Chain-Folded Lamellar Crystals of Aliphatic Polyamides. Comparisons between Nylons 4 4, 6 4, 8 4, 10 4, and 12 4

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ABSTRACT: Chain-folded single crystals of the five even−even nylons 4 4, 6 4, 8 4, 10 4, and 12 4 were grown from solution and their structures and morphologies studied using transmission electron microscopy, both imaging and diffraction. Sedimented mats were examined using X-ray diffraction. All these nylons have room temperature crystal structures that relate to that reported for nylon 6 6, yet there are differences, reflecting the differences in the amide group distribution. At room temperature, all the crystals are composed of chain-folded, hydrogen-bonded sheets; the hydrogen bonds within the sheets form a progressive shear pattern, and, in addition, the sheets themselves are sheared progressively parallel to the sheet plane so that they generate triclinic unit cells. The magnitude of this intersheet shear may differ between nylons; it is dependent on the details of the amide decoration pattern on the hydrogen-bonded sheet faces. In all five nylons studied, the two strong and characteristic diffraction signals of the room temperature triclinic structure, at spacings 0.44 nm (projected interchain/intrasheet distance) and 0.37 nm (intersheet distance), move together and merge as they do for single crystals of nylon 6 6. For each of the X 4 nylons, the Brill temperature (lowest temperature where the spacings are equal) is in the range 140−190 °C. In each case, the triclinic structure gradually transforms into a pseudohexagonal structure as the temperature rises. The melting points of solution-grown crystals of this series of even−even nylons decrease with the linear hydrogen bond density. This series of nylons is unique since in each case the chain folds must be in the diamine alkane segment.

Introduction

The implantation of amide groups into alkane chains generates an extended family of important industrial materials: the nylons. The directionally specific interchain hydrogen bonds that are created between near-neighbor amide groups give the nylons improved physical properties and substantially enhanced melting points, compared with the polyolefins and polyesters.

We are investigating the chain-folded lamellar single crystals of even and even−even nylons. These provide a convenient crystalline morphology to investigate structural changes in nylons using selected-area electron diffraction, supplemented by X-ray diffraction on mats prepared by sedimenting lamellar crystals. We believe that the insights gained from a study of these morphologies will lead to a fuller understanding of more complex commercial nylon samples.

Single crystals of a number of even−even and even nylons have been grown from solution, and the structures proposed provide a useful basis for understanding the group of nylons we have investigated. Crystals of nylons 6 6,[1−3] 4 6,[4] and 6 8,[5] and of the even nylons 4,[6] 6,[7] and 8[8] have all been shown to be chain-folded. There are similarities between the solution-grown crystals of all these nylons, although some (e.g., nylon 6 6) are found in a triclinic phase at room temperature and others (e.g., 4, 6, 8, 4 6, and 6 8) in monoclinic phases. In each case, the chains regularly fold back and forth to form sheets; adjacent chains in each sheet are held together by hydrogen bonds. The requirement that the hydrogen bonds between adjacent chains should be linear (or close to linear) is a crucial feature in determining the crystal structure adopted by all these polyamides. The hydrogen-bonding pattern that develops is a function of the stereochemistry of a particular nylon. In the case of nylon 6 6 single crystals, the hydrogen bonds can only be linear if the chains progressively shear within each hydrogen-bonded sheet, as illustrated in Figure 1a, and this is the sheet structure found experimentally.[1−3] In nylons 4, 6, and 8, linear hydrogen bonds can only form if the hydrogen bonds alternate up and down within each sheet. A projection of a hydrogen-bonded sheet of this kind, for example nylon 6, is shown in Figure 1b.

At room temperature, lamellar single crystals of all the even−even and even nylons discussed above consist of these chain-folded, hydrogen-bonded sheets and, in all cases, the sheets are held together by van der Waals forces. It is commonly found that where the hydrogen-bonding pattern is alternating, as, for example, in nylon 6 (Figure 1b), the stacking between adjacent hydrogen-bonded sheets is also alternating up and down; this gives rise to monoclinic unit cells with chains normal to the crystal surfaces.[4−8] In nylon 6 6, where there is a progressive shear in the hydrogen-bond sheet (as shown in Figure 1a), a progressive shear is found also between hydrogen-bonded sheets, creating a triclinic structure with the chain axis lying oblique (42°) to the lamellar surface normal.[1−3] Nylons 4 6 and 6 8 are particularly interesting because of the equal spacing of the amide units along the chain, which means that both the progressive shear in the hydrogen-bond pattern (Figure 1c) and an alternating pattern (Figure 1d) are possible. In fact, in both nylons, it is the alternating pattern that is found in single crystals grown from 1,4-butanediol,[4,5] and the hydrogen-bonded sheets shear alternately up and down as they stack, creating monoclinic unit cells.

Thus, the structures of lamellar single crystals of all these nylons are basically the same: chain-folded, hydrogen-bonded sheets held together by van der Waals forces. However, and this is important, there are detailed differences in hydrogen-bond patterns from one nylon to another, first, because of the details of the stereochemistry of a particular nylon coupled with the

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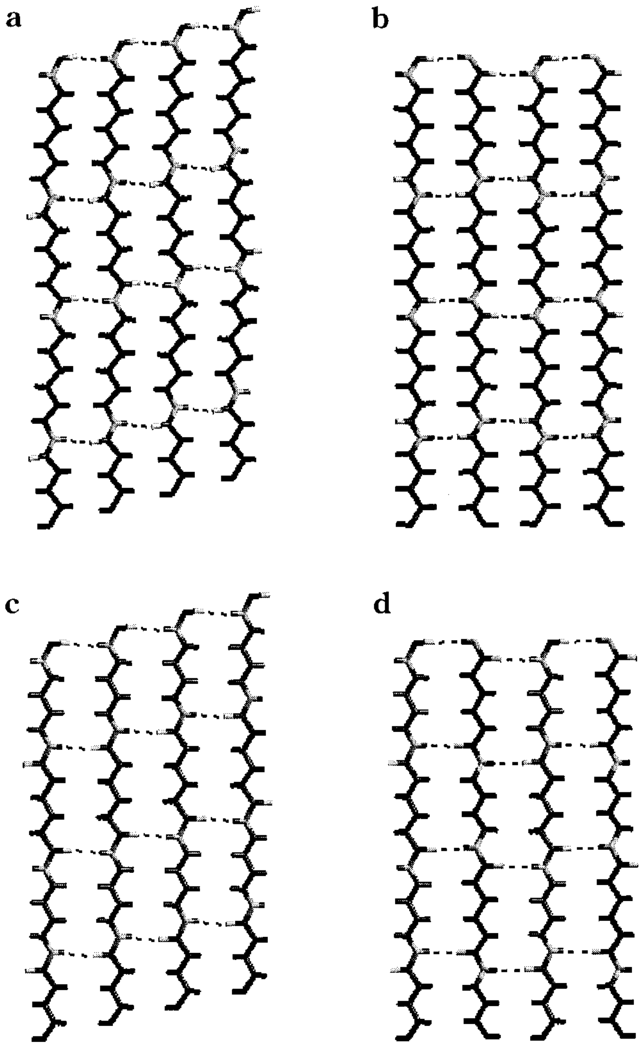

Figure 1. Projections of various aliphatic polyamide hydrogen-bonded sheets normal to the sheet surface; this is the *ac* plane with the chain axis (*c*) direction vertical. The methylene units are in black, the amide units are in gray, and the hydrogen bonds are indicated with dashed lines. (a) Nylon 6 6 showing the progressive shear of the chains within a sheet. Note for *syncephalic* (head-to-head/tail-to-tail polymerized) polymers of this kind, there is no polarity to the chain; they are apolar. Ajacent re-entry folds *must* be via the alkane segments. (b) Nylon 6, showing the alternating nature of the interchain shear. This polar-chain structure imposes the condition that adjacent chains have opposite polarity. This would be consistent with adjacent re-entry chain folding and the tight fold could either be via an alkane segment or contain an amide unit. (c) The progressively sheared sheet structure for nylon 4 6. (d) The alternating sheared sheet structure for nylon 4 6. This structure was discovered in chain-folded single crystals.[4] In this structure each fold must contain an amide unit if the hydrogen-bonding pattern is to be achieved.

requirement that hydrogen bonds between adjacent chains should be linear, and, second, because in some cases the sheets stack with a progressive shear (triclinic unit cell, nylon 6 6) and in others with alternating up and down shear (monoclinic unit cell, e.g., nylons 6 and 4 6).

For room temperature lamellar single crystals of all the nylons discussed above, two strong diffraction signals are observed, at spacings of 0.44 and 0.37 nm. These two strong diffraction signals represent a projected interchain distance within a hydrogen-bonded sheet (actual value 0.48 nm) and the intersheet distance, respectively; they are characterisic signals for even−even and even nylons at room temperature. (They are indexed as 100 and the 010/110 pair for nylon 6 6[1].)

There are further similarities between these nylons which become apparent on heating. In each case the two strong diffraction signals move together with increasing temperature, the rate of change in the 0.37 nm intersheet distance being greater. For some nylons (e.g., 6 6, 4 6, and 6 8[5]) the two signals meet and merge to give a single signal at 0.415 ± 0.005 nm. This signal originates from a high-temperature pseudohexagonal phase. The crystals of other nylons melt before the diffraction signals actually meet (nylons 4,[6] 6,[9] and 8[8]); the structures move toward a pseudohexagonal phase but do not fully achieve it prior to melting.

In this paper, we report on our investigations of lamellar single crystals of a group of nylons of the generic type X 4. We have examined nylons 4 4, 6 4, 8 4, 10 4, and 12 4. The chemical repeating sequences of these nylons are shown in Figure 2. There are two methylene groups between adjacent C═O groups for each nylon, while the number of methylene groups between adjacent NH groups increases by two for each successive member of the series.

As far as we know there are no previously published studies of nylon X 4 single crystals where X is even. We know only of one study of an X 4 nylon, the odd−even nylon 1 4,[10] but in odd−even nylons the hydrogen-bonding patterns are quite different.

Experimental Section

Single-Crystal Samples. The nylons used were made previously by Dr. Pat Dreyfuss, and the detailed syntheses are given in ref 11. The polymers had been stored in the dark, sedimented mats in dry bottles and crystals in suspension in 1,4-butanediol. We do not have sufficient material to measure molecular weights directly with GPC. However, these are high-viscosity materials, and oriented fibers could be drawn. Our previous experience leads us to believe that the molecular weights are in excess of 10 000.

All the nylons were recrystallized for the present study, and, in some cases, it was found that larger crystals could be grown from 2-methyl-2,4-pentanediol following solvent exchange. Details of the crystallization conditions that produced good single crystals of each nylon are given in the captions to the various parts of Figure 3.

Transmission Electron Microscopy. Samples suitable for transmission electron microscopy (TEM) were prepared by placing crystal suspensions in 1,4-butanediol (nylons 6 4 and 10 4 were also crystallized in 2-methyl-2,4-pentanediol) onto carbon-coated TEM copper grids, drying and subsequently annealing in a vacuum oven at 100 °C for 24 h. The samples were examined, in both imaging and diffraction modes, using a Philips 301 TEM operating at 80 kV. Some crystal preparations were shadowed with platinum/palladium to enhance the contrast of the images and allow the diffraction patterns to be calibrated. Some crystals were decorated with polyethylene vapor, following the method of Wittmann and Lotz.[12] Crystals of nylon 4 4 were heated to melting with the *in situ* hot stage and electron diffraction patterns recorded at regular intervals in the range from room temperature to the melting point. The temperature of the hot stage could be controlled to within ±2 °C. Relative measurements were accurate to 2 °C and absolute values to within ±5 °C. The hot stage was calibrated by observing the melting of substances of known melting point. The structural changes of all the nylons were also monitored using sedimented mats and X-ray diffraction (for details, see below).

X-ray Diffraction. The sedimented mats were annealed in a vacuum oven at 100 °C for 24 h. X-ray diffraction patterns were obtained by directing a point-collimated beam parallel to the surface of the mat. Calcite (d_B = 0.3035 nm) was dusted onto selected samples for calibration purposes. For room temperature wide-angle studies, Ni-filtered Cu Kα radiation

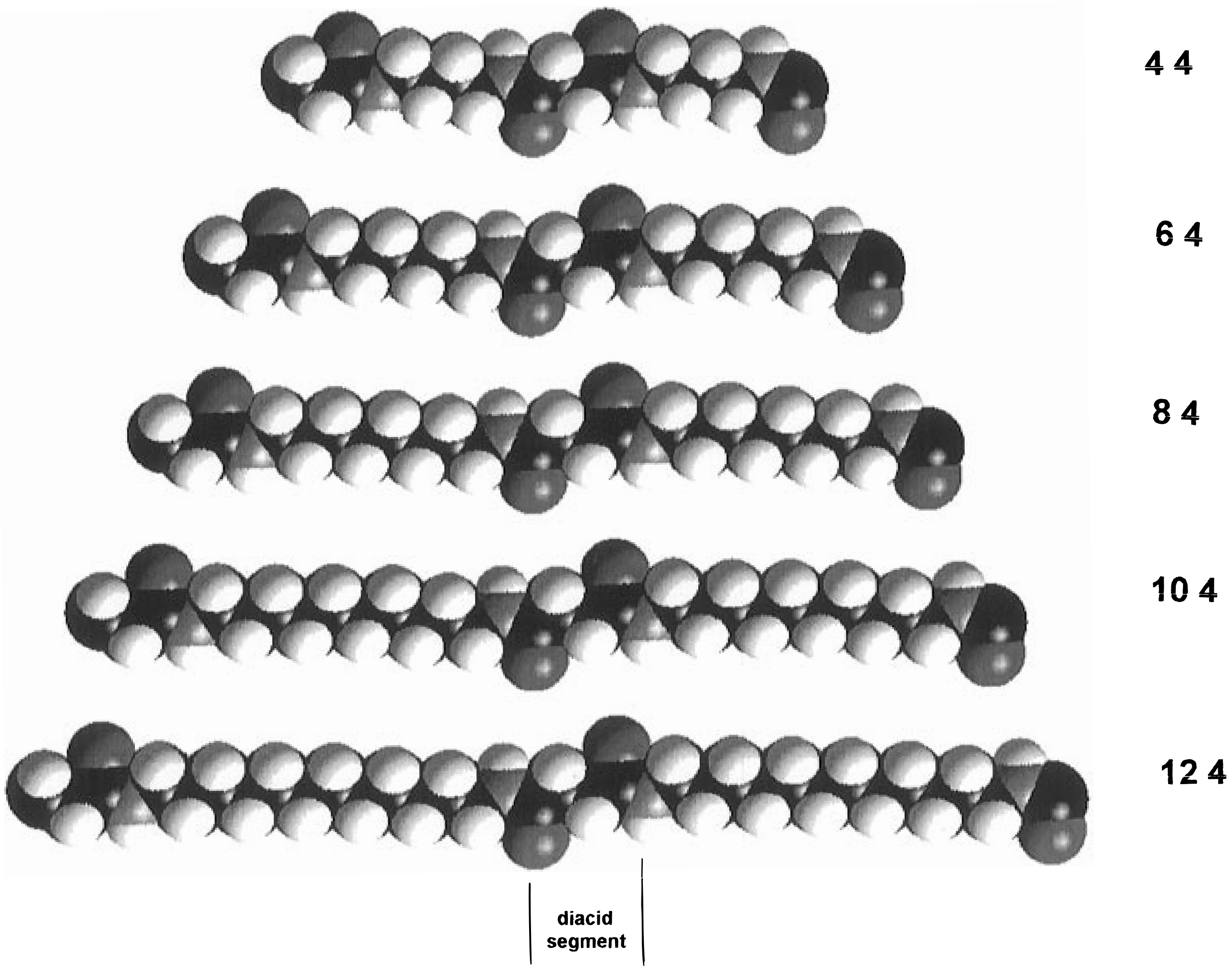

Figure 2. Computer-generated "realistic" space-filling structures of nylons 4 4, 6 4, 8 4, 10 4, and 12 4. Color code: carbon atoms black; hydrogen atoms white; nitrogen atoms light gray; oxygen atoms dark gray. The figure highlights the constant diacid (four-carbon atom) segment in the center of each molecule and the increasing lengths, in jumps of two methylene units, of the diamine segments in the series.

from a sealed-beam Philips generator and an evacuated flat-plate camera were used. The elevated temperature results were recorded using a monochomatized Cu $K\alpha$, point-collimated beam from an Elliot GX-21 rotating target generator and Siemens GADDS two-dimensional detector; the samples were heated in a Linkam T300 hot stage. The low-angle diffraction patterns were recorded on film using a point-collimated Rigaku-Denki low-angle camera and an Elliot GX-21 generator.

Details of the method by which the unit cells were calculated from the diffraction data are given below in the X-ray Results section.

The experimental X-ray diffraction patterns were compared with simulated X-ray diffraction patterns, computed from the unit cells using the Diffraction Module of Cerius 2 version 1.6 (Biosym/Molecular Simulations Inc.). The appropriate Lorentz and polarization factors were included in the simulations.

Differential Scanning Calorimetry (DSC). Melting temperatures of the nylon sedimented mats were measured using a Perkin-Elmer DSC 7 flushed with nitrogen and with a heating rate of 10 °C/min.

Results

Transmission Electron Microscopy. Figure 3 shows typical crystal morphologies for all the X 4 nylons investigated. It is clear that the crystals are elongated and they are often multilayered. The Wittmann and Lotz polyethylene decoration procedure (e.g., Figure 3f) indicates that the chain-folded, hydrogen-bonded sheets lie along the long axes of the crystals. The same is found for other even and even−even nylons.[1,2,4,5,8]

For all the X 4 nylons, the selected-area electron diffraction of room temperature single crystals showed only a single diffraction spot (observed as a pair), at a spacing of 0.44 nm. In longer exposures from a larger selected area containing many crystals, two electron diffraction rings were obtained: a strong ring at spacing 0.44 nm and a much weaker ring at spacing 0.375 nm. Similar results are obtained from nylon 6 6 single crystals,[3] and on the Bunn and Garner[1] triclinic lattice they are indexed as the 100 and 010/110 reflections, repectively. The fact that only one strong diffraction signal is obtained favors the Bunn and Garner[1] type triclinic crystal structure[23] since the (100) planes are only tilted 13° relative to the beam direction, and therefore captured by slight tilts of the crystals, whereas the (010) and (110) planes are tilted at large angles.[1−3]

X-ray Diffraction. The X-ray diffraction photographs from single-crystal mats (an example is shown in Figure 4) confirm the model deduced from electron diffraction: that, in all cases, the chain direction is oblique to the lamellar crystal normal. The 00*l* diffraction signals occur on the meridian, together with orders of the low angle. The 100 diffraction signals (0.44 nm) occur ±6° above and below the equator and the 010/110 diffraction signals (0.37 nm) at ±40°. These results

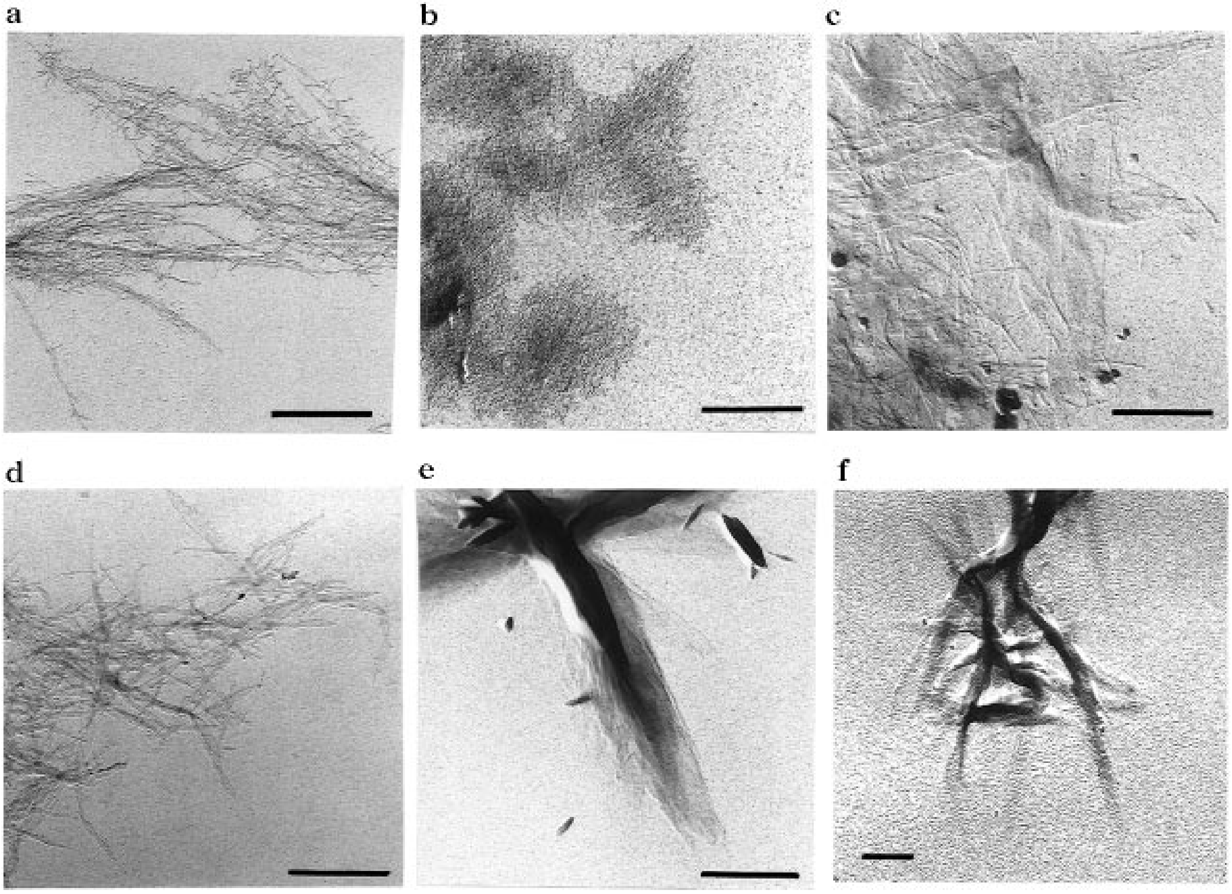

Figure 3. Micrographs of lamellar crystals of X 4 nylons grown from dilute solution. All the crystals were shadowed with Pt/Pd. Micrographs a−e are at the same magnification; the scale bars represent 1 μm. (a) Crystals of nylon 4 4, crystallized from 1,4-butanediol; the solution was held at 115 °C before cooling to 60 °C. (b) Crystals of nylon 6 4 crystallized from 1,4-butanediol at 120 °C. The sample appears to be made up of groups of very small, needlelike crystals roughly oriented in two directions at right angles. (c) These relatively large crystals of nylon 8 4 were thermally crystallized from 1,4-butanediol at 120 °C after seeding at 140 °C. The solution was hot filtered at the crystallization temperature. (d) Crystals of nylon 10 4 crystallized from 2-methyl-2,4-pentanediol at 126 °C. (e) Crystals of nylon 12 4 grown from 1,4-butanediol after seeding at 140 °C followed by thermal crystallization at 120 °C. The solution was hot filtered at the crystallization temperature. (f) Crystals of nylon 12 4, prepared as those in (e) and decorated with polyethylene using the method of Wittmann and Lotz.[12] Note that the polyethylene fibrils are distributed randomly on the carbon film but line up normal to the long direction of the individual nylon crystals. This indicates that the chain-folded sheets lie along the long direction of the crystals (perpendicular to the polyethylene fibrils[12]).

are similar to those reported by Atkins *et al.*[2] for sedimented mats of nylon 6 6, except, of course, that the *c* spacings change as a function of the number of methylene groups. The unit cell dimensions for the X 4 nylon series, deduced from the diffraction data (Table 1a), are tabulated in Table 1b together with the calculated densities. The values are compared with those of nylon 6 6.

The unit cells were determined as follows: the *a* and β values were set at 0.49 nm and 77°, respectively, in accordance with the requirement that the hydrogen bonds should be linear within the sheets. For each X 4 nylon, the *c* value was set at $(0.125N - 0.02)$ nm, where N is the number of backbone bonds, consistent with an all-trans conformation for the polyamide chains. (The 0.02 nm is subtracted because of the inclusion of one nitrogen in each backbone repeat.) The *b*, α, and γ values could then be calculated from the measured d_{100}, d_{010}, d_{110}, and d_{001} spacings. The resulting unit cells were all similar to that of nylon 6 6, differing by only ±0.02 nm in *b* and ±2° in α and γ, respectively. The simulated X-ray diffraction patterns computed from the unit cells agreed with the experimental patterns to within the accuracy in the measured *d*-spacings. The simulated pattern for nylon 12 4 is shown in Figure 5c and should be compared with the experimental pattern in Figure 5a.

Behavior on Heating. The melting points of the five X 4 nylons, measured by DSC, are listed in Table 2. Note that the melting points increase with increasing linear hydrogen bond density of the nylons. Nylon 4 4 single crystals degrade rather than melt. Degradation has been previously observed in other nylons with high linear hydrogen bond densities.[13,14]

On heating the X 4 nylons, the two characteristic 0.44 and 0.37 nm diffraction signals move together with increasing temperature, eventually meeting at a spacing of 0.42 nm. These changes are illustrated in Figure 5. This type of behavior was first observed by Brill for nylon 6 6,[15] so the lowest temperature for which the two spacings are equal is termed the “Brill temperature”. For nylon 6 6[16,21] and for other even−even nylons that we have studied as a function of temperature, the phase above the Brill temperature is pseudohexagonal.[5,15,16] Table 2 lists the Brill temperatures recorded for lamellar single crystals for the various X 4 nylons using X-ray diffraction, together with their melting temperatures determined by DSC. The density of the nylons in the pseudohexagonal phase is less than the room temperature triclinic phase; for example, for nylon 6 6 it is 1.10

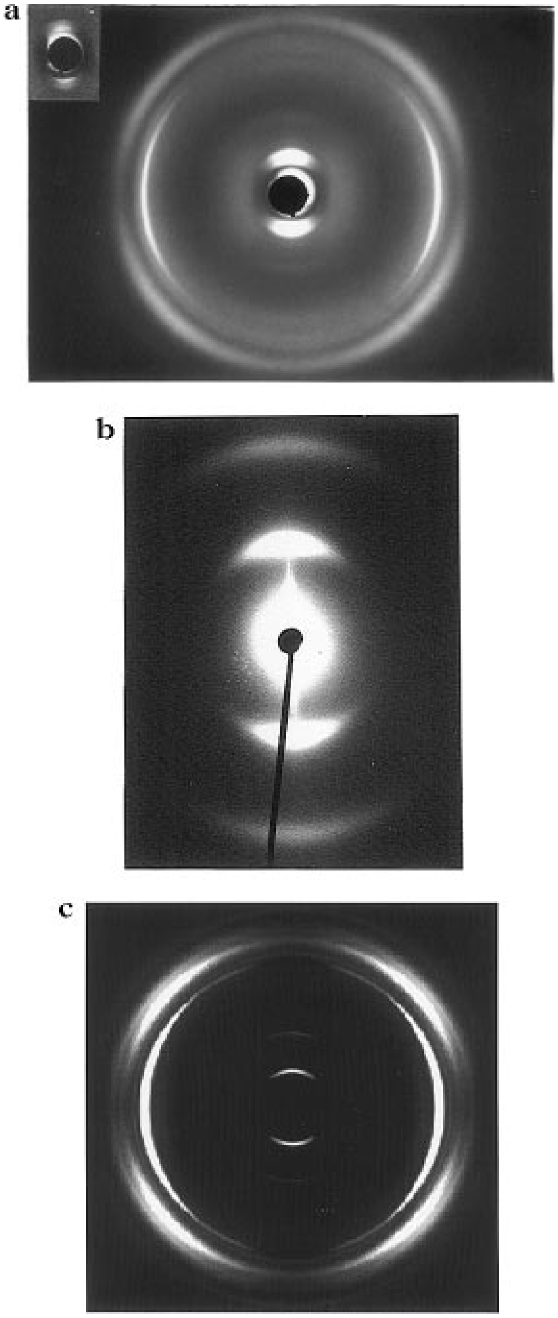

Figure 4. (a) Wide-angle X-ray diffraction pattern obtained from sedimented mats of nylon 12 4 (taken with the X-ray beam parallel to the mat surface; mat normal vertical). The strong 100 arcs spaced at 0.44 nm are centered ±6° above and below the equator (horizontal bisector) but they run into each other, giving the false impression of equatorial arcs. The 010 and 110 arcs, at 0.37 nm, appear in the 40−50° angular range. The 001 diffraction signal, at spacing 1.66 nm on the meridian, is straddled and swamped by the strong third and fourth orders of the low-angle diffraction series emanating from the lamellar stacking period of 5.62 nm. Thus the strong broad meridional arc, just clear of the beam stop flare, is indeed the third and fourth orders of the low-angle diffraction (see inset) straddling the weaker 001 signal. (b) The first two orders of the low-angle diffraction series of nylon 12 4, with a fundamental of 5.62 nm, the lamellar stacking period. (c) Simulated X-ray diffraction pattern of nylon 12 4, based on the unit cell deduced from the experimental data (Table 1). This corresponds closely with the experimental pattern, Figure 4a. However, only the 001 diffraction signal appears on the meridian of the simulated pattern because the computer simulation does not generate signals due to the low-angle, lamellar stacking, periodicity.

g/cm^3,[15] which is 89% of the density of the room temperature structure. In some crystal preparations, a faint 0.42 nm diffraction arc, indicating a trace of the pseudohexagonal phase, was observed between the strong 0.44 and 0.37 nm diffraction arcs in the patterns obtained at room temperature.

Discussion

The overall behavior of all the X 4 nylon series, in both terms of structure and structural changes as a function of temperature, is similar to that of nylon 6 6. At room temperature, the lamellar single crystals exhibit the two characteristic interchain and intersheet diffraction signals at spacing 0.44 and 0.37 nm, respectively, typical of even−even and even nylons. The crystals are found in the triclinic phase, as would be expected from the chain structure if the hydrogen bonds are to be linear. For example, the chain-folded, hydrogen-bonded sheets for nylons 4 4 and 8 4 are shown in Figure 6.

The melting temperatures of the crystals increase as the linear hydrogen bond density increases. This is again as expected[18] since it is the hydrogen bonds that hold the crystals together long after the alkane portions of the chains have become mobile (locally melted). Nylon 4 4 degrades before it melts, in common with other nylons with high linear hydrogen bond density.[13,14] The degradation temperature of nylon 4 4 is in excess of 300 °C, above the melting point of nylon 6 4, the adjacent member of the X 4 series. Note that the nylon 8 4 has the same linear hydrogen bond density as nylon 6 6 and their melting temperatures are similar.

On heating, all the X 4 nylons exhibit behavior like that of nylon 6 6. It seems that for single crystals of these nylons, the higher density triclinic crystal forms are more stable at room temperature. However, pseudohexagonal structures are more stable at high temperatures and the triclinic crystals move toward the pseudohexagonal phase on heating. We believe that as the temperature increases, the alkane segments increase their mobility until they effectively melt locally. However, the structure is still held together by the hydrogen bonds, some of which rearrange, flipping ±60° out of the original sheets[5,8,19−21] and the structure shifts toward the high-temperature pseudohexagonal phase. We intend to discuss these changes in more detail elsewhere.

The Brill temperatures of lamellar single crystals of the X 4 nylons appear in the range 140−190 °C. We have found previously, for single crystals of nylon 8[8] and nylon 6,[9] that the Brill temperature of a crystal preparation is quite strongly dependent on the crystallization conditions. Nylon 8 single crystals normally melt at about 180 °C. When the crystals have been slowly crystallized or annealed, the two characteristic diffraction signals move together on heating, but melting takes place before they actually meet. However, if the crystals are crystallized very rapidly (for instance by fast cooling from the solvated state) or if the crystals contain solvent, then the two characteristic 0.44 and 0.37 nm diffraction signals move together noticeably more rapidly and a Brill temperature is recorded below the melting temperature. The results from nylon 8[8] indicate that there is not one fixed Brill temperature for a particular nylon, but the Brill temperature can vary with the perfection (as well as with the solvation) of the crystals; Ramesh *et al.*[16] have found similar behavior in melt-crystallized nylon 6 6. Hence we are not surprised by the apparent fluctuations of the measured Brill temperature as a

Table 1[a]

A. Nylon X 4 Diffraction Data

nylon	100 spacing (nm) ± 0.003	010 spacing (nm) ± 0.003	001 spacing (nm) ± 0.01nm
4 4	0.428	0.372	0.92
6 4	0.428	0.367	1.14
8 4	0.429	0.373	1.33
10 4	0.434	0.375	1.48
12 4	0.435	0.373	1.66
6 6	0.436	0.369	1.28

B. Nylon X 4 Unit Cell Parameters

nylon	*a* (nm)	*b* (nm)	*c* (nm)	α (deg)	*β* (deg)	*γ* (deg)	calcd density (g/cm^3)
4 4	0.49	0.55	1.23	49	77	62	1.28
6 4	0.49	0.53	1.48	51	77	62	1.26
8 4	0.49	0.54	1.73	51	77	62	1.21
10 4	0.49	0.55	1.98	49	77	63	1.19
12 4	0.49	0.55	2.23	49	77	63	1.17
6 6	0.49	0.54	1.72	49	77	63.5	1.24

[a] The data for nylon 6 6 is from ref 1.

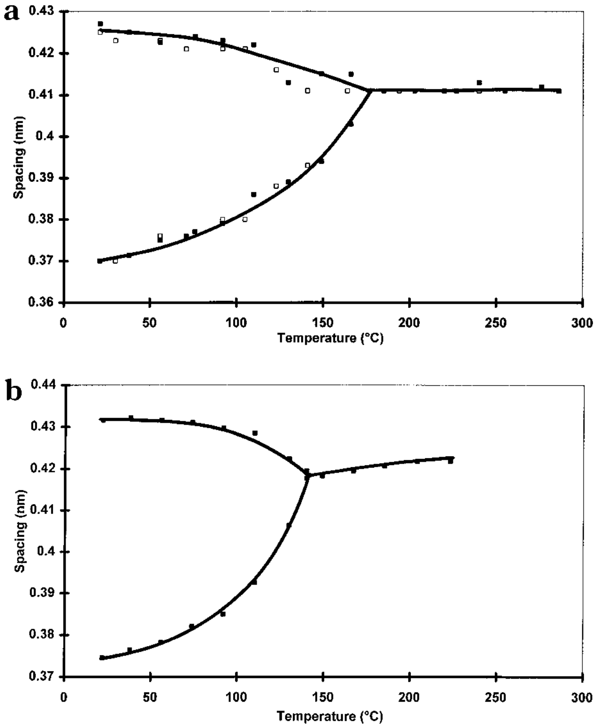

Figure 5. Graphs showing variations to the 100 and 010/110 spacings as the single crystals are heated from room temperature to the polymer melting temperature for (a) nylon 4 4 and (b) nylon 12 4: (■) WAXD data; (□) electron diffraction data.

Table 2. Thermal Data and Brill Spacings for the X 4 Nylons

nylon	Brill temp (°C)	mp (°C)	Brill spacing (nm)
4 4	170	degrades	0.415
6 4	190	275	0.42
8 4	190	254	0.42
10 4	160	242	0.42
12 4	140	237	0.42
6 6	220[a]	265	0.42[a]

[a] Data from ref 21.

function of the different nylon X 4 crystal preparations. In addition, we might expect changes of Brill temperature because of variations in the location and distribution of the amide groups within the polymer backbones.

We have previously shown that nylon 8[8] and nylon 6 8[5] lamellar crystals grow in the high-temperature phase. Spherulitic samples of nylon 6 6 have recently been shown to grow in the high-temperature pseudohexagonal phase.[16] Nylon 8 crystals usually transform to the hydrogen-bonded sheet structure on cooling, but the high-temperature phase can be observed at room tempertature in crystals which have been quenched from the crystallization temperature to below the glass transition temperature.[8] The observation, at room temperature, of faint traces of the pseudohexagonal phase in some of our nylon X 4 single crystals is consistent with the hypothesis that these crystals, too, grow in the pseudohexagonal phase which is more stable at high temperatures.

We can draw definite conclusions about the chain folding in lamellar crystals of these nylons of the *X*4 group. In these materials, as for nylon 6 6, there is no polarity to the chain and this means that, if the hydrogen bonds are to be linear, adjacent re-entry folds must be via the alkane segments (see Figure 6 and also 1a which show the analogous case for nylon 6 6). Nylon 6 6 can fold in either of the two alkane sequences.[2,22] However, this cannot be the case for the X 4 nylons. A previous study of nylon 4[6] has shown that it is not possible to achieve a chain fold in an alkane segment as short as three methylene units; for nylon 4 the amide group has to be in the fold because each alkane segment is too short to complete a fold. The X 4 nylons have only two methylene units in the diacid alkane sequence, so folding in this part of the chain is certainly impossible. Because each fold must lie in an alkane segment in order to achieve linear hydrogen bonding, the folds, in every case, have to lie in the diamine alkane segments. This sequence is shortest, four methylene units, in nylon 4 4, and this is just long enough to achieve a fold;[6] folding will be easier in all higher X 4 nylons. Thus, this series of nylons is unique in that we can be sure of the folding; in each case, the fold must be in the diamine alkane chain segment. The form of the folds is shown in Figure 6 for nylons 4 4 and 8 4. It is clear from the figure that the fold in the diamine alkane chain segment is only just possible for nylon 4 4; the hydrogen bonds adjacent to the folds show some strain.

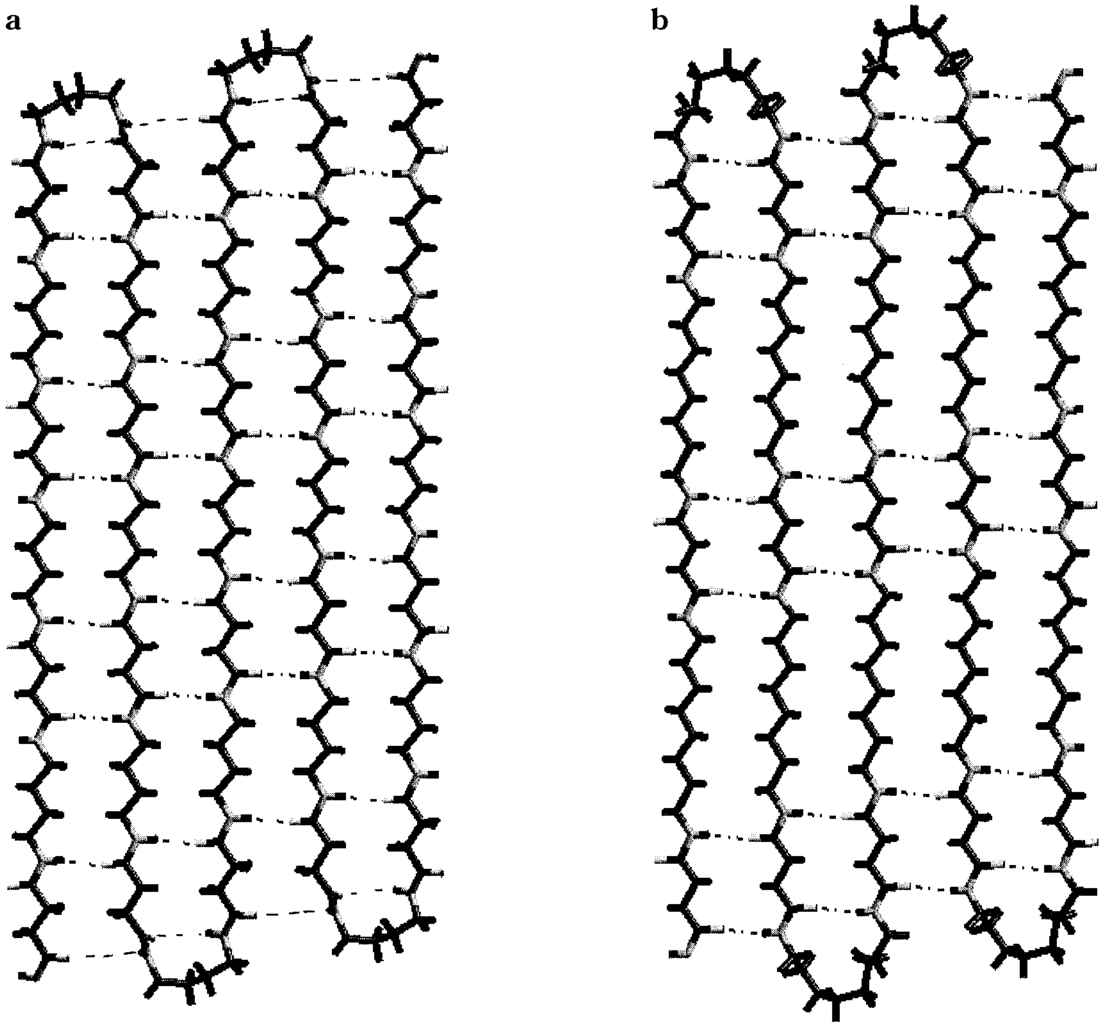

Figure 6. View of the chain-folded hydrogen-bonded sheets in the *ac* plane of (a) nylon 4 4 and (b) nylon 8 4. The methylene units are in black, the amide units are in gray, and the hydrogen bonds are indicated with dashed lines. These polyamides must fold through alkane chain segments to maintain the hydrogen-bonding pattern; they have to fold in the diamine alkane segments because the diacid alkane segments are not long enough to complete the fold. The hydrogen bonds adjacent to the folds in nylon 4 4 can be seen to be strained.

Conclusions

(i) Single crystals of five members of the nylon X 4 series have been grown. All are chain-folded lamellae with lathlike shapes, but there are differences in detailed morphologies. These five nylons all behave similarly with respect to their room temperature crystal structures and behavior on heating.

(ii) At room temperature the crystals are composed of chain-folded, hydrogen-bonded sheets, the hydrogen bonds form a progressive shear pattern, and the sheets are sheared progressively parallel to the sheet plane so that the unit cells are triclinic. All have crystal structures closely related to that of nylon 6 6.

(iii) As is the case for single crystals of other even−even nylons on heating, the two strong diffraction signals (characteristic of the triclinic structure) move together and meet at temperatures between 140 and 190 °C. In each case, the triclinic structure gradually transforms into the pseudohexagonal phase as the temperature rises and the Brill temperature is well below the melting temperature.

(iv) In all these respects, the single crystals of these five nylons from the X 4 group are similar to nylon 6 6, and their behavior is as we would predict from our previous studies of even−even nylons.

(v) The melting points of solution-grown crystals of the various X 4 nylons increase with increasing linear hydrogen bond density. Nylon 4 4 crystals degrade before the extrapolated melting temperature is reached.

(vi) In this series of nylons, we can be sure that the folds must be in the diamine alkane segments of the polyamide chains.

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