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Comparison of Structures and Behavior on Heating of Solution-Grown, Chain-Folded Lamellar Crystals of 31 Even−Even Nylons

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ABSTRACT: A wide-ranging and varied group of 31 even−even nylons, in the form of adjacent, re-entry chain-folded lamellar crystals, are compared and contrasted with respect to their room-temperature structures and behavior on heating. In this comparison, various relationships and trends emerge that provide a clearer understanding of the salient features that control the competitive interplay between the nylon chemistry, the crystal structure of the lamellar core, and the nature of the folds. For even−even nylons with differing alkane segment lengths, only one type of hydrogen-bonded sheet is found; for those with equal alkane segment lengths ($2N$ $2(N+1)$ nylons), two types of hydrogen-bonded sheet are found and there is direct coupling with the fold chemistry. In some cases the fold chemistry and/or stereochemistry dictate the sheet structure (e.g., nylon 4 6), while in other cases the reverse is true (e.g., nylon 4 4). There is no chain directionality in these even−even nylons, and it transpires that the two distinct alkane segments, diamine and diacid, can independently influence the final structure and behavior on heating. Relatively high intrachain amide density molecules (e.g., nylon 2 4) need to incorporate amide units within the adjacent, re-entry folds, and the fold geometry can bear a resemblance to the folding found in apβ-sheet proteins. For molecules with short, dimethylene, diamine alkanes (2 Y nylons) the proximity of the intrachain amide units perturbs the all-trans conformation; however, for molecules with similarly short, dimethylene, diacid alkanes (X 4 nylons) the all-trans conformation occurs. Nylon isomer pairs with inverted amides (nylons X Y and $Y-2$ $X+2$) form sheets with the same hydrogen-bonded lattice parameters; however, these pairs usually exhibit different sheet stacking and behave differently on heating. Comparisons are made between the behavior on heating, including the Brill transformation, of the 31 even−even nylons.

Introduction

We are interested in the interplay between chain-folding and the straight-stem crystallography of nylon crystals. The even−even nylons are a prominent group within the nylon family where contiguous amide units along the chain are in a syncephlic (i.e., head to head) arrangement, creating diamine and diacid alkane segments of lengths which differ between the various members of the group,[1] as shown in Figure 1. As a consequence, the even−even nylon chains have no overall directionality. This is helpful in the case of chain-folded, adjacent re-entry lamellar crystals since it removes considerations of chain directionality and allows us to focus more succinctly on how the interchain interactions correlate with the detailed distribution of amide units and the consequences that this has for the chemistry of the fold.

Even−even nylon chain-folded lamellae precipitated from dilute solution were examined by Geil,[2] who showed that nylons 6 6 and 6 10 give diffraction signals corresponding to spacings of 0.44, 0.41, and 0.37 nm; the latter two occurring only occasionally. The 0.44 and 0.37 nm ($hk0$) spacings are characteristic of the α- and β-structures of nylons 6 6 and 6 10 previously determined by Bunn and Garner[3] from fiber systems. Holland[4] showed that nylon 6 6 polymer chains are tilted at a substantial angle to the lamellar surface. Dreyfuss and Keller[5] sedimented lamellar crystals to form oriented mats and, on the basis of X-ray diffraction results, showed that the diffraction signals indexed on the Bunn and Garner unit cell[3] but that the chain direction (c axis) is inclined at 42° to the lamellar normal, such that the $00l$ planes are parallel to the lamellar surface. These planes give rise to the characteristic meridional diffraction signals observed in the wide-angle X-ray diffraction pattern from oriented mats, when the incident X-ray beam is parallel to the mat surface and the mat normal is vertical. The nature of the meridional diffraction signals has been investigated by several authors. Dreyfuss[6] compared the spacings of these $00l$ diffraction signals to the low-angle X-ray diffraction signal, corresponding to the lamellar stacking periodicity (LSP), and

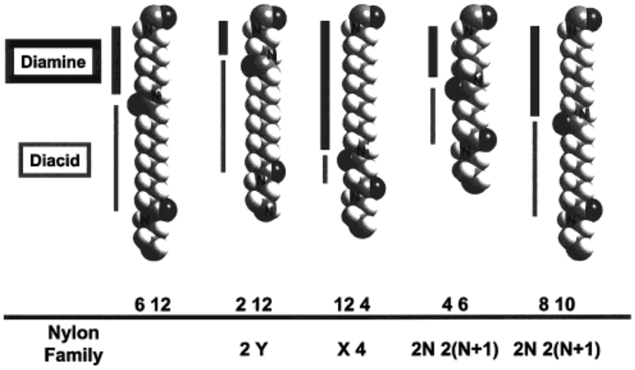

Figure 1. Computer-generated space-filling models of selected nylons from the overall group investigated. The diamine and diacid alkane segments have been highlighted by black (double thickness) and gray lines, respectively. The amide units are in a head to head arrangement; thus, the chain has no overall directionality. The groups to which these nylons belong are indicated, e.g., 2 Y, X 4 and $2N$ $2(N+1)$. Color code: hydrogen, white; oxygen, dark gray; carbon, medium gray. The nitrogen atoms are labeled "N".

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Y \ X	2	4	6	8	10	12
4	forms 1 & 2 1) β_a–phex 0.41, 0.39 $T_{Deg} > T_B$ 2) 0.48, 0.38 N. A.	α_p 0.44, 0.37 $T_{Deg} > T_B$	α_p 0.44, 0.37 $T_M > T_B$	α_p 0.44, 0.37, $T_M > T_B$	α_p 0.44, 0.37, $T_M > T_B$	α_p (phex) 0.44, 0.37 $T_M > T_B$
6	α_p–phex 0.42, 0.39 $T_M > T_B$	β_a 0.44, 0.37, $T_M > T_B$	α_p (β_p) 0.44, 0.37 $T_M > T_B$	α_p (β_p) 0.44, 0.37, $T_M > T_B$	α_p β_p 0.44, 0.37, $T_M > T_B$	α_p (β_p) 0.44, 0.37 $T_M > T_B$
8	α_p–phex 0.42, 0.39 $T_M > T_B$	α_p β_p (phex) 0.44, 0.37, $T_M = T_B$	β_a 0.44, 0.37 $T_M > T_B$	α_p (β_p) 0.44, 0.37 $T_M > T_B$	α_p β_p (phex) 0.44, 0.37 $T_M = T_B$	α_p (β_p) 0.44, 0.37 $T_M = T_B$
10	α_p–phex 0.42, 0.39 $T_M > T_B$	α_p β_p (phex) 0.44, 0.37 $T_M = T_B$	α_p β_p (phex) 0.44, 0.37 $T_M = T_B$	α_p (β_p) 0.44, 0.37 $T_M > T_B$	α_p β_p 0.44, 0.37 $T_M = T_B$	α_p β_p (phex) 0.44, 0.37 $T_M = T_B$
12	α_p–phex 0.42, 0.39 $T_M > T_B$	α_p β_p (phex) 0.44, 0.37 $T_M = T_B$	α_p β_p (phex) 0.44, 0.37 $T_M = T_B$	α_p (β_p) 0.44, 0.37 $T_M = T_B$	α_p β_p 0.44, 0.37 $T_M = T_B$	α_p β_p (phex) 0.44, 0.37 $T_M = T_B$
18			α_p β_p 0.44, 0.37 $T_M = T_B$			

Figure 2. Comparison of the even−even nylons studied. They are classified as follows. (i) The room-temperature structures: "α", "*β*", and "phex" refer to the α-, *β*-, and pseudohexagonal structures present at room temperature. Subscripts "$_p$" and "$_a$" denote the progressive or alternate *c*-axis shear of chains within the chain-folded sheets. Structures in parentheses are minority phases. The projected interchain and intersheet diffraction spacings are also listed, all spacings are in nanometers, e.g., α_p (β_p), 0.44 (0.37). The 2 *Y* nylon group have structures between the room-temperature structure of even−even nylons (either α_p-structure or, for nylon 2 4, β_a-structure) and the high-temperature pseudohexagonal structures. This is indicated as "α_p-phex" (see text for more details). (ii) The behavior on heating: if either $T_M = T_B$ or $T_M > T_B$ (real or extrapolated); T_M and T_B are defined in text. T_{Deg} represents the degradation temperature. Since nylon 2 4, form II, has smectic ordering, it cannot be classified in terms of the usual even−even nylon structures.[22]

used this to assess the number of chemical repeats per lamellar thickness. Atkins et al.[7] took this analysis one stage further, by examining the subsidiary maxima between the 001 and 002 diffraction signals of nylon 6 6 lamellae sedimented into oriented crystal mats. They found that the best fit for their experimental data occurred for 3.5 chemical repeats per lamellar thickness, with adjacent, re-entry chain folds in the diacid alkane segments.

There have been few detailed structural analyses of even−even nylon lamellae precipitated from dilute solution. However, there have been extensive infrared spectroscopic studies undertaken on films and fibers.[8−13] Most authors have applied the existing structures for even−even nylons, usually the Bunn and Garner[3] structures of nylons 6 6 and 6 10, and studied lamellar thickness and chain folding. Notable exceptions to this are the structure determination of nylon 12 10 by Franco and Puiggali[14] and recent work on other even−even nylons by ourselves.[15−22] We have, over the past few years, compiled structural and morphological data on solution-grown lamellae of 31 even−even nylons, which are presented in Figure 2.[15−22] In this paper we compare the structures of all these nylons at room and elevated temperatures. By studying the structure and properties of even−even nylons with the varying chemical composition, we endeavor to ascertain the relationships between their chemical features and physical properties. On the basis of this information, we have sought to arrange the even−even nylons into a number of groups with related properties and chemical structures, e.g. the 2 *Y* nylons[19] and the 2*N* 2(*N* + 1) nylons.[20] The synthesis of all nylons investigated was confirmed by elemental analysis and infrared spectra. All molecular weights were in excess of 10 000. The details of synthesis and experimental procedures are given in refs 15−22 and references therein.

In this paper, we show the overall similarities and patterns of structures found within this extensive group of even−even nylons. We find that there are subtle differences in structure, owing to the interplay between the important factors of hydrogen bonding, alkane segment length and distribution, chain folding, and van der Waals forces.

General Discussion of Even−Even Nylons

Chain-folded Hydrogen-Bonded p-Sheets and a-Sheets. Hydrogen bonding plays a key role in the crystallization and structure of aliphatic polyamides.

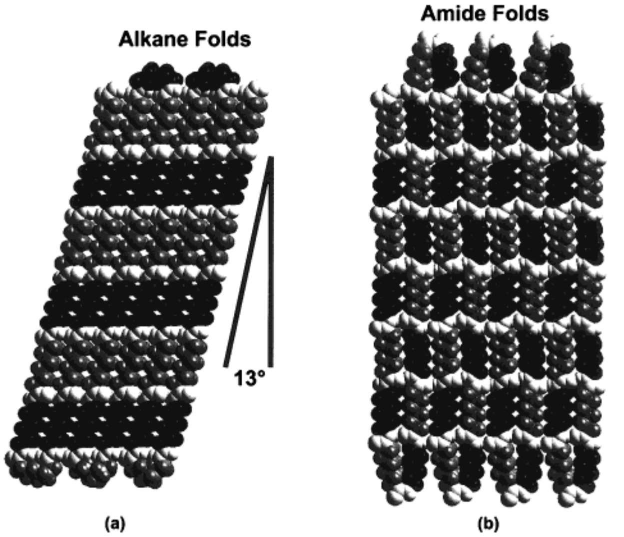


Figure 3. Two possible projections of nylon 6 8 hydrogen-bonded sheets. Color code: diamine alkane, black; diacid alkane, dark gray; amide units, white. (a) View orthogonal to a p-sheet, illustrating the invariant progressive shear of chains by 13° and the adjacent re-entry chain folds, containing an alkane segment; either the diamine (upper fold surface) or diacid alkane (lower fold surface). (b) View orthogonal to an a-sheet, illustrating the alternating shear of the chains and adjacent, re-entry chain folds containing an amide unit.

Repetitive sequences of $>C{=}O\cdots H{-}N<$ hydrogen bonds occur at regular intervals between the chains, and these hydrogen bonds have the lowest energy when they are linear. At room temperature, lamellar crystals of even−even nylons are usually composed of stacks of chain-folded sheets.[3] Most even−even nylons can only form chain-folded sheets with linear hydrogen bonds in the manner shown in Figure 3a; these sheets are called p-sheets.[20] The hydrogen bonds, and therefore the chains, progressively shear by 13° parallel to the chain axis (*c* direction) within each hydrogen-bonded sheet. We know, from our previous studies, where the precise lamellar thickness has been calculated from subsidiary maxima,[19,7] that there is insufficient room for loose switchboard-type chain folds to be incorporated within the space allowed by the lamellar stacking periodicity (LSP). Even when the straight-stem crystallography conspires to suppress the intensity of subsidiary maxima, we have good reason to believe that tight, adjacent re-entry chain folds are adopted by these solution-crystallized nylon lamellae. Adjacent re-entry folding is, of course, consistent with structures utilizing all the possible hydrogen bonds. For the hydrogen bond pattern found in p-sheets to be sustained in adjacent re-entry chain-folded lamellar crystals, each fold must contain an alkane segment. Should the alkane sequences be very short, it would also be possible to have three alkane segments (plus two amide units) in each fold.[20,22] This fold geometry bears a resemblance to the γ-folds reported in apβ-sheet proteins.[23]

Those even−even nylons with equal numbers of methylene groups in both the diacid and diamine alkane segments, i.e., the nylon $2N$ $2(N+1)$ group, also have the opportunity to form chain-folded sheets with alternately sheared chains, known as a-sheets[15,16,20,22] (Figure 3b). For this hydrogen bonding pattern to be sustained in adjacent re-entry chain-folded lamellar crystals, each fold must contain an amide unit at the apex of the fold.[22] These a-sheets are not possible for even−even nylons with different numbers of methylene units in the two alkane segments. We have studied five nylons of the $2N$ $2(N+1)$ group, nylons 2 4,[22] 4 6,[15] 6 8,[16] 8 10,[20] and 10 12.[20] In the case of nylon 2 4, with alkane segments consisting of only two methylene units, stereochemical restrictions occur, and it will be more convenient to discuss it later. Of the other four $2N$ $2(N+1)$ nylons, solution-crystallized lamellae of nylons 4 6[15] and 6 8[16] consist of a-sheets at room temperature, while solution grown crystals of nylons 8 10 and 10 12 are found to crystallize in p-sheets.[20] For the p-sheet hydrogen-bonding pattern to be achieved, the fold must be completed in a single alkane segment. The shorter alkane segments of nylon 4 6 are not long enough to achieve complete, unstrained folds in a single alkane segment; however in the case of nylons 8 10 and 10 12, the alkane segments are sufficiently long for the fold to be completed in a single alkane segment. Folds are less demanding in the a-sheet structure, where two alkane segments (plus an amide unit) are included in each fold. Hence, if the folds are to be unstrained, nylon 4 6, with short alkane segments, can only form amide folds and must hydrogen-bond as chain-folded a-sheets. Conversely, nylons 8 10 and 10 12 can make either amide folds or alkane segment folds without straining the polymer chain; thus, both a-sheets and p-sheets are possible for these nylons. The fact that they were found to crystallize into p-sheets indicates that the p-sheet structure generally has the lower energy of the two hydrogen-bonded sheet structures. This is as expected, from consideration of dipole alignment in a-sheets and p-sheets and because of the loss of hydrogen bonds when amide groups are located in the folds.[20] Nylon 6 8 is an intermediate polymer with six methylene units in each alkane segment; we have observed solution-crystallized lamellae of nylon 6 8 in the form of chain-folded a-sheets,[16] whereas other authors have reported fibers consisting of p-sheets.[24] This change from a-sheet to p-sheet structure, with increasing alkane segment length in the $2N$ $2(N+1)$ nylon series, is an instructive example of how, under special circumstances, the nature of the chain fold can affect the crystal structure. This feature reinforces the fact that the folding pattern is regular, adjacent re-entry.

Other even−even nylons, where the diamine and diacid alkane segments are unequal in length, are unable to achieve the a-sheet hydrogen-bonding pattern, and only p-sheets are found. Certain even−even nylons, with short alkane segments, e.g., nylons 4 4 and 2 6, form p-sheets, even though they must chain fold via a single alkane segment. There is no alternative structure with linear hydrogen bonds available to these nylons, and consequently the fold, and the hydrogen bonds close to the fold, must be strained.[17,19]

Sheet Stacking. Chain-folded p- and a-sheets stack together via van der Waals forces. The p-sheets are most commonly found to stack with a progressive shear, as illustrated in Figure 4a; this was referred to as the α-structure by Bunn and Garner for the principal crystalline phase of nylon 6 6.[3] In addition it is possible for the chain-folded sheets to stack with alternating shear (see Figure 4b); this was termed the β-structure by Bunn and Garner.[3] As a consequence, there are four possible types[20] of crystal structure: (1) alkane fold/p-sheets stacked with a progressive shear, α_p-structure; (2) alkane fold/p-sheets stacked with an alternate shear, β_p-structure; (3) amide fold/a-sheets stacked with a

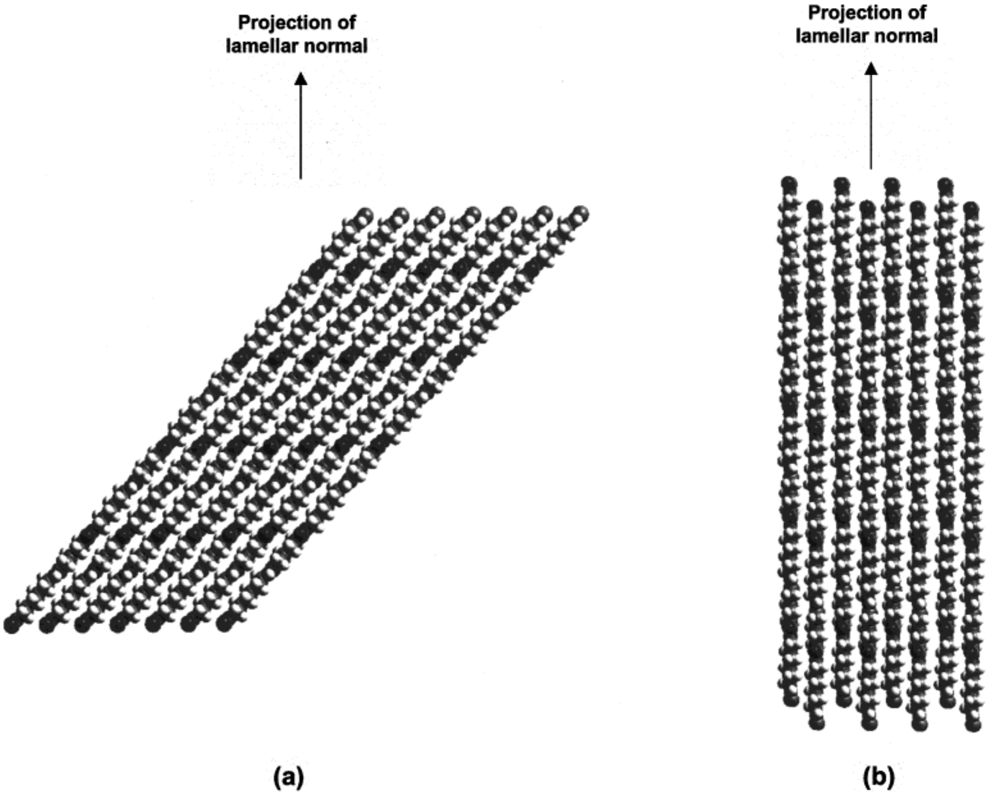


Figure 4. Projections of the even−even nylon sheet stacking. (a) View parallel to the hydrogen-bonded sheets (shown in Figure 3) in the α-structures of even−even nylons, illustrating the progressive intersheet shear. The relative stacking of sheets is controlled by van der Waals forces and can be different for each even−even nylon. (b) View parallel to the hydrogen-bonded sheets in the β-structures of even−even nylons, illustrating the alternating intersheet shear.

progressive shear, α_a-structure; (4) amide fold/a-sheets stacked with an alternate shear, β_a-structure.

We have observed three of these four possible structures in solution-crystallized even−even nylons at room temperature. Lamellar crystal preparations of nylons 4 8, 4 10, 4 12, 6 10, 6 12, 6 18, and 8 12;[18] nylons 8 10 and 10 12;[20] nylon 12 10;[14] and nylons 6 6, 8 6, 8 8, 10 6, 10 8, 10 10, 12 6, 12 8, 12 10, and 12 12[21] have been shown to exhibit the α_p-structure plus varying quantities of lamellae in the β_p-structure. Lamellar crystals of nylons of the type *X* 4 (4 4, 6 4, 8 4, 10 4, and 12 4) show the α_p-structure only, and those of nylons 4 6[15] and 6 8[16] are found at room temperature in the β_a-structure. We have not observed the α_a-structure. All of the four possible structures generate two characteristic diffraction signals, observed at 0.44 and 0.37 nm.[3,20] These aspects are summarized in Figure 2.

Of all the 31 nylons reported here, only lamellar crystals of the 2 *Y* nylons are not found at room temperature in one of the four structures listed previously. The structures adopted by nylons 2 4, 2 6, 2 8, 2 10, and 2 12 will be discussed later, after the high-temperature structures have been described.

Low Intrachain Amide Density Nylons. In nylon crystallization, there is competition between the energy requirements of the amide units and those of the alkane segments. The lowest energy structure of the alkane segments, considered in isolation, would be the all-trans conformation crystallizing in an orthorhombic unit cell, similar to that of polyethylene. For all the nylons discussed so far, it is the amide units that dominate the crystallization, resulting in the hydrogen-bonded structures characteristic of nylons. The bulky C═O groups and the requirement for linear hydrogen bonds hold the chains apart and weaken the van der Waals interactions. However, below a certain density of intrachain amide units, the van der Waals interactions of the alkane segments would be expected to become more important than the interchain interactions of the amide units. Indeed, it can be envisioned that nylons with low intrachain amide density will not form the usual hydrogen-bonded nylon sheet structures, but instead would adopt a “polyethylene-like” crystal structure. The lowest linear amide density nylon structure to have been reported is nylon 18[25] and the lowest that we have studied are nylons 12 12[21] and 6 18.[18] In all these cases, the polymer chains form “nylon-like” sheet structures dominated by hydrogen bonding. To our knowledge, no low amide nylons have yet been observed in a “polyethylene-like” structure but eventually the frequency of amide units must become so low that the conformation will approach that of polyethylene (nylon ∞).

High-Temperature Structures and Brill Transformation. Brill[26] discovered that when crystalline fibers of nylon 6 6 are heated, the two characteristic interchain X-ray diffraction signals at spacings 0.44 nm (100) and 0.37 nm (010), respectively, move together and meet at 0.42 nm (Brill spacing), as shown for nylon 6 6 chain-folded lamellae[21] in Figure 5a, at a temperature (Brill temperature, T_B) below the melting temperature (T_M). This high temperature phase of even−even nylons is commonly referred to as pseudohexagonal since hexagonal symmetry is observed in the plane orthogonal to the chain axis (a^*b^* reciprocal plane).[27−31,16−22] As the temperature increases from T_B to T_M the Brill spacing increases slightly, due to thermal expansion.

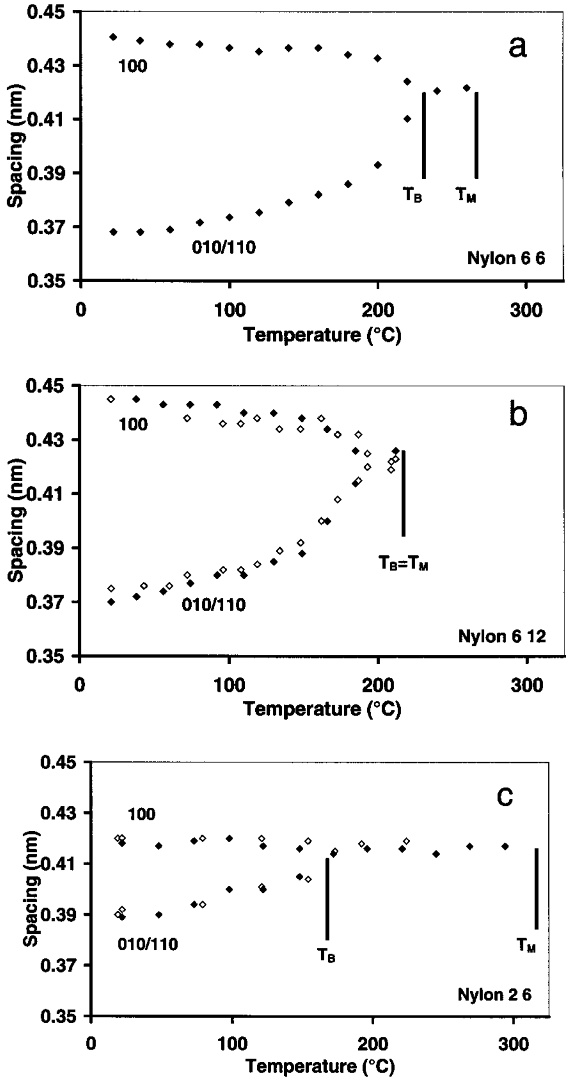


Figure 5. Plots showing changes in the 100 and 010/110 diffraction spacings for selected even−even nylons as the lamellae are heated from room temperature to the melt. The relevant values of T_B and T_M are indicated. Key: (a) nylon 6 6, $T_B < T_M$; (b) nylon 6 12, extrapolated $T_B = T_M$; (c) nylon 2 6, 2 *Y* nylon. Solid symbols: X-ray diffraction data. Open symbols: electron diffraction data.

It has been shown that crystals of nylons 4 6,[32] 6 6,[26,28−30] 6 8,[16] and 6 12[33] grow in the high-temperature pseudohexagonal phase (see Figure 5) and revert to their respective higher density room-temperature structures on cooling. We believe that all even−even nylons crystallize and grow in the pseudohexagonal phase. Only on cooling do the alkane segments become less mobile and eventually settle into the all-trans conformation. Thus, the room-temperature structure is dependent on both the nature of the high-temperature structure found during crystallization and on the manner in which this structure changes during cooling to room temperature.

Structures of 2 *Y* Nylons. Nylons 2 6, 2 8, 2 10, and 2 12, members of the nylon 2 *Y* family,[19,10] adopt room-temperature structures between the room-temperature α_p-structure and the high-temperature pseudohexagonal structure of nylon 6 6. The short dimethylenediamine segments are the only factors common to the whole nylon 2 *Y* series and different from the other even−even nylons that we have studied. Hence, we consider that the unusual room-temperature structures of the 2 *Y* nylons, and the details of their behavior on heating to the Brill temperature (see Figure 5c), must be determined by the diamine segments in the chains, rather than the diacid segments. We believe that the dimethylenediamine segments are restricted in movement,[19] and on cooling after initial crystallization this hinders the transformation from the high-temperature, pseudohexagonal growth phase, to the room-temperature sheet structure found for most even−even nylons. Thus, an intermediate structure remains at room temperature.

Table 1. Brill Temperatures (°C) of All the Even−Even Nylons Studied

	X					
Y	2	4	6	8	10	12
4	240	170	190	190	160	180
6	174	245	230	194	184	183
8	177	250	203	213	222	213
10	181	240	220	185	200	188
12	158	235	215	202	193	181
18			190			

Interestingly, nylon 2 4[22] belongs to both the nylon 2 *Y* and nylon 2*N* 2(*N* + 1) groups and its structure has features reminiscent of both. Nylon 2 4 chain folds into a-sheets, like nylons 4 6 and 6 8.[20] These sheets have been observed to stack in two ways: form I and form II. In form I, they stack to create a structure between the high temperature and room-temperature structures of nylon 4 6,[15] similar to the structures of the 2 *Y* nylons.[19,22] In form II,[22] nylon 2 4 a-sheets stack with smectic A type ordering. The fold geometry has been compared with the apβ-sheet protein folding.[22,23]

When the 2 *Y* nylons, including form I of nylon 2 4, are heated, the two characteristic diffraction spacings move together and meet well below the melting temperatures of the various polymers (or, in the case of nylon 2 4, the degradation temperature). However, the rate at which the diffraction signals move together over the 40 °C or so before the T_B is slower than with α_p-phase nylons. Thus, it appears that some aspects of the Brill structure are incorporated into the room-temperature structure of the 2 *Y* nylons. This suggests that there is less scope for change on heating, and consequently the rates of change of the 2 *Y* nylon structures with temperature are slower than those of the other even−even nylons. Despite this reduced rate of change, the T_Bs for the 2 *Y* nylons are comparable with those of the *X* 4 nylons; see Table 1.

The salient features of the room-temperature structures for all the even−even nylons that we have studied are shown in Figure 2, and the T_Bs values are set out in Table 1.

Melting Temperatures of Even−Even Nylon Lamellar Crystals. Figure 6 shows the melting points of lamellar crystals of all the even−even nylons studied in recent research from our group[16−21] and that of polyethylene,[34] plotted as a function of intrachain amide density. Since crystal thickness influences the melting temperatures (T_Ms), the T_M of polyethylene needs to be the T_M of polyethylene crystals 5−7 nm thick, to be commensurate with the thickness of a typical solution-crystallized nylon lamella. In Figure 6, two melting temperatures are indicated for polyethylene. The first, at 130 °C, is a typical experimental value for solution-grown polyethylene lamellar crystals; the second, at 100 °C, is the theoretical T_M of polyethylene crystals 6 nm thick.[34]

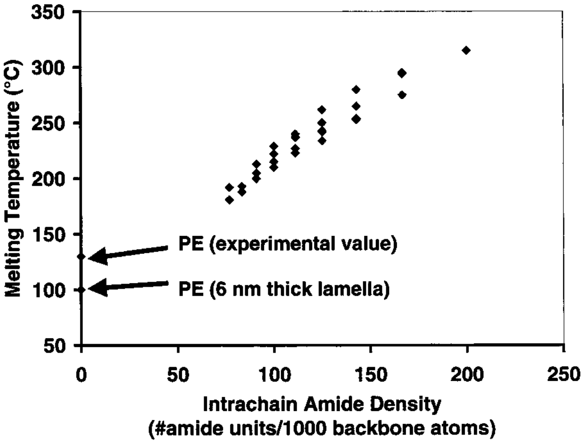


Figure 6. Plot of melting temperatures vs intrachain amide unit density for even−even nylon lamellae. The two points for polyethylene (amide density = 0) correspond to a typical value for a solution-crystallized PE lamella (130 °C) and that estimated for a 6 nm thick chain-folded lamella (100 °C).[34]

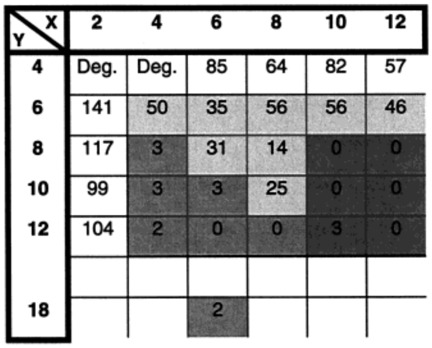
Table 2. Melting Temperatures (°C) of All the Even−Even Nylons Studied

	X					
Y	2	4	6	8	10	12
4	degr[a]	degr	275	254	242	237
6	315	295	265	250	240	229
8	294	253	234	227	222	213
10	280	243	223	210	200	188
12	262	237	215	205	193	181
18			192			

[a] degr: degrades before melting.

The melting point can be related to the intrachain amide density as follows (e.g.[35]): $T_M = x\Delta H/y\Delta S$, where T_M is the equilibrium melting temperature, x is the number of interacting amide units per repeating unit (two for all even−even nylons), ΔH and ΔS are the changes in enthalpy and entropy on melting, respectively, and y is the number of flexible methylene units per repeat. Accordingly, the melting temperature of even−even nylons should decrease with decreasing intrachain amide density.[36] At high intrachain amide densities the nylons thermally degrade before they melt, e.g. nylons 2 4 and 4 4.[17,22,37,38] The melting behavior of low intrachain amide density nylons has not been investigated; the lowest we have studied are nylons 12 12 and 6 18. Surprisingly[36] there is a linear relationship between amide density and T_M, which can be extended from lamellar crystals of nylons 6 6 and 12 12 to the predicted melting temperature of 6 nm thick polyethylene lamellar crystals; see Figure 6 and ref 39. However, it seems likely that very low amide intrachain density nylons will have lamellar thicknesses greater than 5−7 nm and will consequently have enhanced melting temperatures.[34]

Table 2 lays out the T_Ms of the even−even nylons; they decrease with decreasing intrachain amide density.[39,35] Within any particular group, e.g., the *X* 6 group (2 6, 4 6, 6 6, 8 6, 10 6, and 12 6) or the 8 *Y* group (8 4, 8 6, 8 8, 8 10, and 8 12), this can be seen by looking along any row (*X N*) or down any column (*N Y*) of Table 2. However, the detailed variation of melting points is complex and subtle. For instance, within any of the sets of nylons of equal amide density (bottom left to top right diagonals), members of the 2 *Y* family have the highest melting points, presumably because of their short diamine segment and its effect on crystal structure. Additionally for any particular nylon, variations in T_M can occur as a result of, for example, different crystallization conditions which can give different lamellar thicknesses, crystal perfections, and degrees of crystallinity.



Y \ X	2	4	6	8	10	12
4	Deg.	Deg.	85	64	82	57
6	141	50	35	56	56	46
8	117	3	31	14	0	0
10	99	3	3	25	0	0
12	104	2	0	0	3	0
18			2			

Figure 7. Chart listing $T_M - T_B$ values (±3 °C) for the even−even nylons studied. Unshaded region: nylons containing one or two dimethylene alkane segments. Light gray region: $T_B < T_M$. Medium gray region: extrapolated $T_B = T_M$, due to high T_B. Dark gray: extrapolated $T_B = T_M$, due to low T_M (see text for further discussion).

Relationship Between the Brill and Melting Temperatures. It is apparent, from Figure 2, that T_B becomes equal to T_M with decreasing amide density (shaded region in Figure 2). The relationship is not straightforward; for instance, nylons 6 8, 8 8, and 8 10 have unexpectedly low T_Bs. It should be recalled that the measured T_B is dependent on the crystallization conditions. It has been noticed that lamellar crystals of nylon 8[40] and melt-crystallized nylon 6 6[30] show considerable variations in T_B as a function of the crystallization conditions. In practice, a range of values of T_B could be obtained, for a particular nylon, by changing the crystal perfection; hence, if a nylon is to be ascribed a single T_B, then it should be the highest obtainable. The measured crystal melting point is more consistent and less dependent on crystallization conditions than the measured T_B. The melting temperatures are accurate to a few degrees, but for reasons described above, we cannot always be confident that we have the highest possible T_B.

Despite some uncertainty in the measured T_B, general trends are apparent. As previously stated, all even−even nylons with dimethylene alkane segments, the *X* 4 and 2 *Y* groups, have T_Bs well below their T_Ms; see Figure 7. Excluding these groups, nylons with more methylene units in the diacid segment than in the diamine segment (medium gray in Figure 7) all have $T_B = T_M$[18] (see Figure 7; Tables 1 and 2) as a result of the rigidity in the diamine alkane segments.[18] Conversely, nylons with longer diamine segments than diacid segments have either $T_B = T_M$ or $T_B < T_M$ (see Figures 2 and 7).[21] Of this group of nylons, those with extrapolated $T_B = T_M$ (nylons 10 8, 10 10, 10 12, 12 8, 12 10, and 12 12, shaded dark gray in Figure 7) all have T_Ms less than those nylons with $T_B < T_M$ (light gray). Thus, it appears that these nylons (dark gray) have $T_B = T_M$ because their melting temperatures are relatively low. In contrast, nylons 4 8, 4 10, 4 12, 6 10, 6 12, 6 18, and 8 12 (medium gray) have $T_B = T_M$ because of their high T_Bs.

Changes to the 00*l* Diffraction Signals on Heating. When nylon α_p-structure lamellae are heated, the 00*l* diffraction signals (corresponding to the *c* value

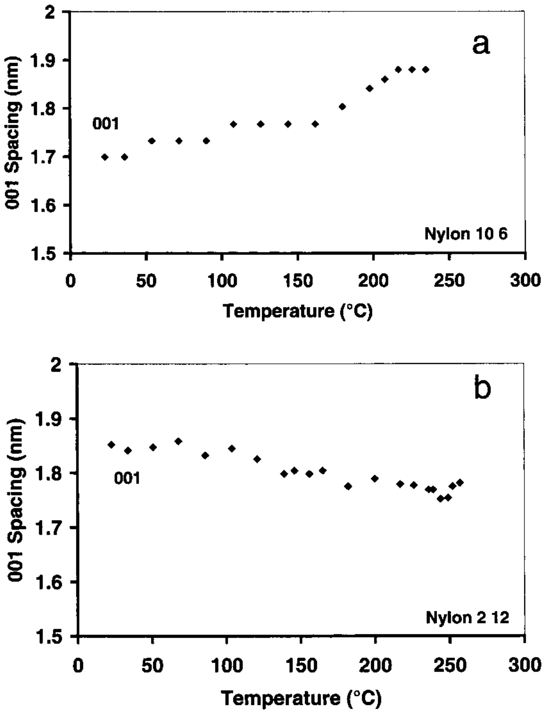


Figure 8. Plots showing changes in the 001 X-ray diffraction spacing as selected even−even nylon lamellae are heated from room temperature to the melt. (a) nylon 10 6 and (b) nylon 2 12.

projected onto the lamellar normal) are observed to change; see Figure 8. This is a consequence of two effects: (1) on heating, the alkane segments become mobile and librations occur, twisting the chain out of an all-trans planar zigzag, and gauche conformations are temporarily formed, causing the c value to decrease; (2) on heating, the chain-folded sheets slip past each other in the c direction. The $c{}^\wedge c^*$ angle decreases, causing the 00l spacings to increase. All the nylons in this study, apart from the nylon 2 Y group, behave like nylon 10 6 (Figure 8a). The 00l spacings are observed to increase on heating (~11%), showing that the tilting of the polymer chains is the dominant mechanism.

At room temperature, the polymer chains in the 2 Y group are tilted at only 30°-34° to the lamellar normal, rather than 42° for nylon 6 6. On heating, the chains have less scope to tilt than those of nylon 6 6, and consequently the twisting of the polymer chains is more important. As a result, the 00l spacings of the 2 Y nylons either remain constant or decrease on heating (~4%, see Figure 8b).

Comparison of Nylon Isomer Pairs with Inverted Amides (NIPIAs). If nylons could be modeled by a planar zigzag backbone with interchain hydrogen bonds, then the direction of the hydrogen bonds should not influence the crystal structure. In this context, it is interesting to compare the 2 Y nylons with the X 4 nylons. Both groups have an alkane segment containing one dimethylene unit, but in the 2 Y group the diamine alkane is short and in the X 4 group the diacid alkane is short. The difference between nylons 2 10 and 8 4 is that the directions of the amide groups within these sheets have been reversed (see Figure 9).[19] As would be expected, both nylons crystallize to form p-sheets; indeed, both stack their sheets with a progressive shear. However, which alkane segment is the shorter crucially affects the resulting crystal structure. The X 4 family of nylons adopt structures similar to the α_{P}-structure of nylon 6 6. In contrast, the 2 Y nylons adopt room-temperature structures between the room-temperature α_{P}-structure and high-temperature pseudohexagonal structure of nylon 6 6. As previously stated, we believe that, like all other even−even nylons, these materials originally crystallize in the pseudohexagonal structure; all nylons of both groups have a pseudohexagonal structure at high temperatures and T_{B}s well below their T_{M}s. However, the manner in which the characteristic interchain diffraction signals move apart on cooling (or, conversely, move together on heating) differ between the 2 Y and X 4 groups. We believe that the reason for this difference in behavior is, at least in part, a result of the difference in flexibility between the diamine (and diacid) dimethylene alkane segments, constrained, as they are, by their two terminal N−H (and C═O) groups. The notion that the environment of the amide unit, i.e., the length of the adjacent alkane segments and location of amide units, determines chain conformation has recently been highlighted in the literature.[41,42]

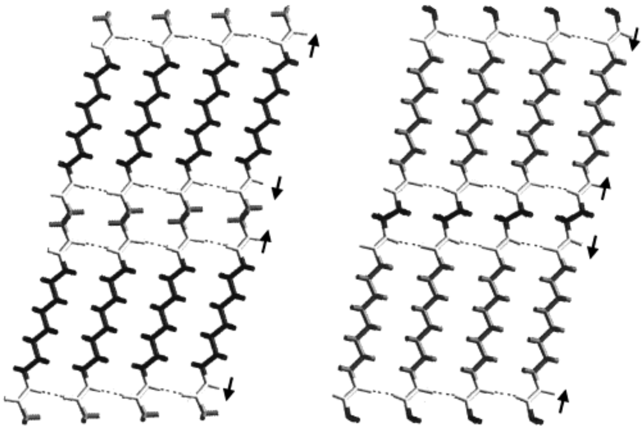

(a) Nylon 8 4 (b) Nylon 2 10

Figure 9. Example of a nylon isomer pair with inverted amides. Hydrogen-bonded p-sheets of nylons 8 4 and 2 10 (shading as in Figure 3). The arrows illustrate the orientation of the amide units (they point toward the carboxyl group). Nylon 8 4 has eight methylene units in the diamine segment and two in the diacid, while nylon 2 10 has two in the diamine and eight in the diacid. As a consequence, the relative hydrogen bond position, within the chain-folded sheets, are identical for these two nylons. However, there are two inherent differences: (1) the direction of amide units (arrowed) and hydrogen bonds are reversed; (2) each alkane segment is affected by the orientation of the amide units straddling it, and consequently, although the alkane segments are chemically identical, their stereochemical environments differ.

The contrast between the 2 Y and X 4 groups is particularly apparent because of the unusual room-temperature structures of 2 Y nylons. In general, one would expect nylon X Y to have an identical intrasheet hydrogen bond arrangement to nylon $Y-2$ $X+2$, e.g., nylons 10 8 and 6 12. We will call nylon isomers of this type nylon isomer pairs with inverted amides (NIPIAs), as shown in Figure 9.[43] For such nylon pairs it might be expected that the sheet stacking and behavior on heating would also be similar. However, from Figures 2 and 7 and Tables 1 and 2, it is clear that the crystal structure and properties of most NIPIAs are different. Some of the nylons in the range $X \geq Y$ and $Y \geq 6$ (light gray and dark gray in Figure 7) have only a trace of β_{P}-phase crystals or $T_{\mathrm{B}} < T_{\mathrm{M}}$, whereas all the nylons in the range $X \leq Y - 4$ and $X \geq 4$ (medium gray in Figure 7) have $T_{\mathrm{B}} = T_{\mathrm{M}}$ and all, except nylon 8 12, have substantial quantities of β_p-crystals. The reason for these different properties probably derives from the relative orientation of amide units with respect to the different alkane segments. We believe that dimethylenediamine units restrict chain motion to a greater extent than short diacid segments and that this accounts for the unusual structures and properties of the 2 *Y* nylon group.[19] It also appears that the short diamine segments of the 4 *Y* nylons (nylons 4 8, 4 10, and 4 12) may account for their high T_Bs.[18] The differences between the 2 *Y* and *X* 4 nylon groups highlights the need to appreciate the subtleties in conformation and distribution of the amide units, to understand the structures of nylons and to predict their properties and behavior as a function of temperature.

Conclusions

The comparison of chain-folded, adjacent re-entry lamellar crystal structures of such a large group of even−even nylons has provided a unique opportunity to ascertain trends and relationships between polyamide chemistry, crystal structure, and fold chemistry and geometry. Within the 31 even−even nylons studied, there is a substantial range in average intrachain amide density, e.g., from nylon 12 12 up to nylon 2 4, and a wide spread in amide distributions, as summarized in Figure 2.

The overall pattern, at room temperature, is that the even−even nylons crystallize in the form of chain-folded hydrogen-bonded sheets stacking via van der Waals interactions to form lamellar crystals. With the exception of the $2N\ 2(N+1)$ nylons, the only fully saturated hydrogen-bonded sheet arrangement available is in the form of p-sheets. Such p-sheets require folding via an alkane segment. In general the p-sheets stack with progressive shear, the α_p-structure, akin to the well-known nylon 6 6 α-structure,[3] although not always with the same degree of intersheet shear. Some alternating intersheet shears, the β_p-structures, are also found to occur in varying amounts. It depends on the particular nylon and to some extent on the crystallization conditions.

The $2N\ 2(N+1)$ nylons, with equal diamine alkane and diacid alkane segments, can also form hydrogen-bonded a-sheets; thus, they have a choice of sheet structure. There is a coupling between fold chemistry and sheet structure. Nylons 2 4, 4 6, and 6 8, where the alkane segments are too short for unstrained alkane segment folding, crystallize in a-sheets and with amide units in the fold. We find that these sheets stack with alternating intersheet shear, the β_a-structure. Nylons 8 10 and 10 12, with their longer alkane segments, crystallize in p-sheets and α_p-crystal structures. Thus, the fold can determine the sheet structure. We conclude that the p-sheets have a lower energy than the a-sheets and therefore the p-sheet/alkane fold is preferred in the $2N\ 2(N+1)$ nylons when the alkane fold is unstrained. Interestingly, the other even−even nylons, with relatively short alkane segments, can only crystallize in p-sheets/alkane folds, e.g., nylon 4 4 and indeed nylon 6 6; these nylons will inevitably have strained folds, yet they still manage to crystallize in adjacent re-entry, chain-folded lamellae.

The melting points of solution-grown crystals of all the even−even nylons investigated decrease with decreasing intrachain amide density. However, the detailed variations in melting point among nylons of equal average intrachain amide density are more complex. For even−even nylons with one or more relatively short alkane segment, the Brill temperature is below the melting temperature ($T_B < T_M$), while for most others the two temperatures are coincident ($T_B = T_M$).

In the 2 *Y* nylons, the close proximity of the diamine amide unit pair introduces a perturbation into the all-trans chain conformation and, as a consequence, the 2 *Y* nylons are unable to access the usual even−even nylon room-temperature structures. Interestingly, an equally short dimethylene diacid alkane segment in the *X* 4 nylons does not perturb the all-trans chain conformation. Other examples of differences between nylon isomer pairs with inverted amides (NIPIAs) are illustrated by noticeable variations in structure and behavior on heating, e.g., NIPIA pairs: nylons 4 8 and 6 6 and nylons 4 12 and 10 6.

A comparison of these 31 even−even nylons shows that localized stereochemistry and environment need to be considered when deriving and predicting relationships between structure and properties.

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References and Notes

(1) By convention, the two numbers defining even−even nylons correspond to the number of carbon atoms between nitrogen atoms in the diamine and diacid segments, respectively. Thus, the number of carbon atoms in the diacid segment always includes the two additional carboxyl carbon atoms. For example, nylon 4 6 actually has four methylene units in both diamine and diacid segments.
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