

Acknowledgements

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