Glycine residues induce a helical structure in polyamides

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We analyse the conformation of copolyamides with regularly alternating glycine and ω-amino acid units (nylons 2/n). These polymers have a crystalline structure with hydrogen bonds running in three different directions; the standard structure of nylons with parallel sheets of hydrogen-bonded molecules is no longer present. The detailed structure depends on whether n is odd or even, which respectively gives rise to trigonal or hexagonal crystalline structures.

(Keywords: glycine; polyamides; nylon)

INTRODUCTION

Aliphatic polyamides (nylons) always crystallize with a structure comprising parallel sheets built from chain molecules and stabilized by hydrogen bonds[1,2]. Polyglycine (nylon 2), the shortest member of the series, is an exception to the rule in the sense that besides the sheet structure[3,4], polyglycine I, it can adopt a second structure[5], polyglycine II, in which hydrogen bonds are formed in three directions at 120° throughout the crystal. No sheets are present in such a structure, and every individual polymer chain is tied to six neighbouring molecules. *Figure 1* illustrates these two different structures.

What will happen when we prepare a copolymer with both types of unit? We have investigated this question in recent years[6–13] and found that the glycine residues invariably play a dominant role, so that the most stable structure of the copolymer is always helical and related to the three-fold helix of polyglycine II. However, the particular symmetry of the helix depends on the exact composition of the copolymer. Therefore in this paper we investigate in detail the chain conformation of these polymers in order to understand the predominance of the helical conformation and its different types. A preliminary account was presented elsewhere[14]. These studies open the way to modify the sheet structure of conventional polyamides into a structure with hydrogen bonds oriented in different directions in space, a fact which undoubtedly will influence the properties of these materials.

CRYSTALLINE FORMS IN 2/n NYLONS

Before analysing in detail the conformation of these polymers we will review the experimental information currently available. Nylons 2/n are alternating copolymers of glycine and a longer ω-amino acid. The nomenclature used follows the recommendations of Kohan[15], and their general formula is as follows:

$$-NHCH_2CONH(CH_2)_{n-1}CO-$$

The two types of structure shown in *Figure 1* have been described for most of these polymers, as summarized in *Table 1*. Form I appears to have a lower stability. It has nearly extended chains and has only been found in some cases, usually in samples epitaxially crystallized onto organic substrates. The most stable form II is a polyglycine II type structure. Single crystals of these nylons can be obtained and examined by electron microscopy. Those of polyglycine itself display hexagonal morphology[16], although sometimes they grow as doughnut shaped structures[17]. Nylons 2/3, 2/3/3 and 2/5 develop triangular lamellae with serrated edges[6,9,11], whereas nylon 2/6 crystallizes nicely with hexagonal habit[8]. The long aliphatic chain copolymers, nylon 2/11 and nylon 2/12, develop irregular lamellar structures with hexagonal tendency[10,12]. In spite of this morphological diversity all these crystals or multicrystalline aggregates exhibit similar electron diffraction patterns, corresponding to the $hk0$ reciprocal zone of an invariably hexagonal lattice with a reticular parameter of 4.79–4.80 Å and 6/mmm point group symmetry. This pattern is easily identified as being produced by a structure such as that depicted in *Figure 1b*, that is with the chain axes placed perpendicularly to the lamellar surface.

Unfortunately it has not been possible, for any of these nylons, to prepare uniaxially oriented samples which would facilitate the analysis of their structure. The reason for this phenomenon is probably related to the organization of hydrogen bonds, which may prevent orientation of the samples by mechanical deformation. Nylons 2/n have no asymmetrical carbon atoms, so either right-handed or left-handed helices are equally probable. For polyglycine[5] and nylon 2/3[7], three-fold helical conformations have been proposed which could be, with the same probability, 3_1 or 3_2 helices. Nevertheless, only helices

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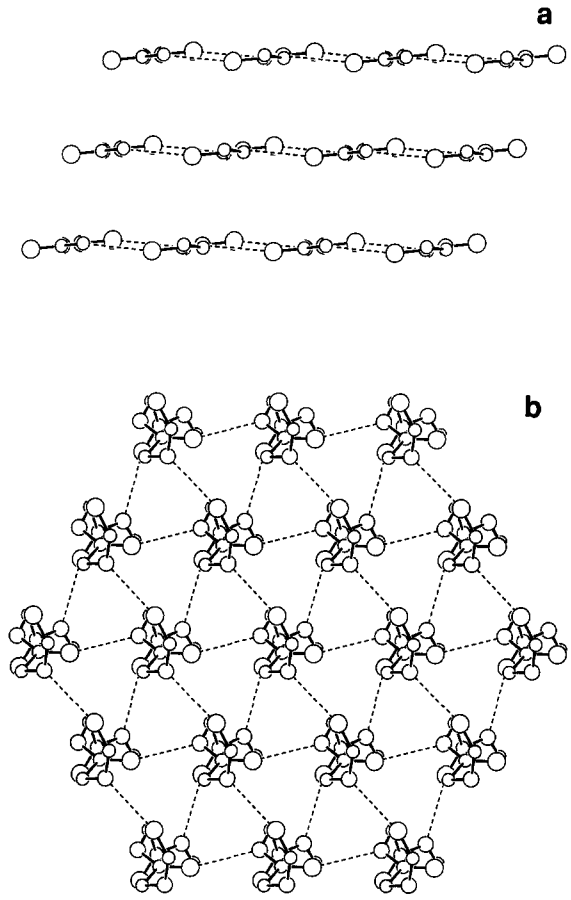

Figure 1 (a) The sheet structure of nylons such as nylon 6; (b) the structure of nylon 2 in its form II (polyglycine II), showing the interaction of each individual polymer chain with its six neighbours. The polymer molecules are projected onto a plane perpendicular to the chain axis. No hydrogens are shown. Hydrogen bonds are indicated by dashed lines

Table 1 Observed crystalline forms in 2/*n* nylons (form I shows extended polymer chains as in the α form of conventional polyamides; form II shows helical molecules related to polyglycine II as described in the text)

Nylons	Form I	Form II	Ref.
2/3	Epitaxial	Triangular	6
2/3/3	Not observed	Triangular	9
2/5	Not observed	Triangular	11
2/6	Ribbon-like lamellae	Hexagonal	8
2/11	Epitaxial	Round/irregular	10
2/12	Epitaxial	Round/hexagonal	12

with the same handedness can be present within a given crystallite, as was already noted for polyglycine[18], in order to correctly place all the hydrogen bonds.

Another characteristic is that we can have either upward or downward helices at every point of the hexagonal lattice. In polyglycine II these two orientations can mix randomly in the whole lattice without disrupting the hydrogen-bonded network, as shown by Ramachandran *et al.*[18]; every chain will form all the hydrogen bonds with its six closest neighbours independently of their mutual arrangement being parallel or antiparallel. As we will show below, in the lamellar crystals and aggregates obtained for the 2/*n* nylons it appears that the chains may also follow this random antiparallel packing.

In view of the difficulties found in preparing oriented samples, an oligomer of nylon 2/3 was synthesized and crystallized in our laboratory[13] in order to obtain direct structural information. It also exhibits a polyglycine II type structure and the most interesting fact about its conformation is that the torsion angles around the glycine residues are those of polyglycine in its form II ($\varphi = 71°$ and $\psi = -149°$), whereas the β-alanyl segment is practically fully extended (all *trans*). We have recently crystallized an oligomer of nylon 2/6 in which the glycine units also have these conformational angles[19].

The crystal structure and chain conformation of these oligomers have allowed us to obtain a common general model for the 2/*n* nylon family, which explains the different morphologies observed in single crystals as well as the common electron diffraction pattern in the *hk*0 zone for all of them. This model shows structural characteristics completely different to those of the standard α, β and γ forms of nylons[1,2], and constitutes an identifying mark of one family of polyamides with crystal structures closely related to the form of polyglycine II. In this work we will use the term 'form Δ' to refer to such a structure.

METHODOLOGY

In the construction of the models and calculation of structure factors the l.a.l.s. (linked-atom least-squares) methodology has been used[20]. The description of one generic residue of nylon 2/*n* is shown in *Figure 2*. Assuming standard bond lengths and angles, the only parameters needed to define the chain conformation are the two glycine torsion angles, φ and ψ, plus the ω-amino acid torsion angles φ', ψ' and v_1 to v_{n-2}. The amide torsion angles have been kept in *trans* conformation for all the models studied. Two additional parameters are needed in packing analysis to position every molecule in relation to its neighbours: the azimuthal angle μ and the mutual vertical displacement between antiparallel chains *w*.

Models with satisfactory stereochemistry have to be consistent with the packing constraints due to the unit cell dimensions of the particular nylon under study, and every chain has to be able to make hydrogen bonds with its neighbours, both in parallel and antiparallel arrangement, following the scheme of *Figure 1b*. When available, diffraction data have been used to test and improve the quality of the model. An occupancy of 50% of up and down chains at every position of the lattice is then used.

RESULTS

Structural model for nylon 2/3

Using the bond parameters of the crystalline structure of the oligomer, acetyl-(glycyl-β-alanyl)$_2$-*N*-propylamide, we can easily build a model for the polymer. The chain conformation of the oligomer structure is shown schematically in projection in *Figure 3a*. The main feature is that the glycyl residue produces a rotation of 120° on the hydrogen-bonding direction and the amide planes orientation, whereas the β-alanyl residue does not change that direction and keeps the amide planes parallel. We will refer to such rotations as $\Phi_{Gly} = 120°$ and $\Phi_{\beta\text{-Ala}} = 0°$. For an infinite chain a 3_1 (or 3_2) helix can be generated in this way. The statistical lattice model can be easily constructed by placing two chains running in opposite

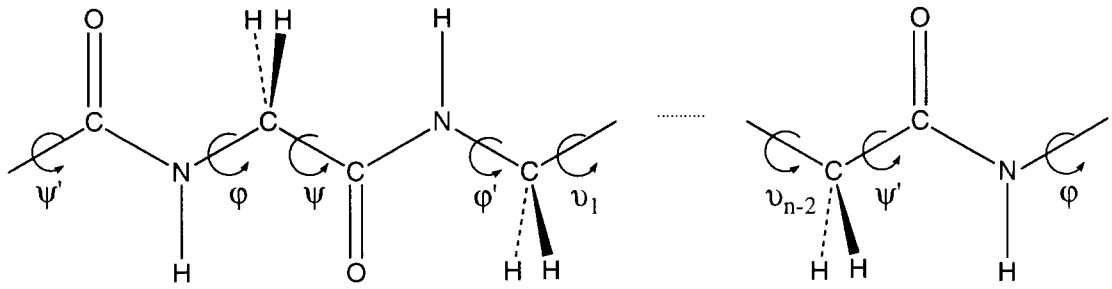

Figure 2 Generic residue of nylon 2/*n*, with the torsion angles used in the refinements. Equivalent peptide units are shown at either end of the residue

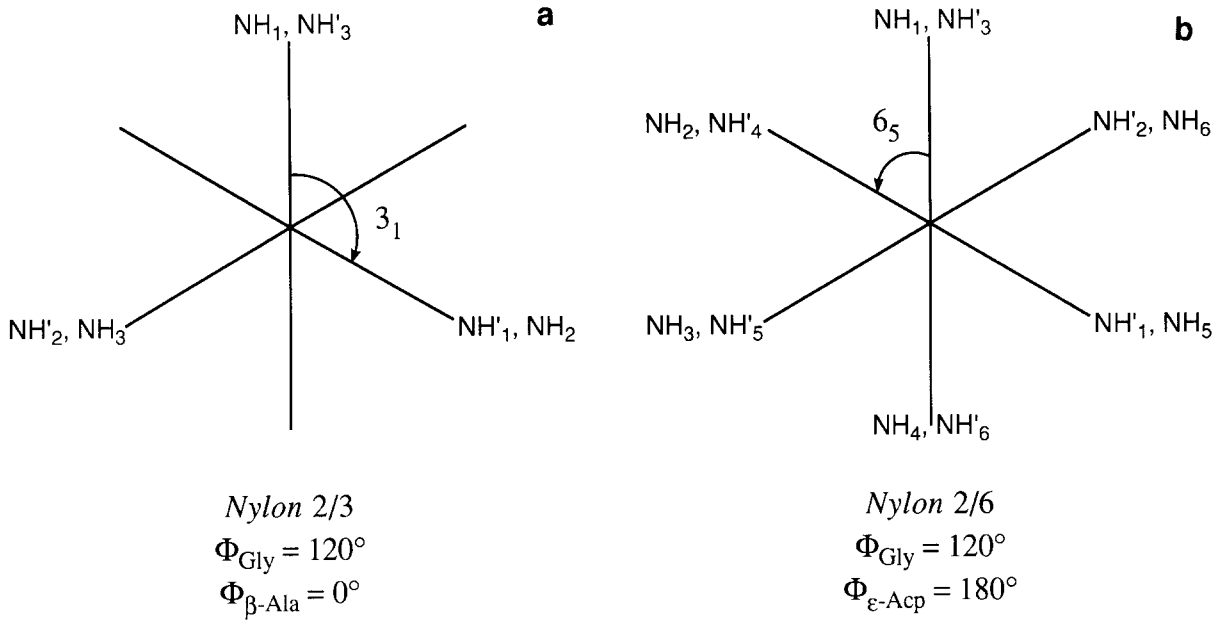

Figure 3 Schematic equatorial projection of the helical conformations of (a) nylon 2/3 and (b) nylon 2/6. The parameters describing the helical symmetry are indicated on the figure

directions per unit cell, coaxially and with 0.5 occupancy each, according to the space group $P3_121$ or $P3_221$. A unit height of 7.4 Å is used, in agreement with the diffuse ring observed in X-ray powder patterns[6].

Two models of nylon 2/3 have been tested against stereochemical criteria. In the first model, which we call Δ_T, the β-alanyl segment has been kept rigid in an all-*trans* conformation, mimicking the oligomer conformation. With this conformation a reasonable packing model can be built with all the helices in parallel, just as they appear in the oligomer structure[13], but when antiparallel packings have been analysed it has not been possible to achieve reasonable hydrogen bonding stereochemistry. Unrestraining the conformation of the β-alanyl torsion angles, φ', ψ' and v, a different model arises from the imposition of antiparallel packing requirements. This second model, Δ_y, has a more satisfactory hydrogen bond stereochemistry both in the parallel and antiparallel case. The final conformation obtained by us for the –CONH–$(CH_2)_2$–CONH– residue is $TST\bar{S}T$, where *S* means *skew*, that is in the range $120 \pm 30°$.

In *Table 2* we compare these two models with a model previously proposed[7] for nylon 2/3. In that model the ϕ and ψ angles chosen for the glycine residue are seldom found in proteins[21]. As we can see, the new Δ_y model constructed on the basis of stereochemical criteria agrees much better with the sparse observed data, even before l.a.l.s. refinement. Similar improvement has not been possible using the previous model. In fact it is a local minimum produced by an inversion of the values of the conformational angles φ and ψ with respect to the respective Δ_y angles. *Figures 4* and *5* show different views of nylon 2/3 chains packed both in parallel and antiparallel mutual arrangement.

A similar model can be built[22] for nylon 2/3/3. In this case we have a duplicate set of β-alanyl torsion angles (*Table 2*), and their resulting conformation is $TST\bar{S}TST\bar{S}T$, so $\Phi_{\beta\text{-Ala}'} = 0°$ too. An identical analysis could be made for both nylons using left-handed helices, which are related by mirror symmetry to those found in the right-handed case.

Structural model for nylon 2/6

The main features of the Δ form of nylon 2/3 allow us to build a model for the even 2/*n* nylons, represented here by nylon 2/6. As shown in *Figure 3a*, the glycyl residue introduces a rotation of 120° on the main chain of nylon 2/3 as well as on the hydrogen-bonding directions, whereas the β-alanyl residue makes a 0° rotation. In the Δ model for nylon 2/6 the glycyl residue also makes a 120° turn, but the ε-aminocaproyl segment places the two amide planes antiparallel, and rotates the

Table 2 Torsion angles, crystallographic symmetry and R factor for different models of nylons 2/n

	Model[a]	φ (deg)	ψ (deg)	ω (deg)	φ' (deg)	ν_i (deg)	ψ' (deg)	ω' (deg)	Symmetry	R (%)
Nylon 2/3	C	151.4	−87.1	180.0	76.4	119.7	−147.9	180.0	Trigonal	23
	Δ_T	86.3	−151.3	180.0	180.0	180.0	180.0	180.0	Trigonal	n.d.
	Δ_γ	76.8	−153.9	180.0	116.6	−164.9	−123.2	180.0	Trigonal	12
Nylon 2/6[b]	Δ_γ	88.2	−151.8	180.0	105.9	166.7	−105.8	180.0	Hexagonal	n.d.
						−171.9				
						170.2				
						−168.4				
Nylon 2/3/3[c]	Δ_γ	79.7	−150.6	180.0	99.4	−165.3	−90.8	180.0	Trigonal	n.d.
					105.3	175.5	−117.5	180.0		
Polyglycine	II	76.9	−145.3	180.0					Trigonal	n.d.

[a] The different models analysed are discussed in detail in the text. Model C was suggested by Muñoz-Guerra *et al.*[7] for the nylon 2/3. In model Δ_T the methylene groups are in all-*trans* conformation, whereas the most adequate model Δ_γ has a *skew* conformation in the φ' and ψ' torsion angles

[b] Nylon 2/6 has four aliphatic angles ν_1 to ν_4

[c] In nylon 2/3/3 there are two sets of β-alanyl angles, φ'_1, ν_1, ψ'_1 and φ'_2, ν_2, ψ'_2

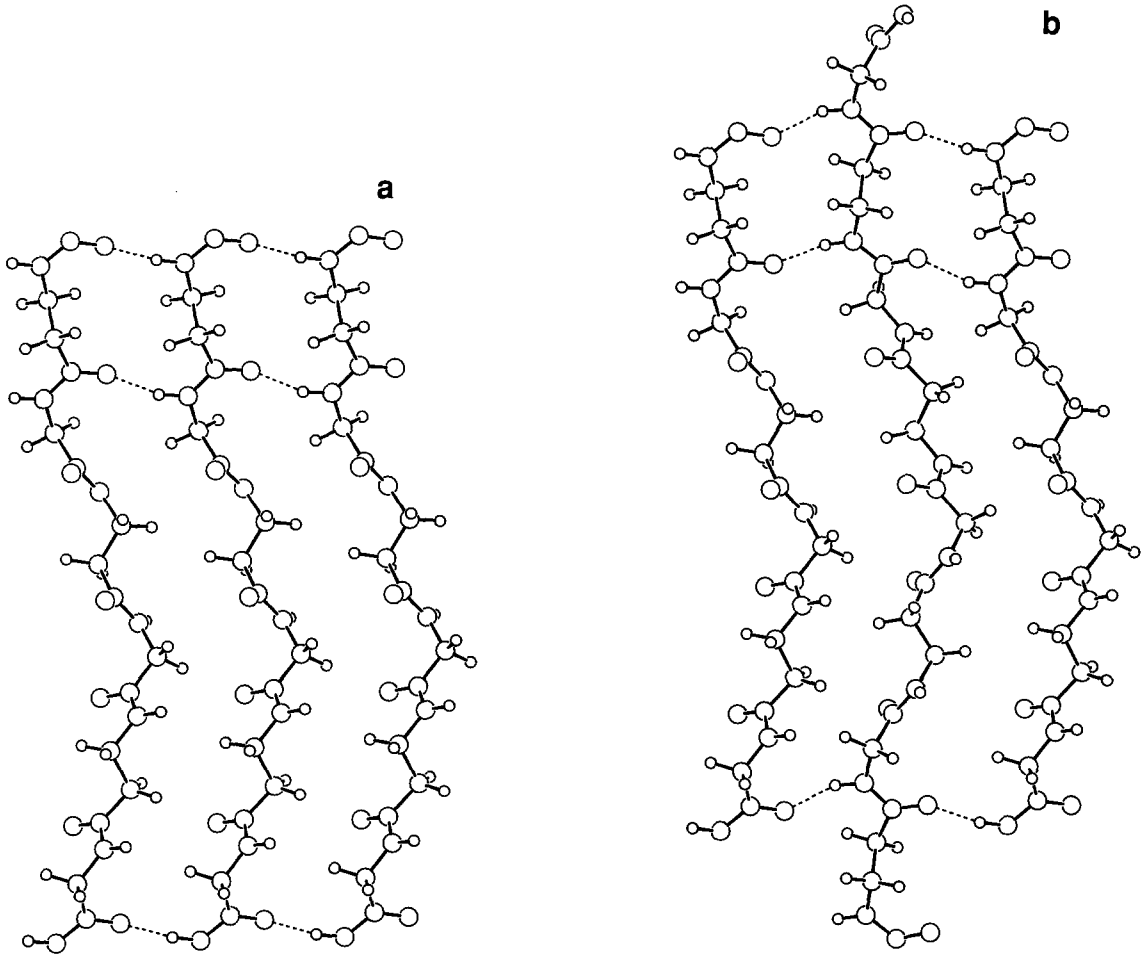

Figure 4 Hydrogen bonding between neighbouring molecules of nylon 2/3: (a) parallel relative orientation; (b) antiparallel relative orientation

main chain and the hydrogen-bonding directions by 180° (*Figure 3b*), either in the T_6 or $TST_4\bar{S}T$ conformations. As a result, the helical symmetry of nylon 2/6 is six-fold, 6_5 or 6_1, depending on the sense of the helix. The crystal structure will be made of hexagonal helices with the molecular axes arranged in a two-dimensional lattice, similar to polyglycine II (*Figure 1b*). Here there are six equivalent hydrogen-bonding directions instead of the three found in nylon 2/3 or in polyglycine II. We can expect the same random antiparallel packing in odd nylons 2/n, so every lattice point in *Figure 1b* will contain one helix pointing upwards and one pointing downwards, each one with an occupancy of 0.5. The resulting symmetry of the [001] projection is *p6mm*, and the average space group for the three-dimensional model is then $P6_522$ or $P6_122$, depending on helix sense.

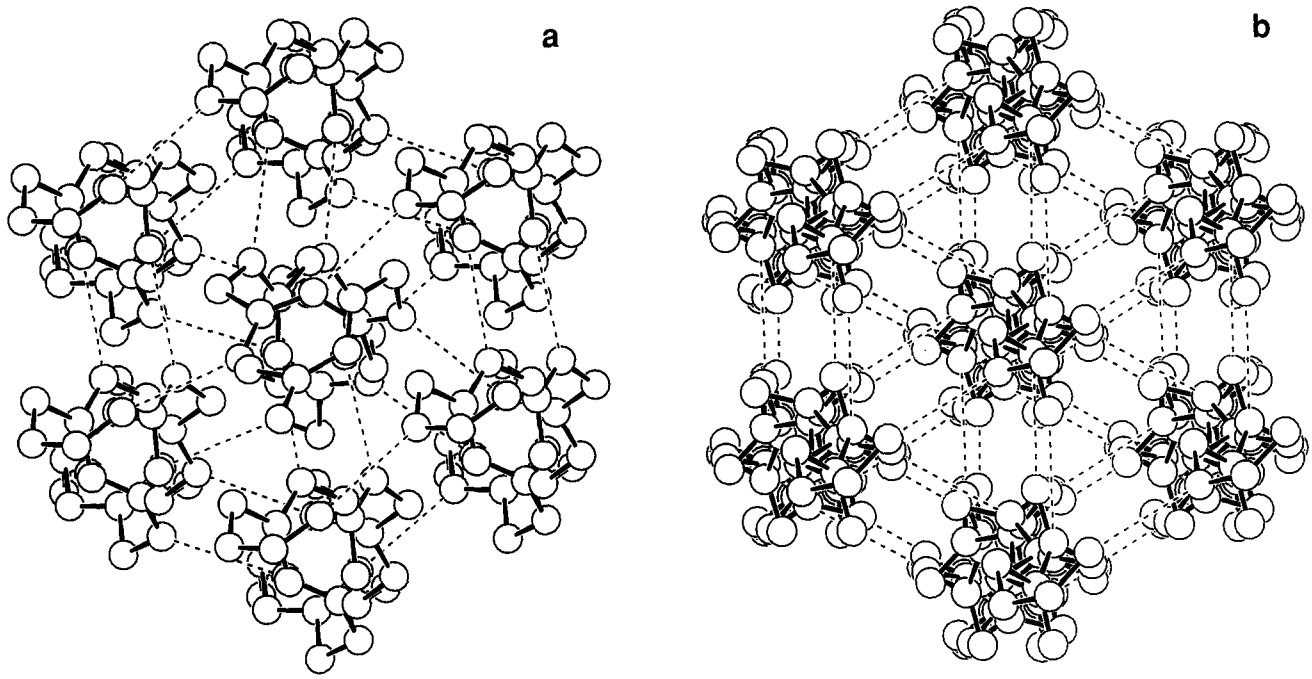

Figure 5 Equatorial projection of the Δ_γ model of (a) nylon 2/3 and (b) nylon 2/6. In (a) the central chain is in relative antiparallel orientation to its six neighbours. The six outer molecules show hydrogen bonding between chains in parallel. In (b) all chains are shown parallel. Hydrogen atoms are not indicated

In order to build a nylon 2/6 model we need to know the residue height, which is one-sixth of the *c* crystallographic repeat. No oriented X-ray diagrams are available for nylon 2/6, therefore this repeat has to be calculated from powder diagrams. In these diagrams there is a strong and well-defined ring at 4.15 Å, corresponding to the 100 interplanar spacing, several more or less well defined rings mainly due to [10*l*] reflections and a diffuse ring at 11.5 Å which, after recrystallization of the sample, can split into two (or occasionally three) very well defined rings[8]. This diffuse ring at 11.5 Å corresponds to the required unit height of nylon 2/6.

Assuming this unit height, the resulting *c* axis becomes 69 Å, and using this repeat two models with different conformations of nylon 2/6 have been considered, one with the ε-aminocaproyl residue kept in all *trans* (T_6) and the other with free torsion angles. Again the Δ_T model turns out to be inconsistent with a polyglycine II type structure, in particular for antiparallel packing: the amide groups are unfavourably oriented to make hydrogen bonds between neighbouring chains. When the torsion angles of the pentamethylene segment are allowed to move freely against the hydrogen bonding restraints, the final conformation obtained is $TST_4\bar{S}T$, analogous to that shown by the β-alanyl segment of nylon 2/3. Either parallel or antiparallel arrangements are possible. *Table 2* shows the final torsion angles for this Δ_γ conformation. *Figure 5* shows an equatorial view of this model. Lateral views are similar to those given in *Figure 4* for nylon 2/3.

DISCUSSION

From the results presented here we can establish a general model for the chain conformation of nylons 2/*n* in the crystalline form which is related to the polyglycine II structure. We propose to call it Δ form. The main feature that determines this molecular arrangement is the local conformation around the glycyl residue. This amino acid introduces a 120° rotation ($\Phi_{Gly} = 120°$) both in the polymer chain and in the hydrogen-bonding direction. The torsion angles on this residue show characteristic values of roughly $\varphi = 80°$ and $\psi = -150°$ (or their opposite in the enantiomorph helices), for all the nylons analysed in their Δ form (*Table 2*). Isolated glycyl residues can adopt these values in globular proteins[21]. Furthermore, this is the typical glycine conformation in collagen and in polyglycine II.

It is interesting to note that the same 120° rotation could be obtained with the 'inverse' conformation for the glycyl residue, $\varphi = -150°$ and $\psi = 80°$, equally possible in a classical conformational map for the glycyl residue[23]. However, inspection of local conformations of the glycyl residue in proteins shows that between these two conformations there is a clear preference for the first one[21]. Furthermore, *ab initio* quantum mechanics calculations on the Ramachandran map for *N*-formylglycylamide demonstrate that there is an internal energetic reason for such preference[24].

Concerning the ω-amino acyl part, in all the 2/*n* nylons analysed the best conformational model, according to the available data, is that in which the –CONH–$(CH_2)_{n-1}$–CONH– segment adopts the $TST_{n-2}\bar{S}T$ sequence, where the initial and final *trans* torsion angles are those of the amide groups ($\omega = 180°$) and the two *skew* angles, φ' and ψ', are adjacent to amide groups. This conformation produces a 0° overall rotation with *n* odd, as in nylon 2/3 and nylon 2/5, and 180° with *n* even, as in nylon 2/6. Likewise the most satisfactory model[22] for the nylon 2/3/3 shows the same local conformation in the two β-alanyl segments as nylon 2/3 in its two β-alanyl segments. The resulting helical conformations are three-fold for nylon 2/3, 2/5 or 2/3/3, and six-fold for nylons 2/6 and 2/12, in exact correlation with the observed morphology of their single crystals.

This helical conformation is entirely compatible

with a random arrangement of chains running up and down interconnected through a three-dimensional network of hydrogen bonds. As a result, the chain $-CONH-(CH_2)_{n-1}-CONH-$ cannot keep an all-*trans* conformation. The *skew* conformation is also present in the γ-form of nylons, like nylon 7,7[25] ($TST_6\bar{S}TST_4\bar{S}$) or nylon 6[26] ($TST_4\bar{S}T$). Both in γ nylons and Δ nylons, those torsion angles introduce a 100–120° twist between the plane of the amide groups and the average plane of the methylene zigzag. Furthermore, with this local arrangement, the amide group planes in Δ nylons are tilted 30–35° with respect to the helix axis. This is also found both in the polyglycine II and the γ nylon structures. The most plausible explanation is in the fact that all these nylons make hydrogen bonds between chains at the same relative level in the crystal structure (with hexagonal or pseudo-hexagonal unit cells). The α and β forms of nylons are characterized by fully extended chains and consequently the amide planes are aligned with the chain axis. With such an arrangement the neighbouring molecules need to be displaced along the chain direction to make hydrogen bonds. For example in nylon 6,6 the vertical displacement between two adjacent molecules is 1.2 Å and the resulting unit cell is triclinic[1], with a characteristic unit cell angle of 77°.

CRYSTALLINE HABIT

The Δ model for the 2/*n* nylons is fully compatible with the observed morphology of lamellar single crystals obtained from solution. When *n* is even, the space group symmetry of the model is $P6_522$ or $P6_122$ and the expected morphology for single crystals is hexagonal, as observed in nylon 2/6[8] and 2/12[12]. When *n* is odd, the space group symmetry of the model is $P3_121$ or $P3_221$ and the expected morphology in single crystals would be triangular or hexagonal-like depending on the actual relative growth speed of two sets of non-symmetrical crystal faces. An approximately triangular morphology has in fact been observed in nylons 2/3[6], 2/3/3[9] and 2/5[11].

In a very qualitative way we can also propose simplified models for the homogeneous nucleation and crystal growth of single crystals of 2/*n* nylons. The most developed faces will be those with lowest growth speed, and in polyamides such faces are usually parallel to the hydrogen-bonding directions. In 2/*n* nylons the planes that contain hydrogen-bonding directions are $\{10\bar{1}0\}$ and $\{01\bar{1}0\}$, which are equivalent in hexagonal symmetry and in $P3_121$ and $P3_221$ space groups. Planes perpendicular to the hydrogen-bonding directions are $\{11\bar{2}0\}$ and $\{2\bar{1}\bar{1}0\}$, also equivalent in true hexagonal symmetry but not equivalent in the trigonal space groups $P3_121$ and $P3_221$.

With *n* even, the expected morphology will be hexagonal, the $\{10\bar{1}0\}$ being the most developed faces. It is easy to generate a simplified model for the growth of one hexagonal single crystal of this kind of nylon, initiated by spiral nucleation (*Figure 6*). The folding directions are parallel to the most developed faces and the hydrogen bonds are formed in the expected directions. The whole crystal will then contain chains running both up and down, randomly distributed, giving rise to the statistical lattice of $P6_522$ or $P6_122$, which has been used in the analysis of the models.

With *n* odd, two families of planes, $\{10\bar{1}0\}$ and $\{01\bar{1}0\}$, contain the hydrogen-bonding directions but the observed morphology is not hexagonal. On the other hand, $\{10\bar{1}0\}$ and $\{01\bar{1}0\}$ faces are related by a two-fold axis perpendicular to the main three-fold axis, and for that reason they cannot give rise to a triangular habit. According to the position of the two-fold axes, the faces with lowest indices compatible with triangular morphologies are $\{11\bar{2}0\}$ or $\{2\bar{1}\bar{1}0\}$, but these planes are not appropriate for chain folding. In a growth model such as that depicted in *Figure 6*, the polymer molecules fold themselves in zigzag mode developing essentially one of two families of faces, in this example $\{11\bar{2}0\}$, whereas the other family is not observed. In this growth model the most developed faces are strictly parallel to neither the chain-folding directions nor the hydrogen-bonding directions, but instead are parallel to their propagation directions. According to this model the most developed faces in the 2/*n* nylons with *n* odd will be more irregular than the faces from crystals following the model with *n* even

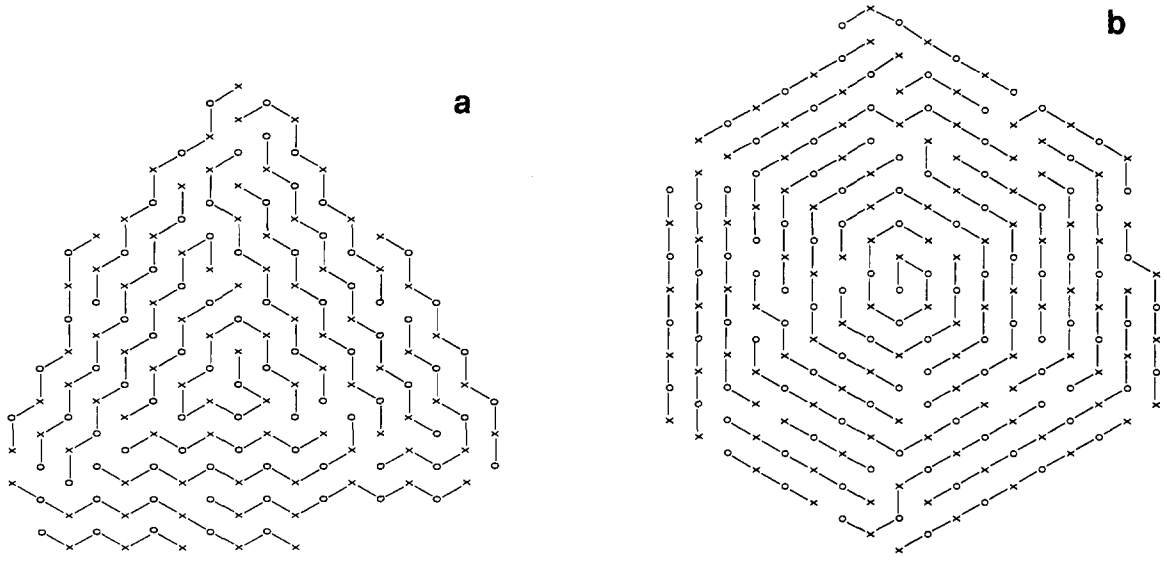

Figure 6 Models of crystal growth for nylons 2/*n* in their Δ form: (a) nylons 2/*n* with *n* odd form triangular lamellae that macroscopically show serrated edges; (b) nylons 2/*n* with *n* even give rise to hexagonal morphology and smooth surfaces

(*Figure 6*). The experimentally observed morphology is consistent with this behaviour: single crystals of nylon 2/6 and 2/12 are nicely defined with well developed faces[8,12], whereas single crystals of nylon 2/3[7], nylon 2/3/3[9] and nylon 2/5[11] have serrated edges.

Finally, we should note that the actual symmetry of the lamellar crystals cannot be truly hexagonal, since they are rather thin, about 40 Å in nylon 2/12[12], for example. Since the height of a monomer unit is 18.8 Å, it is not possible to fit the six units required by the hexagonal symmetry in the thickness of the crystal. Since three different directions of hydrogen bonding already appear with only two monomer units, these polymer crystals should be considered as pseudo-hexagonal. This fact explains why the crystals observed[12] seldom show a perfect hexagonal shape[8].

CONCLUSION

It has been shown that in glycine copolymers this residue induces a crystalline structure with hydrogen bonds running in three different directions; the standard structure of nylons with parallel sheets of hydrogen-bonded molecules is no longer present. Thus the mechanical properties of nylons will be strongly modified by the presence of glycine residues; this aspect is presently under investigation.

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