Structure and Morphology of Nylon 4 Chain-Folded Lamellar Crystals

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ABSTRACT: The structure and morphology of nylon 4 chain-folded lamellar crystals has been investigated using transmission electron microscopy (TEM), selected area electron diffraction, and X-ray diffraction. Solution-grown crystals are seen in the electron microscope in the form of sheaves with lathlike extremities. Electron diffraction patterns show the 0.44 (200) and 0.37 nm (020) reflections which are representative of the interchain distance within a hydrogen-bonded sheet and the intersheet distance, respectively, and are characteristic of the broader family of polyamides. The orientation of the electron diffraction patterns from individual lamellar crystals establishes that the polymer chains lie perpendicular to the lamellar surface and that the folding plane is parallel to the long axis of the crystal. Sedimented mats of the crystals were examined using wide-angle X-ray diffraction in a direction perpendicular to the lamellar normals. The X-ray diffraction patterns confirm that the nylon 4 chains are parallel to the lamellar normal. As a result of these findings and owing to the relatively high amide content of nylon 4, a unique mechanism for folding in nylons is proposed in which an amide group is incorporated in the fold, similar to that recently proposed for nylon 46. The fold exhibits similarity with the β-bend in proteins rather than with the previous folding mechanism for nylons in which the alkane segments are in the fold. The crystallographic unit cell is monoclinic with $a = 0.979$ (± 0.002) nm, $b = 0.831$ (± 0.002) nm, c (chain axis) = 1.225 (± 0.002) nm, and $\gamma = 117°$ and contains four chain segments or two sheet segments, similar to the unit cell of bulk nylon 6 and nylon 46. The effects of temperature on the lattice spacing show that the 200 and 020 reflections converge with increasing temperature but do not meet prior to the melting temperature, and two distinct reflections are observed up to the melt.

Introduction

There are many unanswered questions about the nature of the chain-folded structure of single crystals of polyamides, especially those nylons with a high amide content. The relationship between the crystalline structure of polyamide single crystals and the nature of the lamellar fold is still uncertain. A member of the nylon series with a high concentration of amide groups is poly(pyrrolidinone) or nylon 4. Unlike the more usual commercial nylons, such as nylon 6 or nylon 66, the melting of nylon 4 is accompanied by decomposition and depolymerization, thereby making this engineering thermoplastic difficult to process. The crystal structure of nylon 4, both in the bulk and from solution-grown crystals, has been previously reported.[1-4] X-ray fiber diffraction patterns[2] on uniaxially oriented monofilaments of nylon 4 show that two strong reflections exist at 0.42 and 0.36 nm, with the periodicity along the chain given as 1.225 nm. The crystal structure of nylon 4 is monoclinic with the staggered placement of the hydrogen-bonded sheets and the antiparallel direction of adjoining chains within the sheets. However, little attention has been paid to the nature of the polymer chains at the fold.

The morphology and crystal structure of single crystals of other polyamides have been the focus of numerous investigations but of particular interest with respect to this study are the structure of nylon 6[5] and nylon 46.[6] The X-ray diffraction patterns of nylon 6 have many features in common with those obtained for nylon 4. The two strong reflections occur at 0.44 and 0.37 nm. In the proposed model for the crystal structure of nylon 6, there is no conclusive evidence with regard to the nature of the fold, i.e., whether the alkane segments or amide groups reside in the fold. Recently, the structure and morphology of single crystals of nylon 46 have been investigated.[6] Electron diffraction patterns from the tips of the nylon 46 sheaves show two strong reflections at 0.44 and 0.37 nm, with the hydrogen-bonded sheets running parallel to the long direction of the crystal and the chains within these sheets lying normal to the lamellar surface. An entirely new folding mechanism was proposed, in which the chain-folded lamellae incorporate a complete amide group in the fold and have fold surfaces perpendicular to the chain direction, similar to the β-bend in proteins.[7-9]

In light of the recent investigations and the new chain folding mechanisms proposed for nylon 46, the morphology and chain-folded structure of single crystals of nylon 4 have been examined. These results are consistent with those from previous studies and show similar features in common with nylon 6 and nylon 46. Most importantly, the morphology of nylon 4 has been investigated in an attempt to understand the chain-folded structure of the lamellae, with specific interest in the direction of the polymer chains within each lamella and their relation to the fold surface.

Experimental Section

Single-Crystal Preparation. Solutions of nylon 4 in 1,4-butanediol (0.04% w/v) were prepared, and the crystals were grown isothermally at 150 °C after preheating to 195 °C for 1 h. Upon completion of the crystallization, the solution was hot-filtered with solvent at the crystallization temperature and cooled to room temperature, followed by repeated rinsing with methanol to remove the butanediol. The crystals remained in suspension in methanol until further use.

Electron Microscopy. Transmission electron microscopy specimens were prepared by placing drops of the crystal suspension onto carbon-coated grids. The solvent (methanol) was evaporated, and the crystals were shadowed with Pt/Pd to improve contrast for imaging the crystal morphology and to provide an internal calibration standard for electron diffraction. A JEOL 2000FX transmission electron microscope, operating at 200 kV, was used for both imaging and electron diffraction. To

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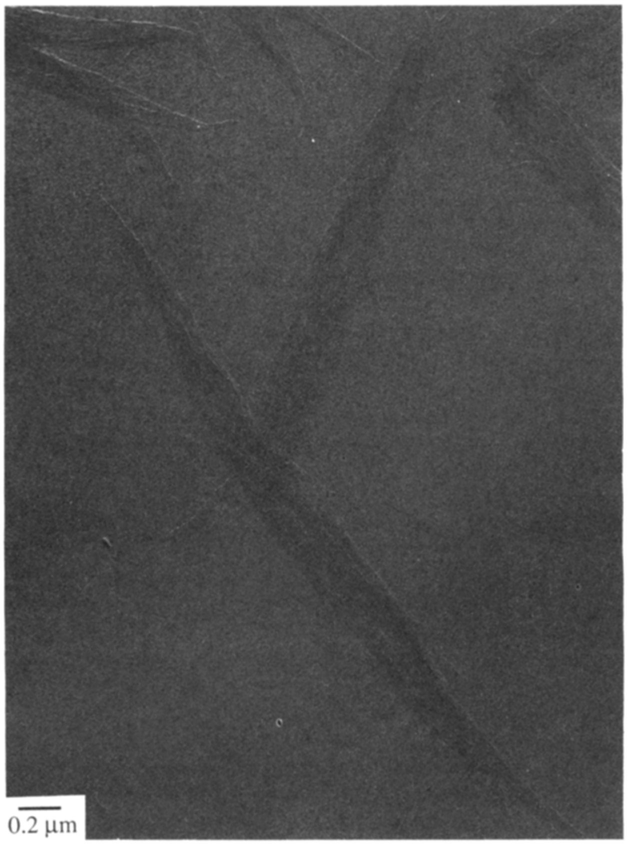
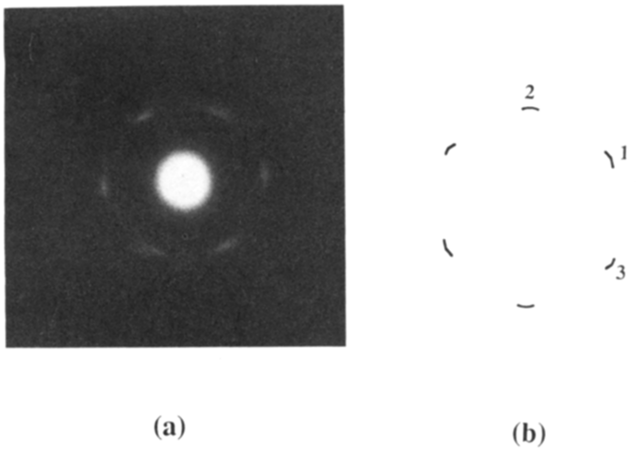


Figure 1. Transmission electron micrograph of sheaves of nylon 4 crystals shadowed with Pt/Pd.



(a) (b)

Figure 2. Selected area electron diffraction from crystals of nylon 4: (a) Electron diffraction pattern of nylon 4 taken at the tip of a sheaf. The diffraction ring is from the metal Pt/Pd shadowing. (b) Schematic representation of the observed reflections.

Table 1. Data from Electron Diffraction of Nylon 4

reflection no.	measd spacing (nm)	index
1	0.415	100
2	0.386	010
3	0.384	1$\bar{1}$0

obtain information on the effect of temperature on the lattice spacings, some crystal specimens were not shadowed. Instead, Pt/Pd was coated on the reverse side of the grid so as not to interfere with the heating process or subsequent changes within the crystals. A JEOL 100 CX transmission electron microscope, operating at 100 kV with a temperature-controlled specimen stage, was used in both image and electron diffraction modes.

X-ray Diffraction. Wide- and low-angle X-ray diffraction techniques were used to examine single-crystal mats prepared by sedimentation. In both cases, pinhole collimation and photographic film were used, using a flat-plate Statton X-ray camera. Ni-filtered Cu Kα radiation sources were employed, and the cameras were evacuated to reduce air scatter. In some cases, the specimens were dusted with calcite and hexatriacontane for calibration purposes.

Results

Morphology and Electron Diffraction. Figure 1 shows a transmission electron micrograph of nylon 4 crystallized in the form of sheaves with lath-shaped extremities, similar to those found in other members of the nylon series. It has been observed that the lamellae have a tendency to orient in similar directions. Electron diffraction patterns from the tips of nylon 4 sheaves, as seen in Figure 2, reveal characteristics of single crystals, as suggested by the nature of the reflections. The closely spaced multiple spots or arcs indicate diffracting crystals in different orientations of the lattice. Figure 2b shows a schematic representation of the reflections, and the measured reciprocal lattice spacings are listed in Table 1. The two strongest reflections at 0.42 (100) and 0.38 nm (010) represent a projection of the interchain distance within the hydrogen-bonded sheet and the intersheet distance, respectively, and lie at an angle of 63° to one another. The hydrogen-bonded sheets run parallel to the long axis of the crystal and lie in the *ac* plane. Twinning of the reflections about the (010) composition plane is sometimes observed for individual lamella. From the reciprocal lattice spacings, *hk*0 reflections only, the values in real space are calculated to be $a = 0.466$ nm, $b = 0.433$ nm, and $\gamma = 117°$. Access to *hkl* reflections from the X-ray diffraction data will show that, in the unit cell, *a* and *b* will need to be doubled, and the unit cell for nylon 4 is therefore monoclonic with $a = 0.932$ nm, $b = 0.866$ nm, and $\gamma = 117°$, with the two strongest reflections, at spacings 0.42 and 0.38 nm, representing the (200) and the (020) planes, respectively. It is evident from the *hk*0 reflections and the orientation of the electron diffraction pattern with respect to the crystal that the nylon 4 chains lie normal to the lamellar surfaces and that the chains are folded in planes parallel to the long axis of the crystal, with a fold geometry similar to the β-bend found in proteins.

X-ray Diffraction. The wide-angle X-ray diffraction pattern from a sedimented mat of nylon 4 crystals is shown in Figure 3, and several features common to nylons exist. There are strong equatorial arcs spaced at 0.436 (200) and 0.370 nm (020), characteristic of the interplanar separations in nylons. The 020 reflection, representing the separation of hydrogen-bonded sheets at 0.370 nm, is not split about the equator in the diffraction pattern of nylon 4 (as it is, for example, in nylon 66 where the chains are not parallel to the lamellar normal). Together with the low-angle results (see below), we are able to establish that the chains are perpendicular to the lamellar surfaces. Two additional reflections at spacing of 0.479 and 0.235 nm are observed and represent the (012) and the (220) interplanar spacings. The character of the 0.479-nm meridional reflection is similar to that observed in sedimented single-crystal mats of nylon 46.[6] The interplanar spacings of the reflections observed in the sedimented single-crystal mat of nylon 4 are listed in Table 2.

The low-angle X-ray diffraction pattern of the nylon 4 sedimented mat is shown in Figure 4. The pattern was taken with the X-ray beam parallel to the mat plane. An arced reflection is observed on the meridian (along the mat normal), indicating stacks of lamellae as is commonly found in nylon crystal mats. The long spacing of this reflection is 6.63 nm. After annealing at 220 °C, the spacing

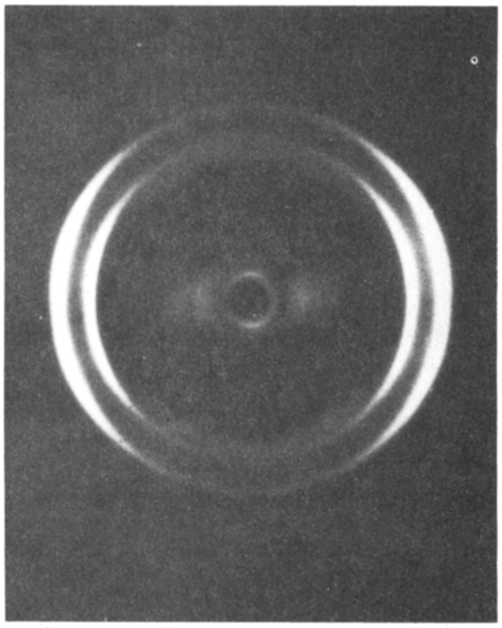


Figure 3. Wide-angle X-ray diffraction pattern of a sedimented mat of nylon 4 chain-folded lamellar crystals. The normal to the mat and the individual lamella is vertical. The lamellae are in a random orientation about the *c* axis or mat normal, exhibiting cylindrical symmetry in the diffraction pattern. Note the two strongest reflections at 0.44 and 0.37 nm are on the equator.

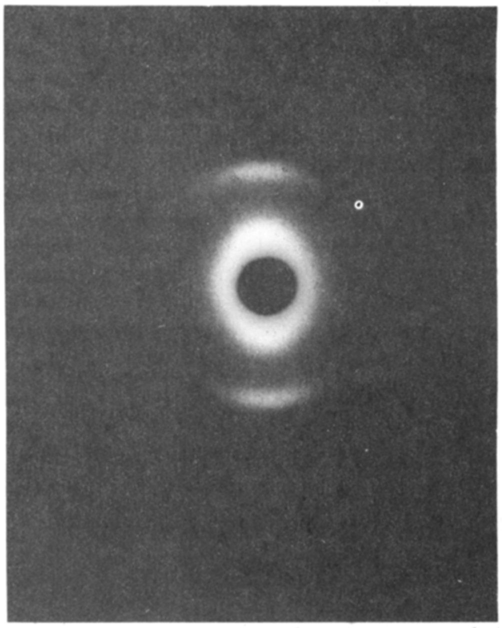


Figure 4. Low-angle X-ray diffraction pattern of a sedimented mat of nylon 4 chain-folded lamellar crystals. On the negative, a weak second order is visible.

Table 2. Data from Wide-Angle X-ray Diffraction of Nylon 4

reflection no.	measd spacing (nm)	index
1	0.436	200
2	0.370	020
3	0.235	220
4	0.479	002

was reduced to 6.33 nm. By analogy with previous investigations on other polyamides, this reduction emanates from improved stacking of lamellae. It should also be noted that the reduction in long spacing may be due to the evaporation of water during heating. Therefore, the lowest or annealed spacing is the closest to the actual lamellar thickness.

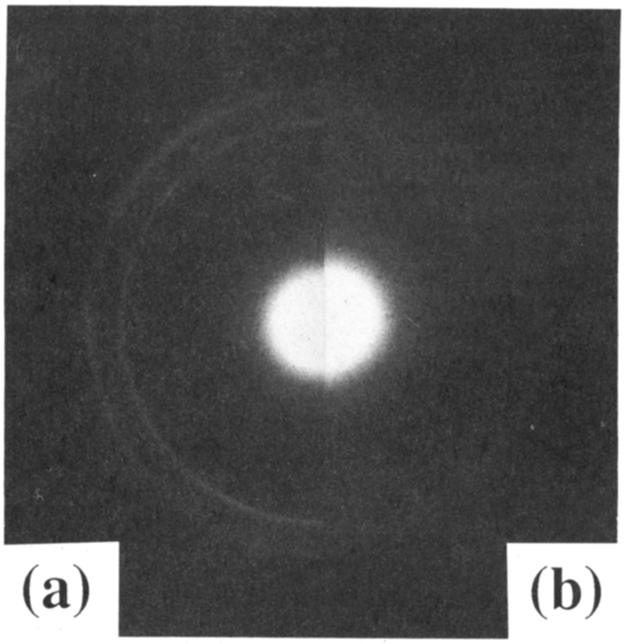


Figure 5. Effect of specimen temperature on the lattice spacings as determined from selected area electron diffraction of nylon 4 crystals: (a) $T = 26$ °C; (b) $T = 251$ °C.

The characteristic long spacing of the stacked lamellae is a unique property for each polyamide due to a combination of the number of hydrogen bonds in the lamellae and the length of a repeat unit.[4] For nylon 4, the length of a chemical repeat unit is 1.225 nm and the long period corresponds to 3% more than 5 chemical repeat units ($5 \times 1.225 = 6.16$ nm) along the chain.

Temperature Dependence of Lattice Spacings. Electron diffraction patterns from single-crystal-like sheaves of nylon 4 at various temperatures are shown in Figure 5. Because the specimens were not shadowed, they were particularly sensitive to the electron beam, especially at elevated temperatures, and it became difficult to capture spot reflections from single crystals; however, ring patterns from multiple nylon 4 crystals could be recorded at all temperatures. It is evident from examination of the ring spacings that an increase in temperature is accompanied by a change in the lattice spacing of the two strongest reflections. As the temperature increases, the 0.42-nm spacing decreases whereas the 0.37-nm spacing increases. In other words, the rings begin to merge, as is observed by comparing the electron diffraction patterns from parts a and b of Figure 5. At higher temperatures it appears as though the rings might converge to a single reflection; however, two distinct rings could always be identified. Figure 6 summarizes the effects of specimen temperature on lattice spacings. It is evident that the (020) interplanar spacing is more significantly affected by elevated temperatures than the (200) interplanar spacing. This is reasonable since the (200) spacing results from the hydrogen-bonded chains in a sheet, while the (020) spacing comes from the separation of the hydrogen–van der Waals bonded sheets, held together by much weaker van der Waals interactions. Extrapolation of the data shows that the lattice spacings converge to a single reflection, approximately 0.41 nm, close to the melting temperature (267 °C) of nylon 4.[10] This type of behavior has been speculated from investigations of the temperature effect on lattice spacings on monofilaments of nylon 4[3] and nylon 6[11] using X-ray diffraction; however, the authors were confined to temperatures below 200 °C.

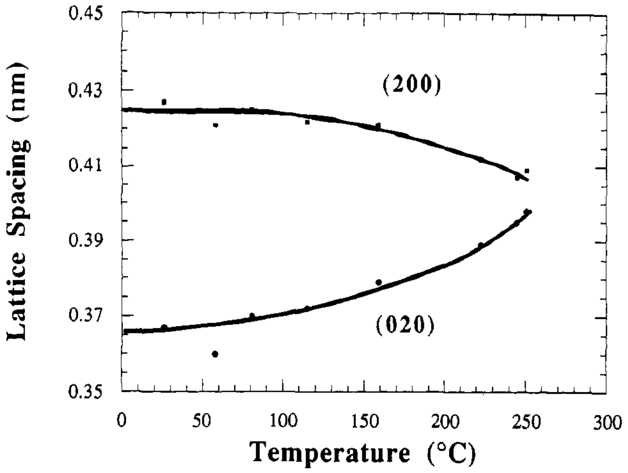


Figure 6. Effect of specimen temperature on the (200) and (020) lattice spacings of nylon 4 crystals.

Discussion

The crystal structure and morphology of nylon 4 single crystals has been investigated and particular attention focused on the direction of the polymer chains within the lamellae and the nature of the structure at the fold. From the electron diffraction data obtained from TEM, we consider the implication of the reflections in terms of the orientation of the chains with respect to the long axis of the crystal and the lamellar surfaces. These results can be directly compared with those recently published for nylon 46. The X-ray diffraction data support the TEM results and provide additional information about the overall crystal structure. The combined results allow a comparison to be made between nylon 4 and other nylons, such as nylon 46 and nylon 6, with special emphassis placed on the chain-folding mechanisms found in these polyamides.

We have established that the polyamide chains lie normal to the basal crystal faces (the *ab* plane) and fold along the hydrogen-bonded sheets, which are in the *ac* plane and run parallel to the long axis of the crystal. Determination of the unit cell is straightforward since direct access to the *hk*0 reciprocal lattice is obtained from the electron diffraction data. The electron diffraction reflections, whose spacing and indexing are listed in Table 1, coincide with a lattice such that a = 0.466 nm, b = 0.433 nm, and γ = 117°. Note that an obtuse angle is used for the real space lattice in accordance with appropriate crystallographic nomenclature. Since the *hk*0 reciprocal lattice is insensitive to shearing of the chains along the c axis, the reciprocal lattice describes a degenerate unit cell containing only one chain segment. Indexing the reflections from the wide-angle X-ray diffraction pattern which provides *hkl* reflections shows that the true unit cell contains four chain segments and that the a and b values of the cell need to be doubled. The electron diffraction values of the lattice spacings differ slightly from those obtained from X-ray diffraction analysis. This is most probably due to interaction of the electron diffraction beam with the sample. This is further noticed by the investigation of the effects of temperature on the lattice spacings of the 200 and the 020 reflections in Figure 6. Thus, it should be noted that the unit cell lattice parameters reflect the measurement obtained from X-ray diffraction, a nondestructive characterization technique. The combined efforts of the electron and X-ray diffraction data give a monoclinic unit cell with a = 0.979 (±0.002) nm, b = 0.831 (±0.002) nm, c = 1.225 (±0.002) nm, and γ = 117°. The values and essential features of the unit cell are similar to those proposed by Fredericks and co-workers[2] from a study on oriented fibers. Thus it is reassuring to find that the unit cell is similar in both chain-folded single crystals and fibers. The values we obtained, except for c which is unique for a particular polyamide, are similar to those obtained for nylon 6[5] and nylong 46.[6]

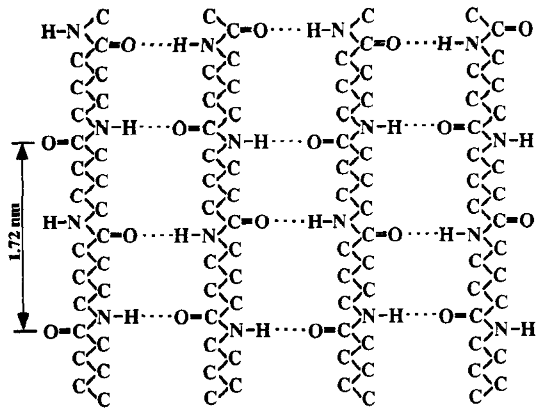


Figure 7. Structure proposed for the hydrogen-bonded sheet of nylon 6.

The proposed model for the crystal structure of nylon 6 is displayed in Figure 7 and has various features relevant to the structure of nylon 4. First, the polymer chains of nylon 6 have a polarity, commonly found in all even nylons, allowing adjacent chains to have opposite stereochemical polarity, or otherwise known as antiparallel, analogous to the antiparallel pleated sheets in proteins. Second, the extended zigzag chains form sheets through linear hydrogen bonds between the amide groups. The hydrogen-bonded pattern within the sheets staggers alternatively up and down between adjacent chains, unlike the progressive shear pattern found, for example, in nylon 66.[12] Last, successive hydrogen-bonded sheets shear with an alternating polarity of the shear vectors, resulting in a two-sheet structural repeat unit.

Extensive work on nylon 6[5] demonstrates a monoclinic unit cell with parameters a = 0.96 nm, b = 0.80 nm, c = 1.72 nm, and γ = 112.5°. Note that the a and b dimensions are effectively doubled and an obtuse angle is chosen in accordance with the accepted crystallographic nomenclature for monoclinic systems. The two strongest reflections, the 0.37 nm (020) and the 0.44 nm (200) spacings, are characteristic of the prominent diffraction signals from the intersheet distance and the projected interchain distance within the hydrogen-bonded sheets, respectively.

A recent study on the crystal structure of nylon 46 has shown this polyamide to be quite different from the structure described for nylon 66[12] but rather similar to the model proposed for nylon 6[5] and described above. The proposed structure of the chain-folded sheet of nylon 46, shown in Figure 8, has characteristic reflections at 0.44 and 0.37 nm representing the (200) and (020) spacings, respectively. The hydrogen-bonded sheets have characteristics similar to those of nylon 6 and again various features relevant to the structure of nylon 4. At any particular hydrogen-bonding site, the neighboring amide group has an opposite polarity and these amide groups stagger alternatively up and down between adjacent chains. In addition, the linear hydrogen-bonded sheets do not progressively shear, as in nylon 66, but alternately shear. The unit cell for nylon 46 is monoclinic with parameters a = 0.96 nm, b = 0.83 nm, c (chain axis) = 1.47 nm, and γ = 115°, containing four chain segments or two sheet segments, similar to the unit cell of nylon 6 and that obtained for nylon 4.

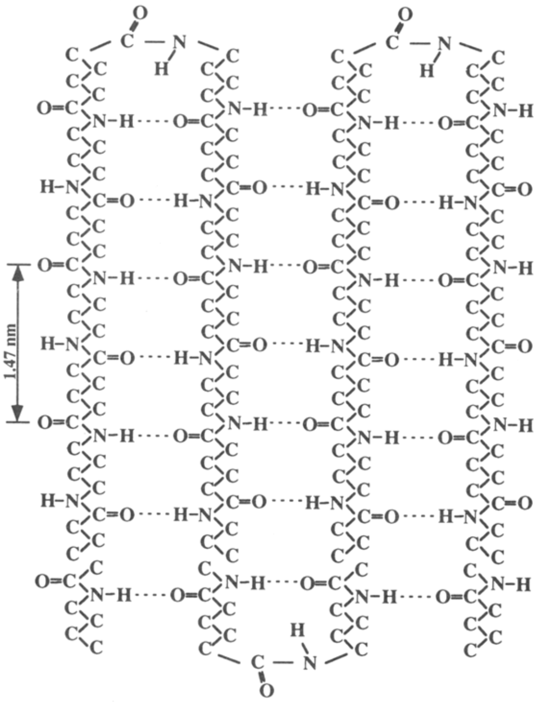


Figure 8. Structure proposed for the chain-folded sheet of nylon 46.

The electron diffraction data and the low-angle X-ray diffraction data of nylon 46 confirm that the polymer chains lie normal to the lamellar surfaces. A new model for the adjacent reentry chain-folding mechanism in polyamides with a high amide content was proposed for nylon 46 in which an amide group is present within the actual fold. This is stereochemistry feasible[13] since the extra CH_2 units on either side of the amide group in nylon 46 make folding easier in comparison to the related hairpin folds or β-bends in proteins, which involve even more stereochemical constraints on the straight stem segments.[7-9] Nylon 4 is similar in structure to proteins such as polyglycine, or nylon 2, with the addition of two extra methylene units along the backbone chain. From the low-angle X-ray data, it is observed that the lowest value of the long spacing, 6.33 nm, is only marginally greater than an integral number of repeat units (5 repeats or 6.16 nm), and therefore it is unlikely that the chain folds are loose but are rather tight or hairpin-like as found in proteins and most recently in nylon 46.

In general, two possibilities exist for the placement of atoms within the fold of nylon 4 crystals: either the alkane segments or an amide group are in the fold, as shown in Figure 9. In the broad family of polyamides, it is likely that the chains will fold along the alkane segments owing to the relatively large number of flexible methylene units between amide groups. However, as the number of methylene units between amide groups decreases, a change in the folding mechanism would be anticipated, as was observed for nylon 46.[6] Examination of Figure 9a shows an amide group within the actual fold. The straight stem of the lamellar crystals is unaffected by the structure of the fold, and the hydrogen-bond distance maintains its classical value for nylons. However, placement of the alkane segment within the fold disrupts the straight-stem hydrogen-bonded crystal structure. If the crystal structure is constrained, as prescribed by the electron and X-ray diffraction results, the two carbon atoms of the alkane segment are too far apart (0.243 nm) for conventional bonding between carbon atoms (0.154 nm) to occur, as shown in Figure 9b. This is the minimum distance of approach allowed stereochemically. The proposed structure of the fold in nylon 4 chain-folded lamellar crystals, as shown in Figure 9a, incorporates an amide group in the actual fold.

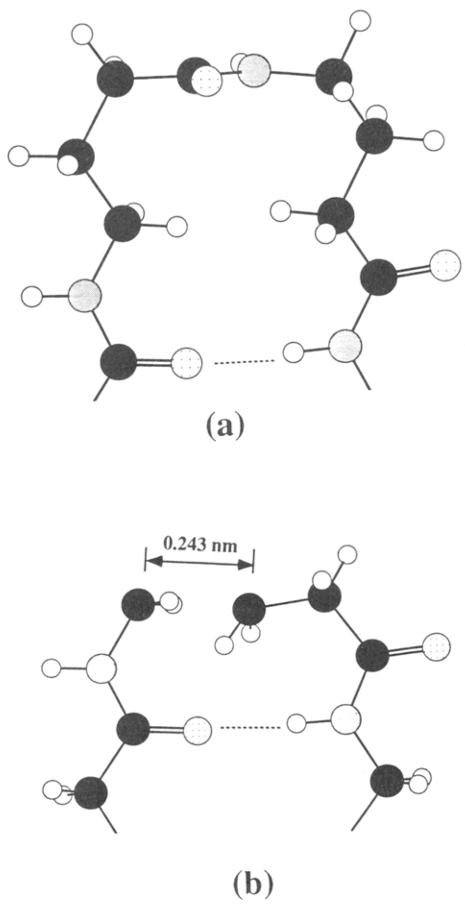


Figure 9. Structure proposed as the fold of nylon 4 chain-folded lamellar crystals: (a) amide group in the fold; (b) alkane segment in the fold.

It has not escaped our attention that another arrangement of atoms containing the amide group in the fold may possibly exist. In Figure 9a, the folding entity of the polymer chain contains 10 atoms. However, it is also possible to have a fold with only 8 atoms by a 180° rotation of the chains in the straight stems. This configuration is highly unlikely owing to thermodynamic considerations of the 8-member fold. The structure of the proposed chain-folded sheet of nylon 4 is shown in Figure 10 and favors an amide group with 10 atoms in the structure of the fold. Thus, the folding behavior of nylon 4 provides a connection between chain folding in nylons and proteins.

The effects of temperature on the lattice spacings of nylon 4 were examined in an attempt to determine the existence of a high-temperature pseudohexagonal crystalline structure. The crystal forms of nylon 6 and nylon 66 are quite different at high temperature, although they exhibit similar molecular packing at room temperature. For example, the (100) and (010) interplanar spacings converged with increasing temperature by 160 °C for nylon 66; however, such a process did not occur before melting in nylon 6.[14] A metastable crystalline phase has been proposed for nylon 6.[15] The author suggests that, in addition to the hydrogen bonding which commonly exists within a sheet of extended chains (antiparallel), intersheet hydrogen bonds between parallel sheets may also exist, similar to a pseudohexagonal crystallline structure.

Figure 6 summarizes the effects of temperature on the lattice spacings of the 200 and 020 reflections. Although

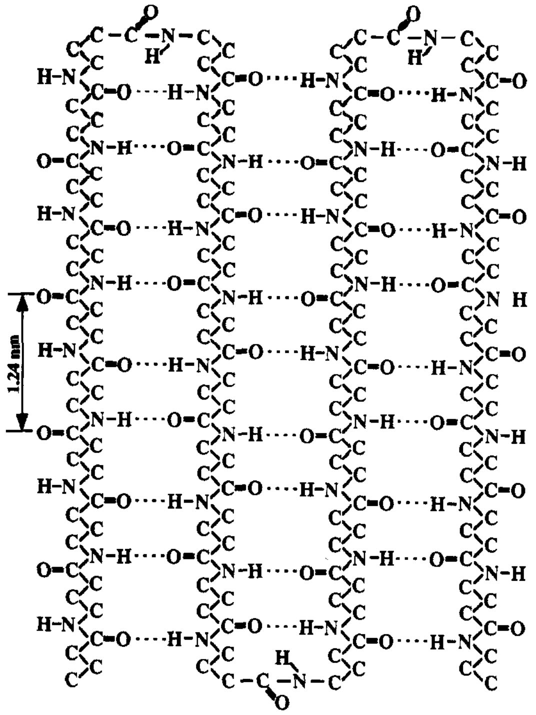


Figure 10. Proposed structure of the chain-folded sheet of nylon 4.

the lattice spacings seem to converge, two distinct reflections are observed up to 251 °C, close to the melting temperature of nylon 4. Similar to that proposed for nylon 6, it is possible that a metastable crystalline phase exists for nylon 4 at temperatures close to the melt. The high-temperature, three-dimensional crystalline structure of nylon 4 is currently under investigation.

Conclusions

Experimenal evidence from electron and X-ray diffraction shows that the chains of nylon 4 crystals lie normal to the lamellar surfaces and form hydrogen-bonded sheets, similar to the structure of proteins and that proposed for both nylon 6 and nylon 46. The reflections index on a monoclinic unit cell with parameters a = 0.971 (±0.002) nm, b = 0.831 (±0.002) nm, c (chain axis) = 1.225 (±0.002) nm, and $\gamma = 117°$, containing four chain segments or two sheet segments. Low-angle X-ray diffraction is consistent with five chemical repeats and tight, adjacent reentry folds.

The observed crystal structure necessitates that an amide group rather than an alkane segment must exist in the fold. This folding mechanism, also recently deduced for nylon 46, is completely different from previous chain-folding mechanisms reported for nylons. Thus, as the linear amide density in nylons increases, the chain-folded crystalline structure is similar to that found in β-proteins.

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