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Mesomorphic Form (β) of Nylon 6

Finizia Auriemma,* Vittorio Petraccone, Lidia Parravicini, and Paolo Corradini

Dipartimento di Chimica, Università degli studi di Napoli, via Mezzocannone, 4 80134 Napoli, Italy

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ABSTRACT: The structure of poly (ϵ-caprolactam) (nylon 6) in the β mesomorphic form is here examined. The comparison of the diffraction intensity, calculated on modeled structures, with the experimental profiles, collected by us through an automatic diffractometer, is presented. This analysis has put into evidence the following limiting structural features. (a) The β form of nylon 6 is made of small mesomorphic aggregates of chains (where the matter scatters coherently) with axes arranged in a hexagonal lattice ($a = b = 0.48$ nm; $\gamma = 120°$). (b) The chains have disordered conformations (and do not have a definite chirality, as it is the case for the 2_1 helices in the α and γ forms) with the $-CH_2-$ chains close to nearly all-*trans* (antiperiplanar) and the two dihedral angles adjacent to the amide bond, ±120°) to antiperiplanar (180°). This notwithstanding, the chains are straight and extended. As a result, the mean chain periodicity is close to 0.835 nm. (c) The H-bonds are formed along lines in the [100], [010], and [1$\bar{1}$0] directions; they force neighboring chains within the small mesomorphic aggregates to adjust their conformation in such a way that nearly 100% of hydrogen bonds are always formed, in agreement with the IR data. In the case of the α and γ more ordered forms of nylon 6, such lines are all in a unique direction, leading to hydrogen-bonded sheets (parallel to the chain axis) of enantiomorphous anticlined, alternately up and down chains (in the α form) or of isomorphous isoclined chains, (in the γ form). (d) As a consequence, since the amide groups lie all at nearly the same height along z, in the β form of nylon 6 the lines of hydrogen bonds lie in layers perpendicular to the chain axis and have the same direction within each layer. However, consecutive layers along z may have the lines of H-bonds which are not parallel (e.g., occasionally rotated by +120 or −120° instead of the "normal" 180°). (e) In the β form of nylon 6, disorder arises also from the random substitution of up and down chains in the lattice positions.

Introduction

Although the X-ray structures of the two stable crystalline forms of poly(ϵ-caprolactam) (nylon 6), the so-called α and γ forms, have been well-known for a long time,[1,2] the structure of a third form, called β, which appears as partially disordered (mesomorphic) from the X-ray diffraction patterns, needs, in our opinion, further clarification.

More than 40 years ago, Holmes et al.[1] identified the presence of another "crystalline" form (β) in samples of nylon 6 which were prevailingly in the α form. Later on, the β form was obtained in the absence of the α form in melt spun fibers by Ziabicky.[3] A few years later, Tsuruda et al.[4] obtained for the first time the pure γ form, by treating fibers in the α form with I_2−KI water solutions.

In this context we will conventionally call "up" or "down" chains those nylon 6 chains with the C(=O)- - -N bonds directed toward a positive or a negative chain axis direction, respectively. According to the standard nomenclature, two chains which are both up or both down are indicated as isoclined; if not, they are indicated as anticlined.[5] We recall that, in the α and γ crystalline forms of nylon 6, the chains are organized in sheets where hydrogen bonds are formed. As shown in Figure 1, hydrogen bonds are between anticlined chains in the α form,[1] and are between isoclined chains in the γ form.[2] In the γ form, sheets of all up or all down chains alternate[2] (see Figure 1). In both of the crystalline polymorphs, chains are 50% up and 50% down. Both structures were described in terms of monoclinic cells assuming b as the unique axis, parallel to the chain axis. Also, in both forms the chain symmetry corresponds to the $s(2/1)$ line repetition group,[5] and the period of the chain includes two monomeric units (see Figure 1): according to ref 1 in the α form the chains are in a all-*trans* planar conformation and correspond to a periodicity of 1.72 nm; according to ref 2 in the γ form the backbone dihedral angles are still in a *trans* conformation, but those adjacent to the amide bonds are around

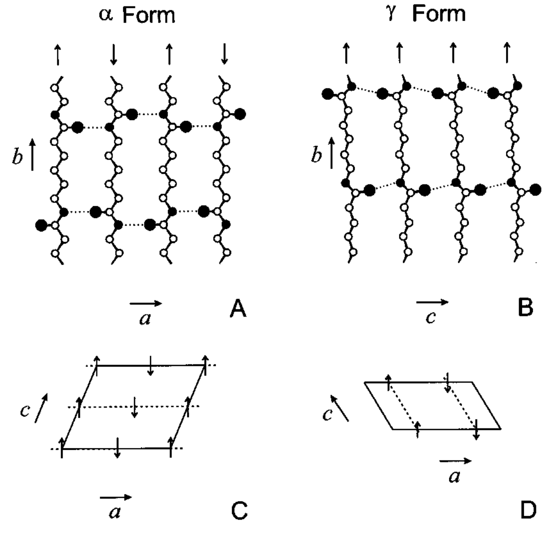

Figure 1. Ordered model structures for the α and the β forms of nylon 6 as proposed in refs 1 and 2, respectively. The unit cells are monoclinic, and b (coinciding with the chain axes) is the unique axis ($a = 0.956$ nm, $b = 1.724$ nm, $c = 0.801$ nm, and $\beta = 67.5°$ for the α form; $a = 0.933$ nm, $b = 1.688$ nm, $c = 0.478$ nm, and $\beta = 121°$ for the γ form). Projections are shown in the ab plane of a sheet of chains, where the hydrogen bonds are formed for the α form (consecutive chains are anticined) (A) and for the β form (the chains are isoclined) (B). The unit cells are shown in the ca projection for the α (C) and the γ (D) forms of nylon 6. The arrows distinguish between up and down chains, and the dashed lines are traces of sheets of hydrogen bonds. In the γ forms sheets of all up and all down chains alternate.

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120° and the periodicity of the chains (lower than in the α form) corresponds to 1.688 nm.

As far as the γ form is concerned, this gives X-ray diffraction patterns similar to those obtained from fibers in the β form except for the fact that the β form is lacking off-meridional and off-equatorial reflections, indicating that disorder occurs to some extent. Ziabicki,[6] from the analysis of X-ray diffraction patterns of oriented (obtained by melt spinning at 3500 m/min) and unoriented (obtained by quenching from the melt) samples of nylon 6 in the β form, suggested a model structure in which chains with a repeating distance of 0.86 nm per monomeric unit are packed in a pseudohexagonal lattice with $a = 0.48$ nm and are randomly rotated around the chain axis; the hydrogen bonds form in all directions, as a consequence (see Figure 20 of ref 6). Up to now, this is the only model of packing proposed in the literature for the β form. The model and the random rotational disorder of the chains around the chain axis do not explain the experimental observation that hydrogen bonds are formed almost 100% as it results from the literature.[7,8] The present paper is aimed at clarifying the nature of the mesomorphic form of nylon 6 through analysis of the X-ray diffraction data, geometrical and energetic considerations on the chain conformation and packing, and Fourier transform calculations on the resulting models.

Experimental Section

Fiber samples of nylon 6, in the β mesomorphic form, were obtained by melt spinning at rates of 3280, 3700, and 4000 m/min and were furnished to us by SNIA of Pisticci (Matera, Italy).

The X-ray photographs were obtained by using a flat camera with Ni-filtered Cu Kα radiation. The samples were identified as in the β form because they present X-ray diffraction photographs lacking off-equatorial and off-meridional reflections.

The X-ray diffraction patterns were obtained by using a Nonius automatic CAD4 diffractometer, with Ni-filtered Cu Kα radiation and were collected always maintaining an equatorial geometry. The measurements have been performed along the equator (i.e. for $\zeta = 0$) in the range $0 < \xi < 9.0$ nm^{-1} at intervals of 0.04 nm^{-1} and along the meridian (i.e. for $\xi = 0$) in the range $0 < \zeta < 9.0$ nm^{-1} at intervals of 0.04 nm^{-1}.

The Lorentz and polarization (Lp) correction, when used (Figures 3B and 4B), is, according to the diffraction geometry, $Lp = (1 + \cos^2 2\theta)/\sin 2\theta)$. It is worth noting that for polycrystalline uniaxially oriented samples it is not sound to compare quantitatively the so-measured intensities of meridional and nonmeridional reflections, since we do not account, in this way, for the real portion of matter contributing to the diffraction with varying ξ, for ξ values close to zero. In this paper we are not concerned about this comparison; however, this is because we mostly are interested in the experimental diffraction intensity distribution along the meridional profile, since this is the only source of information as far as a possible pattern of disorder in the β form of nylon 6.

X-ray Diffraction Analysis

The X-ray diffraction photograph of a fiber, obtained in the β form by melt spinning at a rate of 3280 m/min, is shown in Figure 2 as an example. The X-ray diffraction pattern collected for the other fiber samples of nylon 6 in the β form are very similar. Only equatorial reflections (prominent is the one centered at $\xi = 2.4$ nm^{-1}) and meridional reflections (prominent is the one at $\zeta = 1.2$ nm^{-1}) are apparent.

Figure 2. X-ray diffraction photograph, collected on a flat camera, of a nylon 6 sample in the β mesomorphic form (commercial fiber spun at 3280m/min).

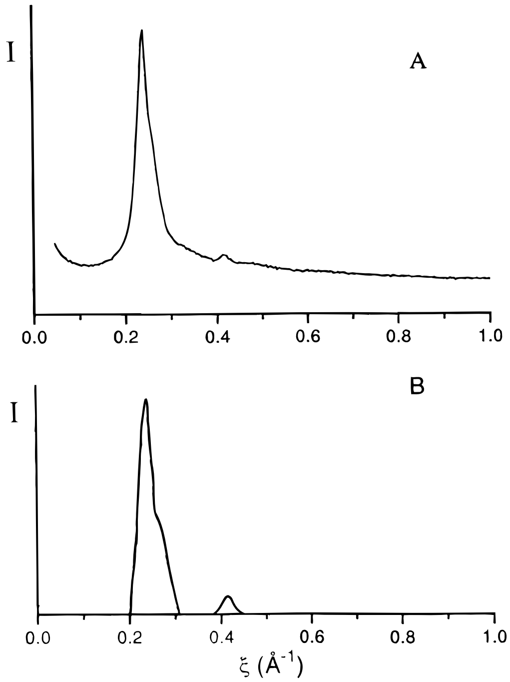


Figure 3. X-ray diffraction profile along the equator of a nylon 6 sample in the β mesomorphic form (commercial fiber spun at 3280 m/min) before (A) and after (B) the Lp correction and the subtraction of the continuous scattering.

Figures 3A and 4A show the equatorial and the meridional diffraction scans, respectively, of the melt spun fiber at 3280 m/min in the β form. The corresponding intensity scans after the subtraction of the continuous scattering and the Lp correction are shown in Figures 3B and 4B. A very intense reflection along the equatorial line is present, at $\xi = 2.4$ nm^{-1}, together with a weaker one, centered at $\xi = 4.1$ nm^{-1} (Figure 3): they can be indexed as (100) and (110) of a pseudohexagonal cell with $a = b = 0.480 \pm 0.005$ nm ($\gamma = 120°$). Also, several meridional reflections are present which can be be indexed as (00l) with $1 \leq l \leq 7$ if a mean periodicity along the chain axis equal to $c = 0.835 \pm 0.01$ nm is assumed (Figure 4). The relative maximum height of (001) and (007) reflections with respect to the intensity of the (002) reflection after the corrections are 4.5 and 1, respectively, when averaged for all the fiber samples (they will be compared with the corresponding calculated quantities for the considered models, in the

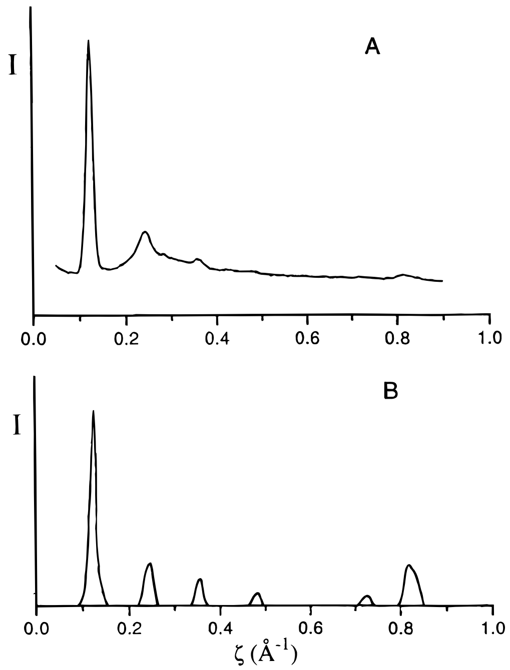


Figure 4. X-ray diffraction profile along the meridian of a nylon 6 sample in the β mesomorphic form (commercial fiber spun at 3280 m/min) before (A) and after (B) the *Lp* correction and the subtraction of the continuous scattering.

following). In the β form of nylon 6, the long-range order is indicated only as far as the positioning of the chain axes positioned at the nodes of a hexagonal lattice and the mean chain periodicity are concerned. The substantial absence of diffraction off the equator and off the meridian indicates that a high degree of conformational disorder is probably present. We also observe that the half-height widths of the meridional reflections (in particular for (001), (002), and (007), which are the most intense ones) increase with increasing diffraction order, as in a paracrystalline model system.[9]

Possible Conformations and Packing Models for the β Form

From the X-ray diffraction data it is seen that the mean chain periodicity in the β form corresponds to $c = 0.835$ nm, i.e. to about $^1/_2$ the chain periodicity in the γ form. In both cases the value of c corresponds to nearly extended conformations.

In accordance with this indication, we have tried to see whether it was possible to model chains of nylon 6 in the β form with disordered, but straight and extended, conformations. In the short range, the conformations of the chains should be locally similar to those in the 2_1 helices of the α and γ forms but should have lost, in the long range, any definite chirality.

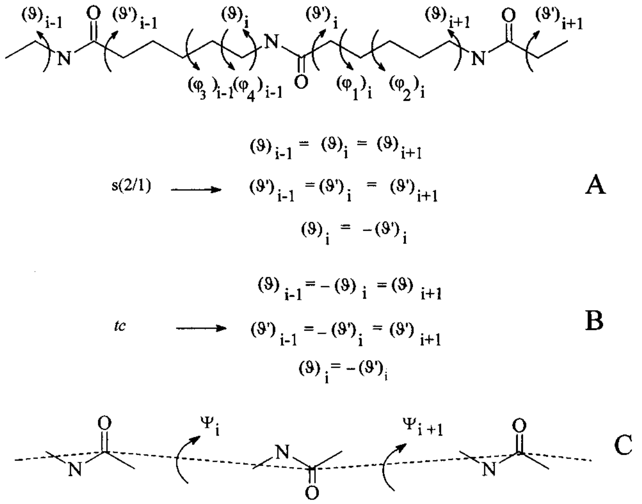
The internal coordinates for the model chains have been chosen in conformity with the following geometrical and energetic considerations.

For the bond lengths and the valence angles standard values of 0.153 nm and 112° have been used for the carbon atoms of the aliphatic portion of the chain. The values for the amide groups have been taken from the literature.[10] All the geometrical parameters are listed in Table 1.

Table 1. Geometrical Parameters for the Polyamide Chains[10]

	bond dist (nm × 10)		bond angle (deg)
C—C(=O)	1.52	C—C(=O)—N	116
C=O	1.23	C—C=O	121
C(=O)—N	1.33	O=C—N	123
N—C	1.45	C(=O)—N—C	122
C—C	1.53	N—C—C	112
		C—C—C	112

Scheme 1



As far as the torsion angles are concerned, the amide groups have been assumed to be rigid and *trans* planar.[10] The torsion angles of the bonds adjacent to the amide bond, i.e., θ (C—C—N—C(=O) and θ' (N—C(=O)—C—C) (see Scheme 1), have low torsion barriers which are 3-fold.[11] These angles have been considered to be variable (in absolute value) in the range 120—180°, according to structural data analysis performed on a variety of amide compounds.[10] Small displacements from the *trans* state for the dihedral angles of the aliphatic portions of chain have been considered.

Model Chains. Extended conformations for nylon 6 are easily constructed when pairs of consecutive dihedral angles $(\theta)_i$ and $(\theta')_i$ (see Scheme 1) have opposite sign. The following geometrical analysis is mainly made for such kind of conformations, starting from the "regular" model chain conformations of the ordered α and γ forms.

The chain conformation for the ordered γ form as well as for the α form of nylon 6 as reported in the literature[1,2] corresponds to chiral 2/1 helices. The angles θ and θ' follow each other along the chain being equal in absolute value, but having opposite sign, according to Scheme 1A. For the α form the chain periodicity corresponds to $c = 1.72$ nm and $|\theta| = |\theta'| = 140°$ (see for instance ref 12); for the γ form the chain periodicity corresponds to $c = 1.688$ nm and $|\theta| = |\theta'| = 120°$. The dihedral angle among the planes of consecutive amide groups along the chain (ψ in Scheme 1C) is equal to 180° whatever the value of $\vartheta (= -\vartheta')$.

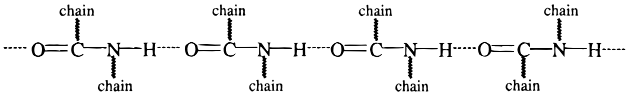
Another set of highly extended, still ordered chain conformations for nylon 6, could correspond to the line repetition group *tc*. Also in this case the dihedral angles $(\theta)_i$ and $(\theta')_i$ are all equal in absolute value and the pairs of consecutive dihedral angles of the kind $(\theta)_i$, $(\theta')_i$ have opposite signs, but the pairs of the kind $(\theta')_i$, $(\theta)_{i+1}$ have the same sign according to the pattern of Scheme 1B. Consecutive planes of amide groups would form an angle Ψ (see Scheme 1C) which is a function of the values of $(\vartheta)_i$ $(=(\vartheta')_{i-1})$. For instance, for $|\vartheta| = 145°$, $\Psi = \pm 120°$ and $c = 1.72$ nm as in the α form, whereas for $|\vartheta| = 109°$, $\Psi = \pm 60°$ and $c = 1.67$ nm as in the γ form. These conformations are unimportant as ordered model chains for nylon 6 in the crystalline α and γ forms, because they correspond to a higher conformational energy than those in $s(2/1)$ symmetry, owing to the unfavorable dipole−dipole interactions among consecutive C=O groups, but can be important as local conformations to model disordered chains for the β form.

Starting from the "regular" models described above, other highly extended regular or irregular chain conformations may be constructed.

A set of perfectly straight but conformationally irregular chains may be obtained if the conditions that all the dihedral angles $(\theta)_i$'s ($(\theta')_i$'s) be equal or have equal moduli but opposite sign is relaxed, and only the condition that the $(\theta)_i$'s be equal to $-(\theta')_i$ is maintained. If this latter condition is relaxed, the chains would become slightly curved, unless slightly correlated and low-energy adjustments are made on the valence and internal rotation angles of the $-CH_2-$ chains, in order to maintain the chain axis straight.[13] It is worth noting that $(\theta')_i \neq (\theta)_{i+1}$ may lead to $(\Psi)_i \neq 180°$, with the result that the C=O bonds would point in all directions, cylindrically distributed around the chain axis. As we shall see, in the following packing models, we shall restrict the values of $(\Psi)_i$ to $180° \pm n60°$ (n integer).

Packing Models. In this paper we have modeled and propose in the following a packing model for the β form, which is based on the hypothesis that the chain conformations are not ordered (not "regular"), yet their axes are straight and parallel, ordered in a pseudohexagonal lattice, and the hydrogen bonds are fully maintained.

In Figure 5 a packing model for nylon 6 in the β form is indicated as an example. The chain axes are placed at the nodes of a bidimensional hexagonal lattice. The H-bonds are formed along lines


$$\cdots\mathrm{O{=}\overset{\overset{\text{chain}}{|}}{C}-\underset{\underset{\text{chain}}{|}}{N}-H}\cdots\mathrm{O{=}\overset{\overset{\text{chain}}{|}}{C}-\underset{\underset{\text{chain}}{|}}{N}-H}\cdots\mathrm{O{=}\overset{\overset{\text{chain}}{|}}{C}-\underset{\underset{\text{chain}}{|}}{N}-H}\cdots\mathrm{O{=}\overset{\overset{\text{chain}}{|}}{C}-\underset{\underset{\text{chain}}{|}}{N}-H}\cdots$$

in the [100], [010], and [1$\bar{1}$0] directions (only two of them are shown in the figure); they force neighboring chains within the small mesomorphic aggregates to adjust their conformation in such a way that nearly 100% of hydrogen bonds are always formed, in agreement with the IR data[7,8] (in the case of the α and γ more ordered forms of nylon 6, such lines are all in a unique direction). As a consequence, since the amide groups lie all at nearly the same height along z, in the β form of nylon 6 the lines of hydrogen bonds lie in layers perpendicular to the chain axis and have the same direction within each layer; however, consecutive layers along z may have the lines of H-bonds which are not parallel (e.g., occasionally rotated by +120° or −120° instead of the "normal" 180°).

The disordered chains of the kind described in the preceding section are suitable for such modeling provided that (i) the angles $(\Psi)_i$ are restricted to assume values equal to $180° \pm n60°$ ($n = 0,1,2$), (ii) the mean chain periodicity c is kept close to 0.835nm, (iii) the conformational disorder is correlated in neighboring chains, in order that 100% of H-bonds are formed.

With reference to point (i), if we want $\Psi_i = 180°$ (neighboring lines of hydrogen bonds are kept parallel), while maintaining the aliphatic chain *trans* planar, then $(\theta')_i + (\theta)_{i+1} \approx 0°$; if we want $\Psi_i = \pm 120°$ (neighboring lines of hydrogen bonds are at an angle of 60°), still maintaining the aliphatic chain *trans* planar, then $(\theta')_i + (\theta)_{i+1} \approx \pm 70°$. We think that conformations with $\Psi = 180°$ should be energetically favored, since they lead the dipole moments associated to the C=O (N−H) bonds to point in opposite directions

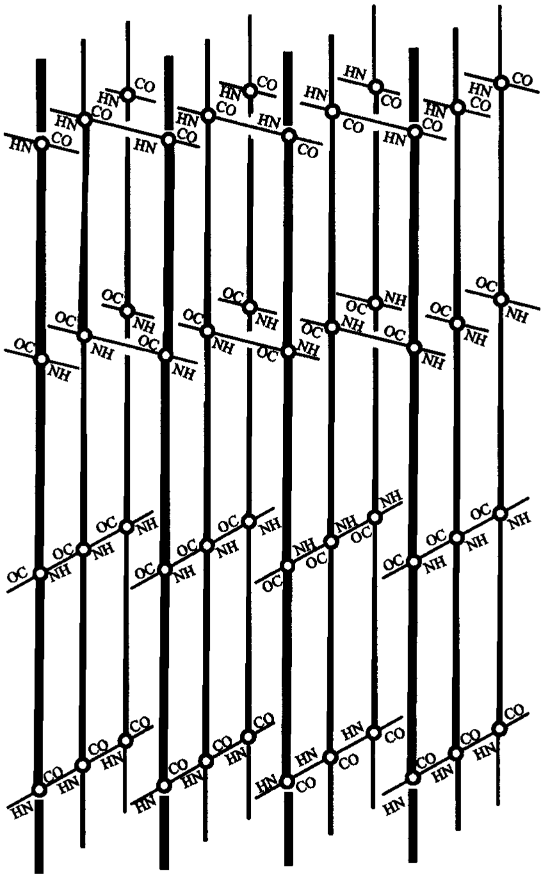


Figure 5. Possible packing model for nylon 6 in the β form. The chain axes are placed at the nodes of a bidimensional hexagonal lattice. The H-bonds are formed along the lattice lines [100], [010], and [1$\bar{1}$0]. Only two of them are shown.

While not exhaustive, it may be of interest to discuss some more ways to build low-energy conformations having $\Psi_i = \pm 120°$, in particular some of them, that lead to small deviations from 180° of the dihedral angles ($(\varphi_1)_i$, $(\varphi_2)_i$, $(\varphi_3)_i$, and $(\varphi_4)_i$; see Scheme 1) in the aliphatic chains. Under the condition that $\Psi_i = \pm 120°$ and the further condition that $(\theta')_i = -(\theta)_{i+1}$, all of the values of φ should be around +165° (or −165°); under the condition that $\Psi_i = \pm 120°$ and the further condition that $(\theta')_i = (\theta)_{i+1} = \pm 120°$ all φ's should be around +167 or −167°; under the condition that $\Psi_i = \pm 120°$ and the further condition that $(\theta')_i = 120°$ (−120°) and $(\theta)_{i+1} = 150°$ (−150°) or vice versa, all φ's should be around +175° (−175°).

In Figure 6 a possible packing model for nylon 6 in the β form is presented, showing the formation of H-bonds along lines which are parallel in planes perpendicular to the chain axis, but not necessarily parallel among different planes. The conformations are adjusted, as discussed above, in such a way that nearly 100% of hydrogen bonds are always formed, and the mean repeating distance per monomeric unit is ≈0.835 nm. A further kind of disorder arises from the possibility of random substitution in the lattice positions of up and down chains. This kind of disorder is easily allowed for in the proposed model structure, as shown in Figure 6.

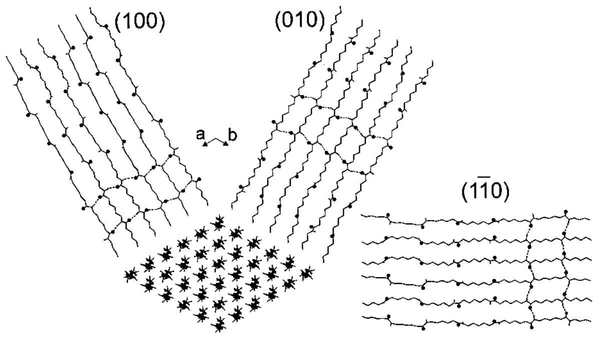


Figure 6. Projections of a possible packing model of nylon 6 chains in the β mesomorphic form showing the concomitant formation of hydrogen bonds in three directions. The lines of H-bonds belonging to consecutive planes perpendicular to the chain axes, run parallel in set of two, just as an example.

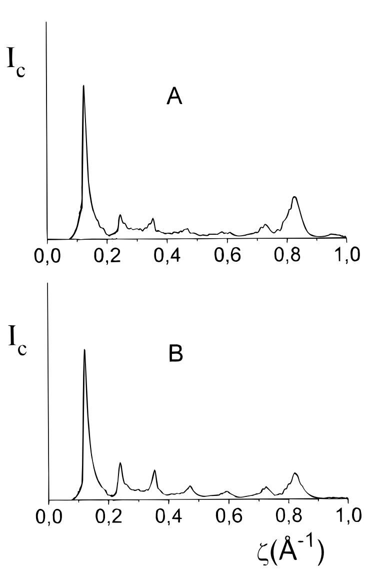


Figure 7. Calculated X-ray diffraction profiles along the meridian for model structures of nylon 6 chains in the β form when only conformational disorder is present (all chains are isoclined) (A) and when conformational disorder and disorder in the substitution of up/down chains in the lattice positions are both present (B). In the calculations $1/\gamma = 5$, $u^2{}_\zeta = 0.04$ nm^{-1}, and $B = 0.02$ nm$^{-2.}$

Fourier Transform Calculations

The calculated X-ray diffraction profiles to be presented and discussed are performed along the meridional profile only, i.e. along the (00*l*) reciprocal line, with *l* being a continuous variable, since the experimental diffraction intensity distribution along the meridional profile is the only source of information as far as a possible pattern of disorder in the β form of nylon 6 is concerned.

The square modulus of the structure factor (I_c), to be compared with the experimental X-ray diffraction data (I), was calculated for bundles of chains which are conformationally disordered. The possibility of random substitution of up and down chains in the lattice positions was also taken into account. Thus, we have calculated the diffraction profiles for such bundles of chains as the sum of the products of three terms. The first term accounts for the interference between couples of atoms

$$f_i f_j \exp(-2\pi i\zeta(z_i - z_j)) \qquad (1)$$

The second term accounts for the finite length of the chains in the bundle and is of the type

$$(1 - 2\gamma)^{O(|z_i - z_j|/c)} \qquad (2)$$

The third term accounts for the paracrystalline disorder (and leads to broaden the meridional maxima, with the increase of ζ) and is of the type (see ref 14, see also ref 15)

$$\exp(-2\pi^2\zeta^2 u^2\zeta|z_i - z_j|/\Delta) \qquad (3)$$

In the sum, the interference of a single monomeric unit in a chain (atomic coordinates z_i; atomic scattering factors f_i) with every other chain in the lattice (atomic coordinates z_j; atomic scattering factors f_j) is considered. This is equivalent to the supposition that the dimensions of the bundles are so large in the directions perpendicular to the chain axis that they do not significantly affect the calculated X-ray diffraction pattern along the meridian. The dimensions of the bundles parallel to the chain axes are taken as smaller, instead, and $1/\gamma$ represents the average number of monomeric units of the chains. According to eq 2, the distribution of the chain lengths is supposed to be of Bernoulli type,[16] O is an operator which takes only the integral part of the ratio $|z_i - z_j|/c$, and c is the mean chain periodicity. In eq 3, $u^2{}_\zeta$ represents the mean square displacement of the atomic coordinate z and Δ is a parameter having the dimension of a distance scaling $u^2{}_\zeta$.

The average value of I_c was determined by iterating the calculation a number of times, each time choosing the reference monomeric unit at random and positioning the other chains along z, in such a way as to have the amide groups at the same height as the reference unit.

The atomic coordinates of the chains (with mean chain periodicity c equal to 0.835 nm, i.e., equal to the mean chain periodicity of nylon 6 in the β form) were determined by introducing conformational disorder according to the rules given in the preceding paragraph.

Thermal disorder was accounted for by multiplying the sum of the interference terms between each couple of atoms by the Debye factor, i.e., $D = \exp(-B_\zeta\zeta^2/2)$.

In the reported Fourier transform calculations $1/\gamma$ is set equal to 5 (the coherent length of the β aggregate of chains along $\boldsymbol{z}$ comprises not more than 5−6 monomeric units, as estimated from the half-height width of the first reflection in Figure 4A through the Sherrer formula.[17] The value of $u^2{}_\zeta/\Delta$ is set equal to 0.04 nm, and the thermal factor B_ζ is equal to 0.02 nm^2.

Results of the Calculations, Discussion, and Concluding Remarks

Figure 7 plots examples of the meridional profiles calculated as discussed in the previous paragraph in the case the chains are supposed isoclined (Figure 7A) and in the case the chains are supposed 50% up and 50% down (Figure 7B).

The presence of the conformational disorder alone already accounts for the main features of the experimental pattern (compare Figure 7A with Figure 4B), although the relative maximum height of (001) and (007) reflections with respect to the intensity of the (002) reflection are ≈6 and ≈1.6 respectively, i.e., higher than the experimental ones (≈4.5 and ≈1). The agreement with the experimental pattern is improved also as far as these latter aspects are concerned, when disorder arising from the random substitution of up and down chains in the lattice position is also included (compare Figure 7B with Figure 4B).

It is worth noting that the agreement with the experimental data is obtained only when the amide groups are placed at nearly the same height along z, in such a way that hydrogen bonds can be properly formed.

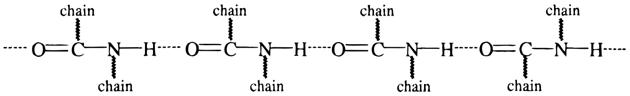
It is also appropriate to note that the only experimental diffraction profile along the meridian could be likewise reproduced also with other models; i.e., if the chains are assumed to be in a regular $s(2/1)$ helical conformation, provided that disorder in the substitution of up and down chains in the lattice sites is included. The validity of the assumption that the conformational disorder is present is based, however, on the appearance of the complete experimental diffraction pattern, i.e., on the absence of off-equatorial and off-meridional reflections.

In summary, the X-ray diffraction intensity data of nylon 6 samples in the β mesomorphic form are in agreement with the following structural features.

(1) The β form of nylon 6 is made of small mesomorphic aggregates of chains with axes arranged in a hexagonal lattice ($a = b = 0.48$ nm; $\gamma = 120°$).

(2) The chains have disordered conformations, however (and do not have a definite chirality, as is the case for the 2_1 helices in the α and γ forms[18]), with the $-CH_2-$ chains close to nearly all-*trans* (antiperiplanar), and the two dihedral angles adjacent to the amide bond, θ and θ', spanning a range of (absolute) values from anticlinical (±120°) to antiperiplanar (180°) (see ref 5). This notwithstanding, the chains are straight and extended, and as a result, the mean chain periodicity is close to 0.835 nm.

(3) Because of the presence of conformational disorder, the H-bonds are formed along lines



$$\cdots\mathrm{O{=}\overset{\overset{chain}{|}}{C}{-}\underset{\underset{chain}{|}}{N}{-}H}\cdots\mathrm{O{=}\overset{\overset{chain}{|}}{C}{-}\underset{\underset{chain}{|}}{N}{-}H}\cdots\mathrm{O{=}\overset{\overset{chain}{|}}{C}{-}\underset{\underset{chain}{|}}{N}{-}H}\cdots\mathrm{O{=}\overset{\overset{chain}{|}}{C}{-}\underset{\underset{chain}{|}}{N}{-}H}\cdots$$

in the [100], [010] and [1$\bar{1}$0] directions. They force neighboring chains within the small mesomorphic aggregates to adjust their conformation in such a way that nearly 100% of hydrogen bonds are always formed, in agreement with the IR data.[7,8] As a consequence, and since the amide groups lie all at nearly the same height along z, in the β form of nylon 6 the lines of hydrogen bonds lie in layers perpendicular to the chain axis and have the same direction within each layer, but consecutive layers along z may have lines of H-bonds which are not parallel (e.g., occasionally rotated by +120° or −120° instead of the "normal" 180°).

(4) In the β form of nylon 6, disorder is present also for the occurrence of random substitution of up and down chains in the lattice positions.

The disorder in the mesomorphic β form of nylon 6 is related to the history of the sample, whereby nonequilibrium situations are kinetically frozen in the fibers, at the end of the drawing process.

As a concluding remark, the extent of ordered features in the β form of nylon 6 is, in our opinion, as follows: (i) the longer range of order is probably connected with the parallelism and the pseudo-hexagonal arrangement of the chain axes; (ii) an intermediate range of order may be referred to the parallelism of lines of hydrogen bonds in layers perpendicular to the chain axis c; (iii) an even shorter range of order refers to the piling up of such layers along c. At variance with the case of the ideal ordered structure of the γ form of nylon 6, along each chain of nylon 6 in the β form the extent of order in the permanence of chirality is probably very low.

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(13) For example, a chain of carbon atoms having identical bond lengths b and torsion angles θ, with these latter slightly displaced from 180°, will have the *uneven* carbon atoms exactly on a line if the bond angles τ are "correlated" in the sense of being slightly larger at the *even* positions (i.e., if the θ values are all equal to 170° (or −170°), and if τ_{2n+1} is tetrahedral ($\tau_{2n+1} = 109.47°$) then τ_{2n} will be 0.83° larger ($\tau_{2n} = 110.30°$)).

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(18) Chirality may be indicated in nylon 6 by negative (>180°) or positive (<180°) values of the torsion angles θ adjacent to the C=O bond. The 2_1 helices in the α and γ forms are chiral, with all "negative" or all "positive" θ angles. In the β form the "chirality" within each chain is maintained over very short ranges.

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