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Chain-folded lamellar crystals of aliphatic polyamides. Investigation of nylons 4 8, 4 10, 4 12, 6 10, 6 12, 6 18 and 8 12

N. A. Jones, E. D. T. Atkins*, M. J. Hill, S. J. Cooper and L. Franco
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK
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Chain-folded single crystals of the seven even–even nylons: 4 8, 4 10, 4 12, 6 10, 6 12, 6 18 and 8 12 have been grown from solution and their morphologies and structures studied using transmission electron microscopy; both imaging and diffraction. Sedimented mats were examined using X-ray diffraction. The solution grown single crystals are lath-shaped lamellae. Diffraction from these crystals, at room temperature, reveals that three crystalline forms are commonly present. The crystals are composed of chain-folded, hydrogen-bonded sheets; the linear hydrogen bonds within the sheets generate a progressive shear of the chains. The sheets are found to stack in two different ways; some of the sheets stack with progressive shear, to form 'α-phase' crystals; other sheets stack with alternate up and down stagger, to form 'β-phase' crystals. Both the α- and β-crystals give two strong diffraction signals at spacings of 0.44 and 0.37 nm; these signals represent a projected inter-chain distance within a hydrogen-bonded sheet (actual value 0.48 nm) and the inter-sheet spacing, respectively. Some crystals also show an additional diffraction signal at 0.42 nm; this signal is characteristic of the pseudo-hexagonal phase, a phase usually only found at high temperatures. The melting points of solution grown crystals of this even–even nylon series decrease with decreasing linear density of hydrogen bonds. On heating, the strong diffraction signals in both α- and β-phases move together and meet, as is the case for other even–even nylons. The lowest temperature at which the two signals first have the same spacing is termed the Brill temperature. For all the nylons of the present study the Brill temperature is coincident with the melting temperature, and the two strong signals meet at the spacing (0.42 nm) of the pseudo-hexagonal phase. The behaviour of these nylons is compared and contrasted with that of nylon 6 6, where only the α-phase is found at room temperature and, on heating, the Brill temperature is found to occur in the range 95–35°C below the melting point at 265°C. © 1997 Elsevier Science Ltd.

(Keywords: even–even nylons; lamellar crystals; diffraction)

INTRODUCTION

The nylons, or aliphatic polyamides, are important industrial materials, valuable because of their good physical properties; for instance, nylons have higher melting points than many other semi-crystalline polymers such as polyethylene. The higher melting points occur because of the formation of hydrogen bonds between chains in nylon crystals, these hydrogen bonds are able to retain the chains in an ordered solid phase after the alkane segments have effectively melted. We are investigating the single crystals of a number of even and even–even nylons. We choose to look at lamellar single crystals because the chain arrangements are well defined and we believe that the insights gained from the study of these morphologies will lead to a fuller understanding of more complex commercial samples, in which chain folding also occurs but in a less organized fashion.

The nylon polymers consist of amide groups separated by alkane segments as shown in *Figure 1*; the number of carbon atoms separating the nitrogen atoms defines the particular nylon†.

Even–even nylons form chain-folded sheets and hydrogen bonds form between amide groups in adjacent chains within the sheets. At room temperature there are no inter-sheet hydrogen bonds. The requirement that the hydrogen bonds between adjacent chains within the sheet should be linear (or close to linear) is a crucial feature in determining the crystal structure adopted by polyamides. The hydrogen bonding pattern that develops is a function of the stereochemistry of each particular nylon. In the case of nylon 6 6 chain-folded single crystals, and for most other even–even nylons, the hydrogen bonds can only be linear if the chains progressively shear within each hydrogen-bonded sheet. Hence the chains are tilted at an angle of 13° to the fold-surface normal, as illustrated in *Figure 2(a)*. These chain-folded, hydrogen-bonded sheets can stack together, either with a progressive shear; termed the α-phase by Bunn

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* To whom correspondence should be addressed

† Nylon chains with a head to head (syncephalic) arrangement of amide groups are defined by two different alkane segments; one between two nitrogen atoms (the diamine segment) and one between the two carbonyl groups (the diacid segment). The, nylon X Y has X carbon atoms in the diamine segment and Y carbon atoms in the diacid segment (including the carbons in the carbonyl groups). All the nylons studied here have both X and Y even and X < Y (i.e. more carbon atoms in the diacid segment than the diamine segment)

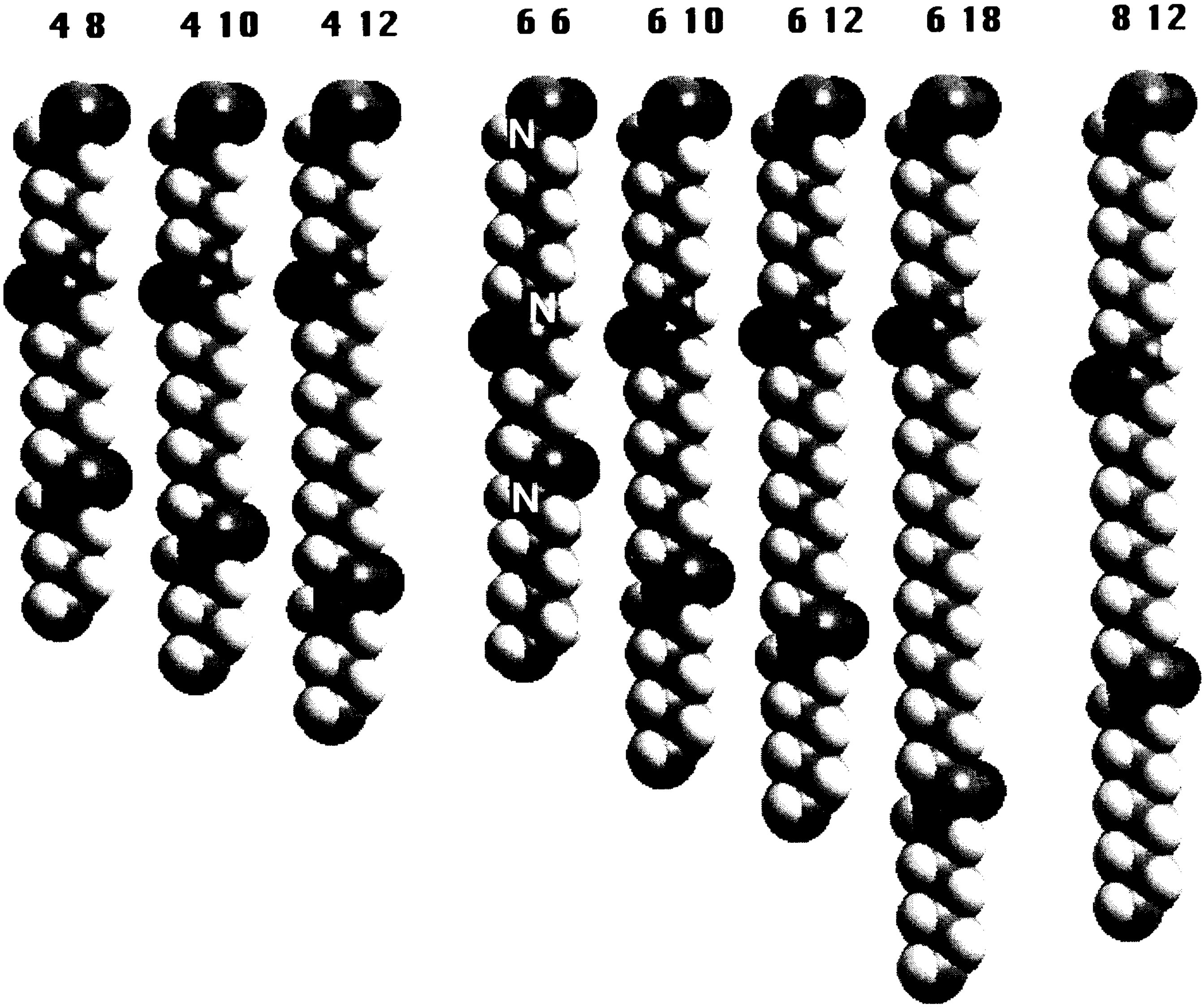


Figure 1 Computer generated space-filling models of the nylons discussed in this paper. The nitrogen atoms are labelled on nylon 6 6 only. Note that the chains have no polarity in these synchephalic even–even nylons, i.e. they are apolar. Colour code: hydrogen, white; carbon, pale grey; nitrogen, mid grey; oxygen, dark grey

and Garner[1] and shown in *Figure 2(a,b)* or with an alternating shear (termed β-phase[1]) as shown in *Figure 2(a,c)*. The α-phase structure is found experimentally for single crystals of nylon 6 6[1–3], for nylon 6 10[1,4,5] and for the other even–even nylons 4 4, 6 4, 8 4, 10 4 and 12 4[6]. Both the α- or the β-phase structures give two strong and characteristic diffraction signals at spacings 0.44 and 0.37 nm, respectively. These diffraction signals represent a projected inter-chain distance within a hydrogen bonded-sheet (actual value 0.48 nm) and the inter-sheet spacing, respectively.

On heating the polymer, the two strong diffraction signals are seen to move together and meet, typically at a spacing of 0.415 nm. A 'Brill temperature' (named after Brill, who first observed this behaviour in nylon 6 6[7] is defined as the lowest temperature for which the projected inter-chain distance within a hydrogen-bonded sheet and the inter-sheet spacing are equal. Above the Brill temperature the single spacing is observed to increase only gradually, as a result of normal thermal expansion. Brill temperatures have been reported for even–even nylons 6 6[7,8a,8b], 4 6 and 6 8[9], 6 10[10], 6 12[11], 4 4, 6 4, 8 4, 10 4 and 12 4[6] and for nylon 11[12].

Of the seven nylons discussed in the present paper we have only been able to find published data on nylons 6 10 and 6 12. Bunn and Garner[1] determined the crystallographic unit cell for nylon 6 10, and found it to be similar, apart from the longer repeat length (c-dimension), to that of nylon 6 6. Previous studies of nylon 6 10 single crystal mats, by Dreyfuss and Keller[4], were consistent with the Bunn and Garner α-phase structure[1]. Geil[5] grew single crystals of nylon 6 10 from glycerine, in the form of rolled up lamellae, and these showed a diffraction signal at 0.44 nm in all cases, and in addition, sometimes at 0.37 nm and occasionally at 0.42 nm. Dreyfuss and Keller grew single crystals of nylon 6 12, from which they prepared sedimented mats[4]. The wide-angle X-ray patterns of these nylon 6 12 mats showed the characteristic X-ray diffraction signals at spacings 0.44 and 0.37 nm and the indexing was consistent with a crystallographic triclinic unit cell similar to that of nylon 6 6 (and that of 6 10) but with the expected increased c-dimension. We can find no reference to a full determination of the crystallographic unit cell for 6 12, or any relevant information for nylons 8 12 and 6 18. Dreyfuss[13] prepared single crystal mats of nylons 4 8,

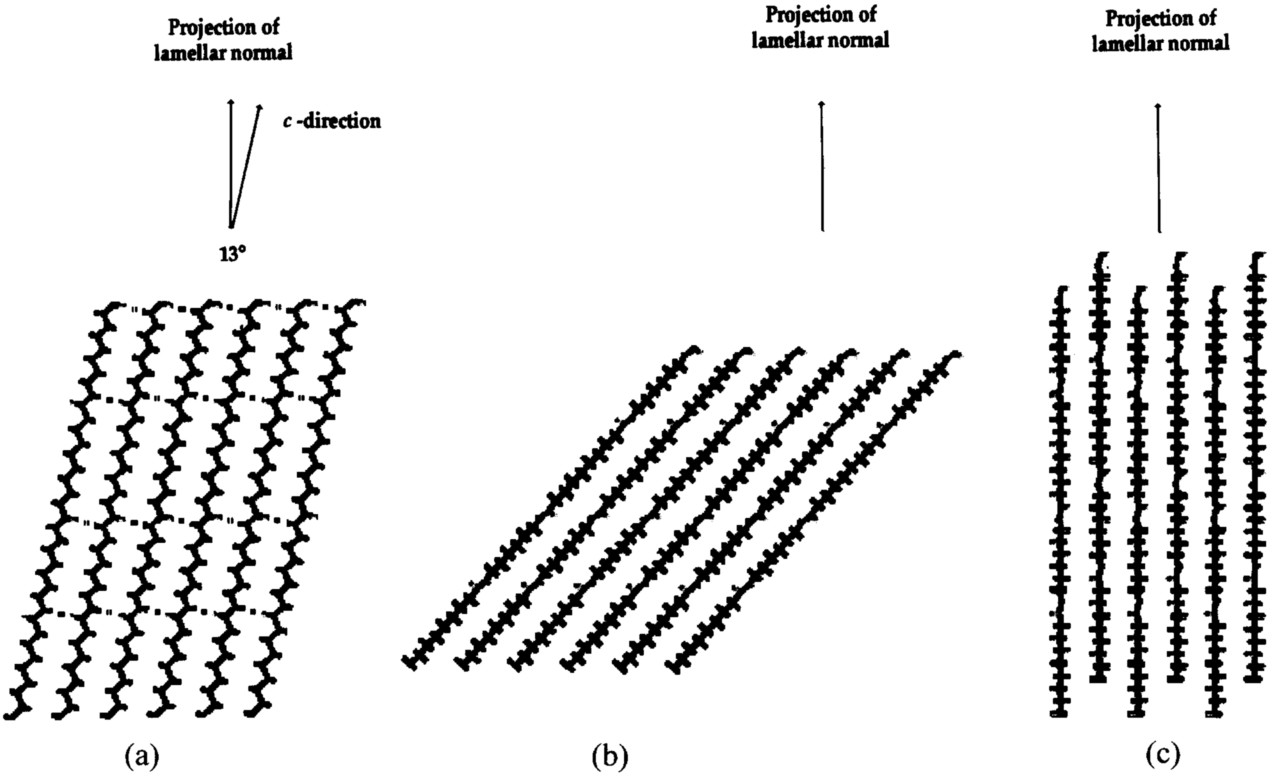


Figure 2 Projections of the nylon 6 6 structures. (a) A view orthogonal to a single hydrogen-bonded sheet, illustrating the progressive shear of chains by 13°. The magnitude of this shear is invarient for all the even–even nylon series since it is a consequence of the linear hydrogen bonds between near-neighbour amide groups. (b) A view parallel to the hydrogen-bonded sheet [shown in (a)] and illustrating the progressive nature of the shear between successive sheets in the α-phase. There is also progressive inter-sheet shear orthogonal to the diagram; thus, the chains are inclined at 41.8° to the lamellar normal in this case. The relative stacking of sheets is controlled by van der Waals forces and can be different for each even–even nylon in the series. For nylon 6 6 the unit cell is triclinic (containing one chain segment) with parameters: $a = 0.49\,\mathrm{nm}$, $b = 0.54\,\mathrm{nm}$, $c = 1.72\,\mathrm{nm}$, $\alpha = 48.5°$, $\beta = 77°$ and $\gamma = 63.5°$[1]. (c) A view parallel to the hydrogen-bonded sheet [shown in (a)] illustrating the β-phase structure; the sheets shear alternately in the c-direction and there is progressive inter-sheet shear orthogonal to the diagram. The unit cell is triclinic, but it contains two chains; the cell parameters are $a = 0.49\,\mathrm{nm}$, $b = 0.80\,\mathrm{nm}$, $c = 1.72\,\mathrm{nm}$, $\alpha = 90°$, $\beta = 77°$ and $\gamma = 67°$[1]

4 10 and 4 12, but only the long spacings (inter-lamellar stacking distance) and crystallographic c-dimensions were reported.

EXPERIMENTAL

Sample preparation

Samples of nylons 4 8, 4 10, 4 12 were prepared previously by Dr Pat Dreyfuss and stored in our laboratory in the form of crystal suspensions in 1,4-butanediol and dry, sedimented crystals mats. Details of sample synthesis and preparation can be found in Ref. 13. The samples were kept in the dark. Nylon 6 10 was a commercial sample obtained from I.C.I and nylon 6 12 was purchased from Aldrich. Nylon 6 18 was a research sample kindly supplied by I.C.I. Nylon 8 12 was synthesized by the condensation of a salt of 1,8-diaminooctane and 1,12-dodecanedioic acid, precipitated from absolute ethanol, dried in a vacuum then polymerized under 3 mbar air pressure at 215°C[14]. Stock solutions of nylons 6 10, 6 12 and 6 18 were prepared by refluxing 20 mg of polymer in 100 ml of 1,4-butanediol at 200°C until dissolution was complete; in each case the solution was allowed to cool to room temperature, during which time the polymer crystallized. Nylon 4 8 chain-folded lamellar crystals were prepared by seeding[15] at 140°C and crystallizing at 110°C. Nylons 4 10 and 4 12 were both seeded at 170°C and crystallized at 135°C. Nylon 6 10 crystals were seeded at 160°C and crystallized at 140°C. Nylon 6 12 was seeded at 190°C and crystallized at 140°C. Nylon 6 18 was seeded at 190°C and crystallized at 160°C. Nylon 8 12 was seeded at 195°C and crystallized at 125°C. The crystal suspensions were hot filtered at their crystallization temperatures.

Electron microscopy

Samples for transmission electron microscopy (TEM) were made by placing drops of crystal suspension on carbon-coated copper grids, drying in a vacuum oven at 100°C and annealing at the same temperature (again in the vacuum oven) for 24 h. Samples were examined in both imaging and diffraction modes, using a Phillips 301 TEM operating at 80 kV. Some crystals were decorated with platinum/palladium to calibrate the diffraction patterns and to shadow the images. Other crystals were decorated with polyethylene vapour, following the Wittmann and Lotz polyethylene decoration technique[16]. Crystals of each polyamide were heated to melting using a hot stage and diffraction patterns, for each nylon, were recorded as a function of temperature, between ambient and the melting point. Relative temperatures were accurate to within ±2°C and absolute temperatures to within ±5°C. The hot stage was calibrated with substances of known melting point.

X-ray diffraction

Sedimented mats of single crystals were prepared by draining crystal suspensions through paper filters,

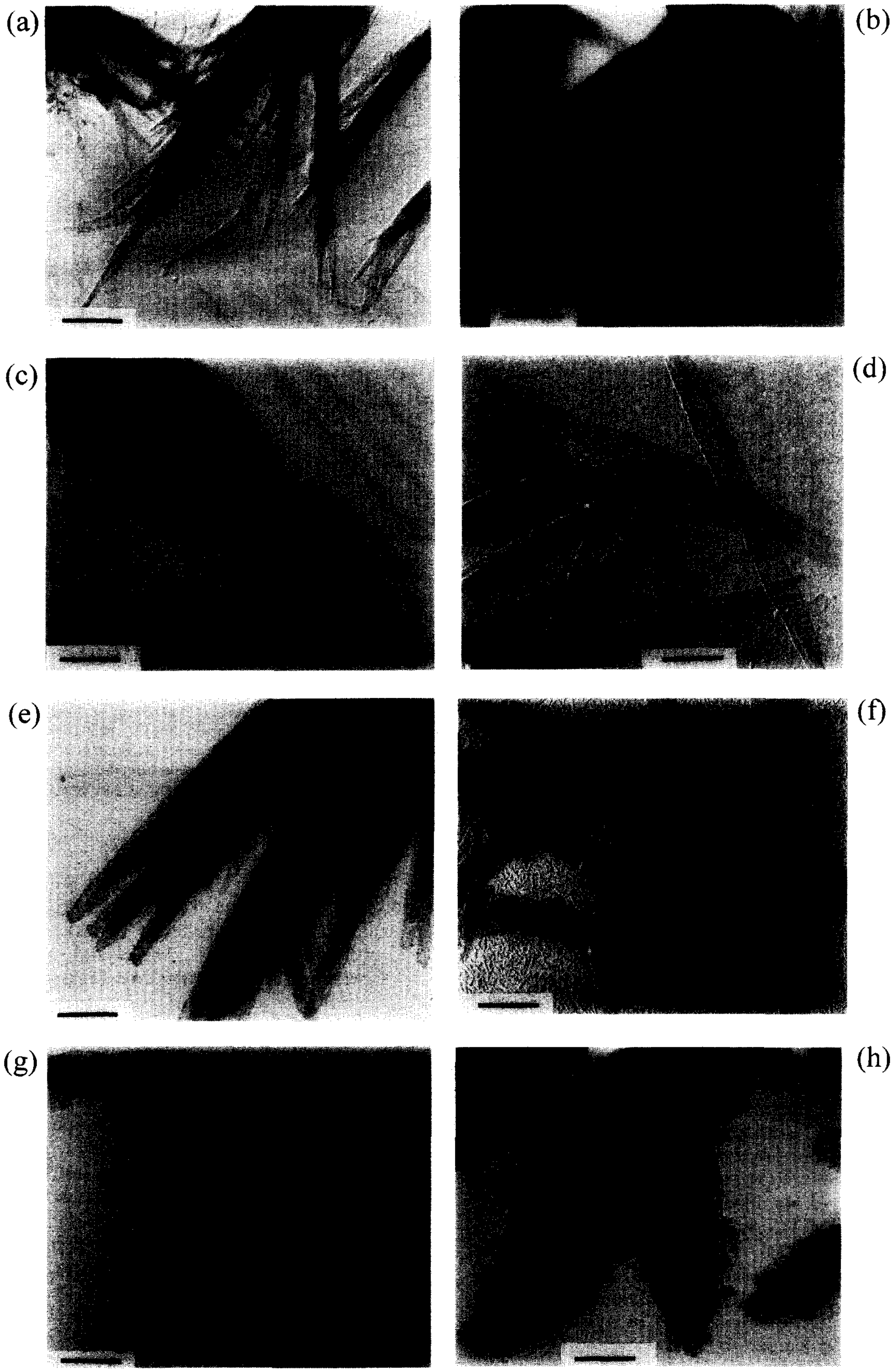


Figure 3 Transmission electron micrographs of lamellar single crystals off all the nylons of this study. All the photographs are printed to the same scale; the scale bar is 1 μm. Nylons crystallized from solution in 1,4-butanediol (a–c, e, h) to give long sheaves with lath-shaped extremities. These crystals are in the form of large multilayers and are not found individually but in groups: (a) nylon 4 8, (b) nylon 4 10, (c) nylon 4 12, (e) nylon 6 12, (h) nylon 8 12. (d) Nylon 6 10 can crystallize from solution to form individual crystals with lath like extremities. If the samples are crystallized from more concentrated solutions multilayered crystals occur; similar to those shown in (e) for nylon 6 12. (f) Crystals of nylon 6 10, prepared as those in (d), decorated with polyethylene using the method of Wittmann and Lotz[16]. The polyethylene fibrils are distributed randomly on the carbon film, but line up orthogonal 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[16]). (g) Nylon 6 18 crystallizes from solution in 1,4-butanediol to give noticeably shorter crystals than the other nylons in this study

Table 1a X-ray diffraction spacings (in nanometres) for nylons 4 8, 4 10, 4 12, 6 10, 6 12, 6 18, and 8 12

	4 8	4 10	4 12	6 10	6 12	6 18	8 12
100 ±0.003 nm	0.438	0.437	0.442	0.439	0.442	0.443	0.446
010/110 ±0.003 nm	0.364	0.365	0.370	0.365	0.368	0.368	0.372
001 ±0.01 nm	1.23	1.48	1.73	1.67	1.86		
002 ±0.006 nm	0.653	0.739	0.862	0.836	0.931		1.030
003 ±0.007 nm						0.798	
Pseudo-hexagonal (RT)[a] ±0.003 nm	0.412	0.409	0.411	0.409	0.412	0.410	0.408

[a] This is the spacing at room temperature (RT), the spacing of this diffraction signal increases on heating (see *Figures 6a* and *b*, and *Table 2*)

followed by annealing in a vacuum oven at 100°C for 24 h. Wide- and low-angle X-ray diffraction patterns were obtained using a point-collimated beam directed parallel to the surface of the crystal mat. At room temperature, diffraction patterns were obtained using a Ni-filtered CuK_α radiation from a Phillips PW2213 sealed beam X-ray generator operating at 35 kV and 40 mA. The X-ray diffraction patterns were recorded on film using an evacuated flat-plate camera. Calcite ($d_B = 0.3035$ nm) was dusted onto selected samples for calibration purposes. Above room temperature, an Enraf-Nonius TN-20 X-ray generator, operating at 40 kV and 20 mA, was used in conjunction with a Metler FR-52 hot stage for nylons 4 8 and 6 10. A point-collimated, monochromatized CuK_α X-ray beam, from an Elliot GX-21 rotating target X-ray generator with a Linkam T300 hot stage was used for nylons 4 10, 4 12, 6 12, 6 18 and 8 12; the data, for this last group, were collected using a Siemens GADDS two-dimensional detector.

Differential scanning calorimetry

Melting temperatures of the sedimented mats were measured using a Perkin Elmer DSC 7 flushed with nitrogen. The heating rate was 10°C min^{-1}.

RESULTS

Electron microscopy

The transmission electron micrographs, shown in *Figure 3*, reveal that these nylons crystallize in the form of lath-like lamellae, similar to those reported for other even–even or even nylons[6,9,17–20]. The Wittmann and Lotz polyethylene decoration technique[16] suggests that the hydrogen-bonded sheets run along the length of the crystals; as they do for many other even–even or even nylons[6,9,17–20].

Figure 4 shows the TEM diffraction patterns from single crystals. The patterns show the two strong diffraction signals at spacings 0.44 nm (indexed as 100 for both α- and β-phases; see unit cell information in *Table 1*) and 0.37 nm (indexed as 010 for α-phase and 020 for β-phase), respectively. The 120 for the β-phase (indexed as 110 for α-phase) also occurs at 0.37 nm spacing. There is also a set of weaker signals at 0.415 nm spacing. In addition to these diffraction signals there are, on some plates, second and third orders apparent. This implies that the polymer chains in the diffracting crystal are tilted only slightly away from the normal to the chain-folded surface, consistent with β-phase crystalline lamellae. In many cases, only the 0.44 nm signal is observed; this implies that the sheets in the diffracting crystal lie at a substantial angle to the lamellar normal, as expected from α-phase crystalline lamellae (see *Figure 2b*). Thus, it appears that both α- and β-phase crystals can be present in these preparations.

X-ray diffraction

The wide-angle X-ray diffraction patterns from sedimented mats of nylons 4 12, 6 12 and 8 12, taken with the X-ray beam parallel to the mat surface and with the mat normal vertical, are shown in *Figure 5*. In the case of α-phase crystalline lamellae the 100 diffraction signals (0.44 nm) should occur ±6° ($\beta^* = 84°$) above and below the equator, and the 010 and 110 diffraction signals (0.37 nm) at ±40° ($\alpha^* = 130°$) and ±33° (angle between [110]* and $c^* = 123°$). For the β-phase crystalline lamellae the equivalent angles are ±14°, ±6° and

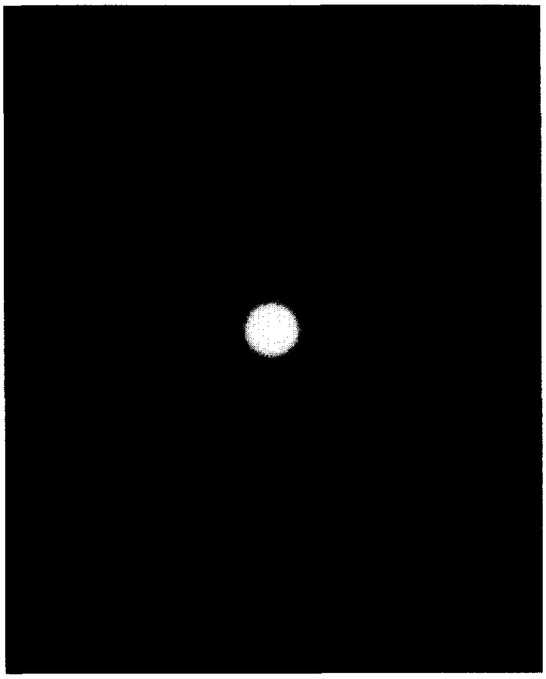
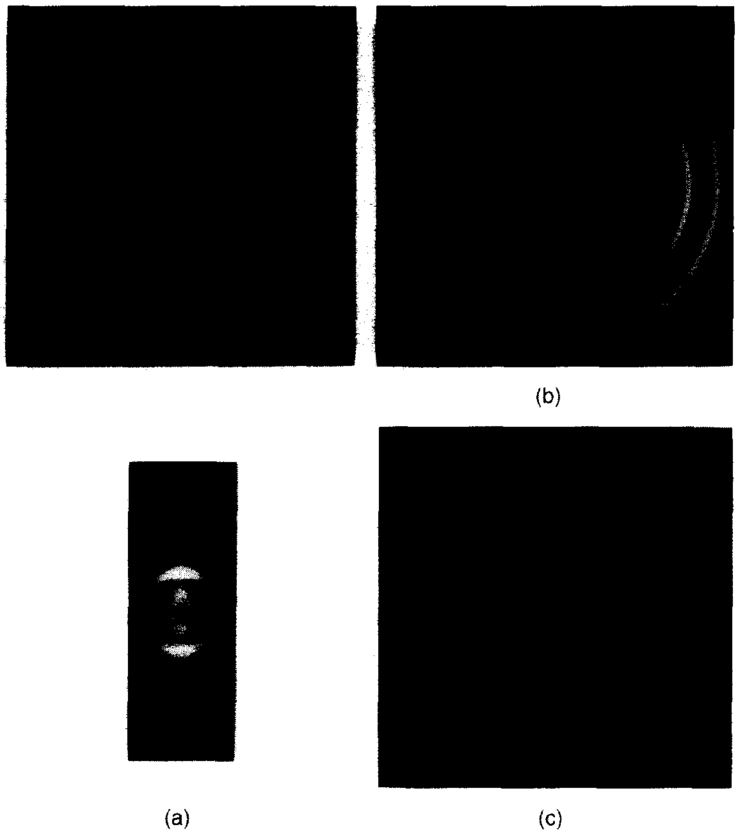


Figure 4 Electron diffraction pattern obtained from nylon 6 10 single crystals. The α-phase gives rise to 100 diffraction signals only in electron diffraction. The appearance of the 020 and 120 diffraction signals, in addition to the 100, indicates that the β-phase is present. We know that both α- and β-phases are present in the diffracting sample because the strength of the 100 reflection is too great, relative to the 020 and 120, for diffraction from the β-phase alone. The arrows indicate three of the faint pseudo-hexagonal spacings at 0.415 nm. The pseudo-hexagonal signals are at 60° to each other, whereas the angles between 100 and 020 and 120 are different. Note that one pair of pseudo-hexagonal signals are aligned with the 020 of the β-phase and, as a result, the other pairs are not aligned with the other two strong signals (120 and 100) of the triclinic phases

Table 1b Unit cell parameters for nylons 4 8, 4 10, 4 12, 6 10, 6 12, 6 18, and 8 12

	4 8	4 10	4 12	6 10	6 12	6 18	8 12
α-phase unit cell							
$a \pm 0.005$ nm	0.490	0.490	0.490	0.490	0.490	0.490	0.490
$b \pm 0.005$ nm	0.523	0.532	0.518	0.530	0.533	0.538	0.534
$c \pm 0.01$ nm	1.73	1.98	2.23	2.23	2.48	3.23	2.73
$a \pm 1$	49	49	51	49	49	48	49
$\beta \pm 1$	77	77	77	77	77	77	77
$\gamma \pm 1$	63	63	64	64	63.5	64	64
β-phase unit cell							
$a \pm 0.005$ nm	0.490	0.490	0.490	0.490	0.490	0.490	0.490
$b \pm 0.005$ nm	0.797	0.800	0.807	0.799	0.802	0.801	0.807
$c \pm 0.01$ nm	1.73	1.98	2.23	2.23	2.48	3.23	2.73
$\alpha \pm 1$	90	90	90	90	90	90	90
$\beta \pm 1$	77	77	77	77	77	77	77
$\gamma \pm 1$	66	66	66.5	66	66.5	67	67

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 nylon. The value of c 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 (0.02 nm is subtracted because of the inclusion of one nitrogen atom in each backbone repeat). The b, α and γ values of the α-phase unit cell 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. β-Phase unit cells were calculated by setting $\alpha = 90°$, $\beta = 77°$, $a = 0.49$ nm and $c = (0.125N-0.02)$ nm. The b and γ values could be calculated from the measured d_{100}, d_{020} and d_{120} spacings. Simulated X-ray diffraction patterns, computed from the unit cell parameters using the Diffraction Module of Cerius; version 1.6 (Biosym/Molecular Simulations Inc.) agreed with the experimental patterns to within the accuracy of the unit cell parameters


(b)

(a) (c)

Figure 5 X-ray diffraction photographs of sedimented mats taken with the beam parallel to the mat surface and with the mat normal vertical. (a) Nylon 4 12 with low-angle pattern underneath; (b) nylon 6 12; (c) nylon 8 12. The strongest signals are marked. The pseudo-hexagonal signals, where present, lie between the 100 and the 010/110 (indexed as 020/120 for β-phase). Note that there is a very sharp reflection on the meridian of the wide angle pattern of nylon 4 12. This is a consequence of non-polymeric material, embedded in and aligned with the mat. The outer speckled ring is a calcite calibration. The strong low-angle meridional diffraction peak [Lx in (a), bottom] represents the lamellar stacking periodicity at a spacing of 6.7 nm; 2.3% more than five projected repeats of nylon 4 12 in the α-phase. The relative intensity of the 002 and 001 diffraction signals is governed by the ratio of distances between the carbonyl groups in the two alkane segments (see *Figure 1*). For nylon 4 12 the two segments are quite dissimilar in length, the 001 reflection is strong diffraction signals and the 002 appears only weakly as a second order. If the distances between the carbonyl groups in the two alkane segments were equal the 001 would be weak because of destructive interference. (It would not be absent, because the positions of the nitrogen atoms would be asymmetric.) In nylon 8 12 the two distances between the carbonyl groups are almost equal; as a result the 001 is weak in comparison with the 002. Nylon 6 12 falls between the two other nylons shown

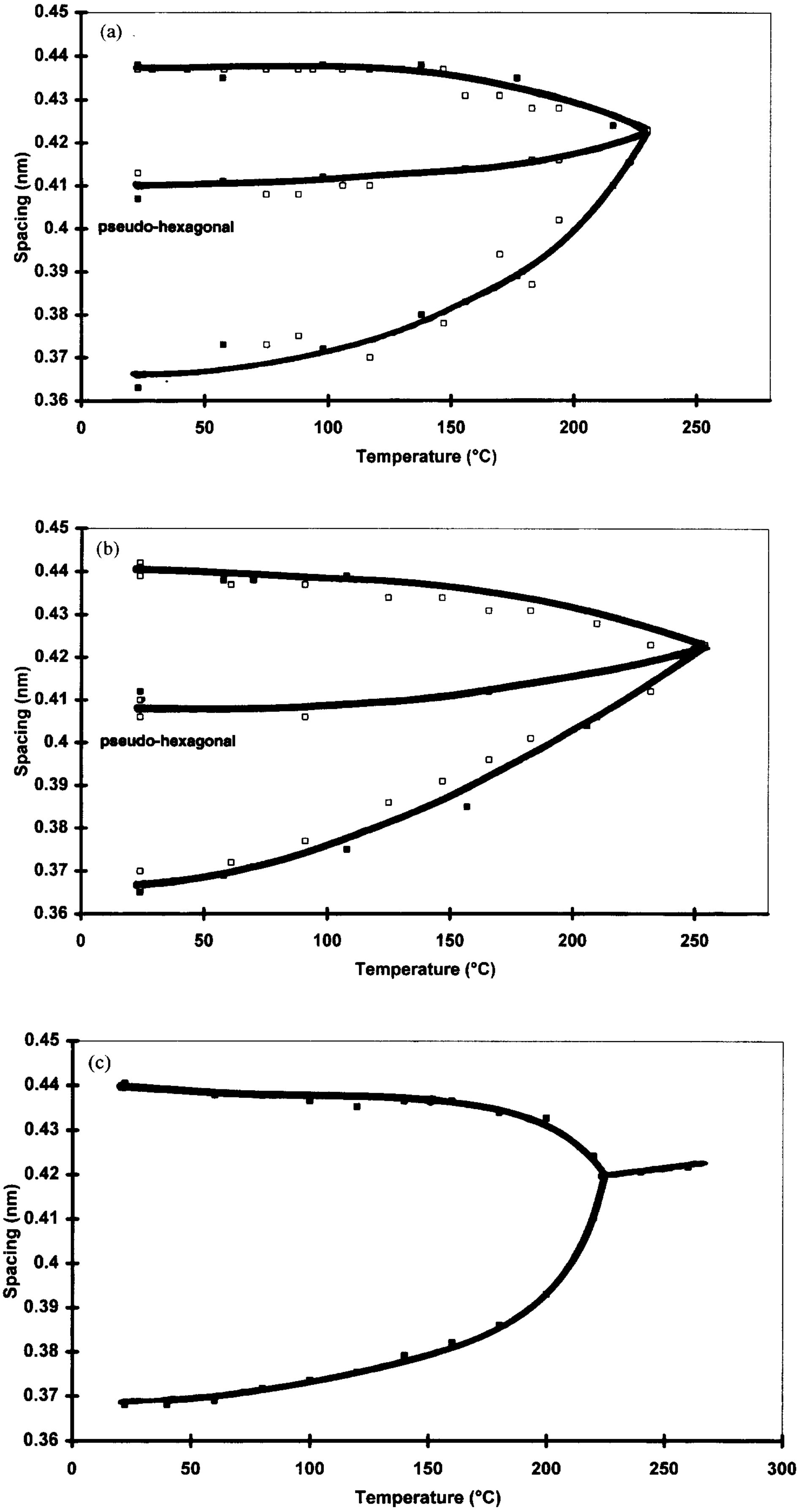


Figure 6 Graphs showing variations to the 100, 010/110 and pseudo-hexagonal spacings (where observed) as single crystals are heated from room temperature to the polymer melting temperature for (a) nylon 6 10, (b) nylon 4 8 and (c) nylon 6 6. (■) Wide-angle X-ray diffraction data; (□) electron diffraction data

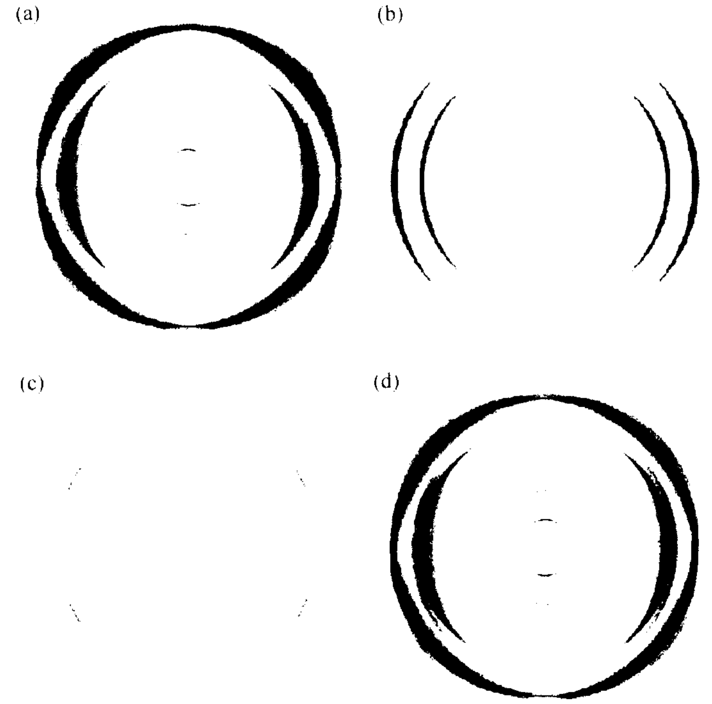


Figure 7 Computer generated simulated X-ray diffraction patterns of nylon 6 12 mats; (a) α-phase, (b) β-phase, (c) pseudo-hexagonal phase. (d) Shows the three patterns combined. In the combined pattern the presence of the β-phase can only be inferred from the relatively greater arcing of the 010/110 and 020/120 (in the β-phase) diffraction signals. Note that the intensities of the β-phase and pseudo-hexagonal phase signals have been reduced (relative to those of the α-phase) to simulate the relative quantities of the three crystal types in the sample from which *Figure 5b* was obtained

±6°, respectively (the latter pair now indexed as 020 and 120 owing to the effective doubling of *b*). Thus, if a mixture of α-phase and β-phase crystalline lamellae occur, arcing of the 100 and 010/110 signals will be greater; this will be more noticeable for the 010/110 arcs at 0.37 nm. Examination of *Figure 5(a–c)* shows that the relative proportions of α-phase and β-phase crystalline in each example is different; the X-ray photograph of nylon 8 12 indicates almost all α-phase. In *Figure 5 (a* and *b)* there is also a weaker signal at an intermediate spacing of 0.415 nm. The diffraction signals on the meridian of the X-ray patterns are the 00*l* series. Between these there are a number of weaker subsidiary maxima, which indicate the number of chemical repeats within the thickness of the lamellar crystal[2]. In each sedimented mat examined, a low-angle X-ray meridional peak, corresponding to the inter-lamellar stacking, was observed. This is shown for nylon 4 12 in *Figure 5a* (bottom). The interplanar-spacings of the observed diffraction signals for the nylon series examined are listed in *Table 1a* and the unit cell parameters are given in *Table 1b*.

Changes in the spacings of the strong diffraction signals at elevated temperatures were monitored using X-ray diffraction (both α- and β-phase crystals) and electron diffraction (β-phase crystals only). Both techniques gave similar results. The variations in spacing as a function of temperature are shown in *Figure 6 (a* and *b)* for nylons 4 8 and 6 10. All the nylons tested exhibit a Brill temperature just prior to melting; in this respect, they behave differently from nylon 6 6, for which the Brill temperature for melt crystallized materials has been reported in the range 170–230°C, well below the melting temperature (265°C)[6,7]. The behaviour of nylon 6 6 single crystals on heating has not, to our knowledge, appeared in the literature. We show in *Figure 6c* our data for nylon 6 6 single crystals; we find that the Brill temperature for these crystals is 220°C. For all the nylons in this study (other than nylon 6 6), the spacing of the 0.42 nm diffraction signal remained constant, or increased very slightly, from room temperature up to the Brill temperature, where all three spacings became equal. Brill temperatures and melting temperatures for these nylons are recorded in *Table 2*.

Differential scanning calorimetry (d.s.c.)

The melting points of the seven nylons studied in this paper, as measured by d.s.c. are listed in the first row of *Table 2*.

Table 2 Melting temperatures, Brill temperatures and spacings at the Brill temperature for the nylons studied

	4 8	4 10	4 12	6 10	6 12	6 18	8 12	6 6
Melting temperature (°C) ±3°C (varies with T_{cr})	253	243	237	223	215	192	205	265
Brill temperature (°C) ±5°C	250	240	235	220	215	190	202	220
Spacing (nm) at Brill temperature ±0.003 nm	0.423	0.431	0.427	0.423	0.422	0.427	0.433	0.418

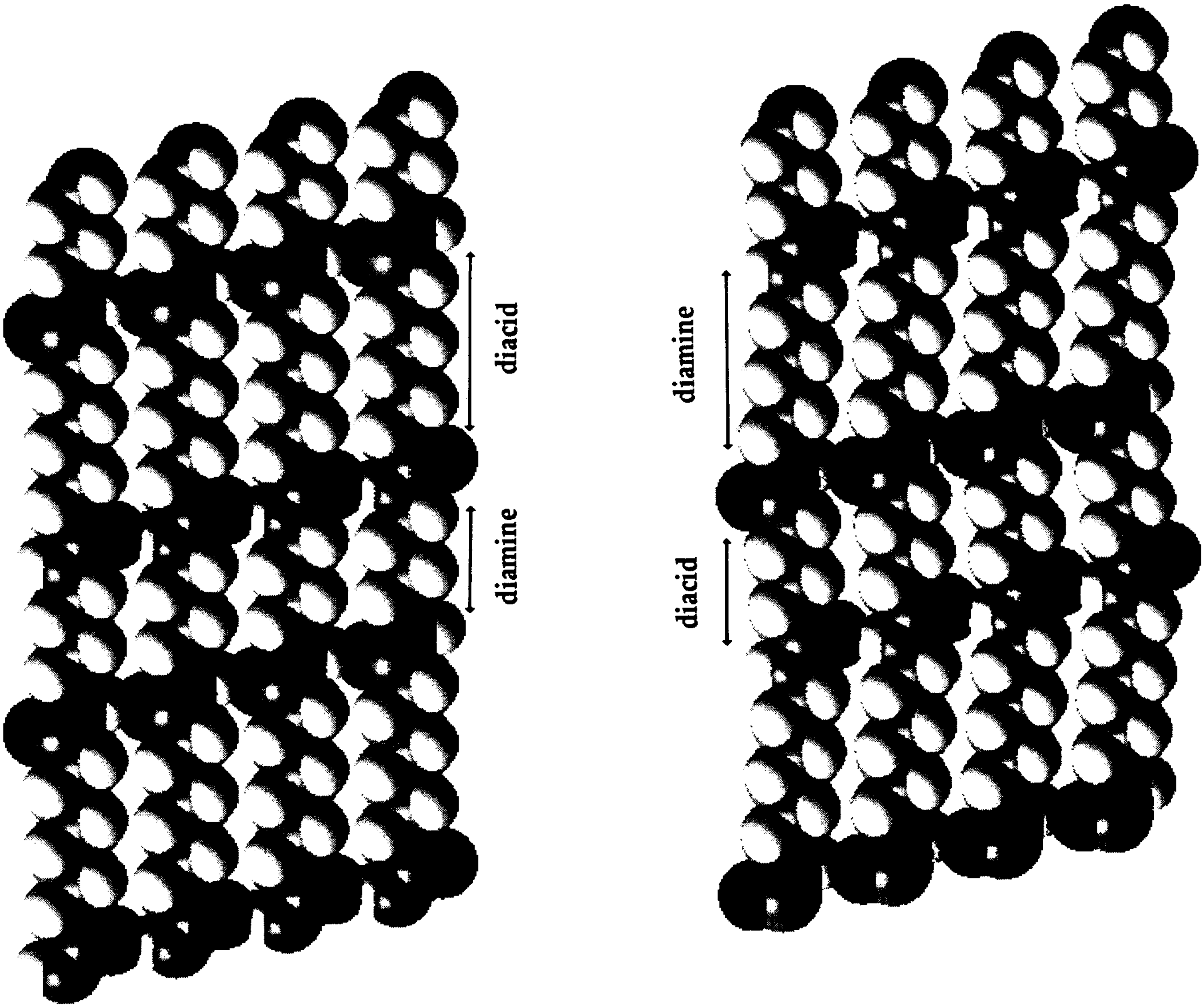


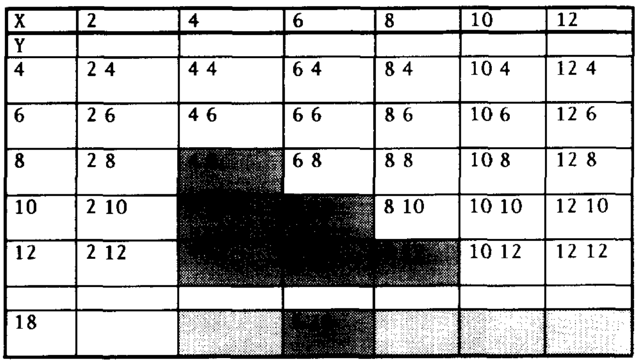
Figure 8 Computer generated 'realistic' space-filling models of *ac* sheets of nylons 6 6 (left) and 4 8 (right). The diacid and diamine alkane sequences are marked on each. The figure highlights the equal spacings of the amides along the chains in these two nylons; effectively, the only difference is the reversal of the amide groups. Colour code: hydrogen, white: carbon, pale grey; nitrogen, mid grey; oxygen, dark grey

DISCUSSION

The melting temperatures of the nylons examined increase with linear density hydrogen bond (see *Table 2*). This is as expected[21] because it is the hydrogen bonds that hold the crystals together at high temperatures, after the alkane segments have melted.

Unit cells for the α-phases of nylons 4 8, 4 10, 4 12, 6 10, 6 12, 6 18 and 8 12, calculated from the electron and X-ray diffraction data (*Table 1*), are similar to those of Bunn and Garner[1] for nylon 6 6 and nylon 6 10, apart from the differing *c*-axis values, which, of course, increase as further methylene units are added in the alkane segments. However, for single crystals of the nylons in this study, unlike those of nylon 6 6, both α-phase and β-phase crystals are often present in the same preparation; the ratios of α- to β-phase vary with crystal preparation. The presence of both α-phase and β-phase crystals has also been reported recently by Franco and Puiggali[20] in the case of single crystals and fibres of nylon 12 10.

α-Phase crystals are observed by electron diffraction, characterized by the observation of the 0.44 nm signal only[3,6]. In the electron diffraction patterns of other crystals, the strength of the signal at 0.37 nm and the presence of a number of higher order diffraction signals show that the polymer chains run nearly parallel to the electron beam (normal to the chain-folded surface), indicating β-phase sheet stacking. These β-phase diffraction patterns usually show the 0.42 nm signal also, at room temperature, as a weak peak between the 0.44 and 0.37 nm signals. The 0.42 nm signal does not index on the Bunn and Garner[1] α-phase or β-phase structure. It is characteristic of the high temperature pseudo-hexagonal phase, normally found above the Brill temperature[7–12,22,23]. It has been shown that some nylons grow in this pseudo-hexagonal phase[8a,8b,9,18] but transform into the appropriate higher density triclinic or monoclinic phase on cooling. However, the pseudo-hexagonal phase can be retained at room temperature by rapid quenching from the crystallization temperature to below the glass transition temperature[9,18]. We believe the nylons of this study also grow in the pseudo-hexagonal phase and that the signals recorded at a spacing of 0.42 nm at room temperature come from regions of the crystal where the high temperature structure has been



X	2	4	6	8	10	12
Y						
4	2 4	4 4	6 4	8 4	10 4	12 4
6	2 6	4 6	6 6	8 6	10 6	12 6
8	2 8	▓	6 8	8 8	10 8	12 8
10	2 10	▓	▓	8 10	10 10	12 10
12	2 12	▓	▓	▓	10 12	12 12
18		░	▓	░	░	░

Figure 9 Chart of the even–even X Y nylons under investigation in our laboratory, with X running horizontally and Y running vertically. The seven nylons reported in this contribution are in the dark-shaded boxes which form part of a triangular region. We anticipate that the other nylons in this triangle (lightly shaded boxes) will have similar properties

frozen in on cooling. It seems that this happens quite readily where both α-phase and β-phase are present. In contrast, unless we have used drastic quenching methods to freeze in the high temperature pseudo-hexagonal structure, we have found traces of the high temperature phase at room temperature much less frequently in nylons showing only the α-phase[6]. The 0.42 nm diffraction signal has not been reported in nylon 6 6 single crystals at room temperature[1–3].

Thus we find, for the nylons of this study, that three crystal phases co-exist at room temperature. Some crystals, or parts of crystals, are in the α-phase, others are in the β-phase and β-phase crystalline material is often also associated with some of the high temperature pseudo-hexagonal phase. The previous observations for nylons 6 10 and 6 12 are entirely consistent with these findings; Dreyfuss and Keller[4] found two different wide-angle X-ray diffraction patterns for sedimented mats of nylon 6 10 crystals. They interpreted these as being the result of differing amounts of twist about the long axis (*a*-axis) of the lamellae, however, the results could equally be interpreted as mixtures of α-phase and β-phase crystals. Geil[5] reported a 0.44 nm diffraction signal for all his single crystals; for some he also observed a signal at 0.37 nm and occasionally a further signal at 0.415 nm. These previously reported results are in complete agreement with our own, but we interpret them differently.

Figures 7a–c show simulated diffraction patterns for α-phase, β-phase and pseudo-hexagonal phase crystals, respectively, and *Figure 7d* shows their superpositioning to give the observed wide-angle X-ray diffraction patterns for nylon 6 12. In the α-phase, the 100 (0.44 nm) signal should appear as two peaks each 6° above and below the equator since the angle β^* is 84°. However, in practice the 100 diffraction signals merge across the equator owing to disorientation (*Figure 7a*). The diffraction signals spaced at 0.37 nm form a ring. This is because the 010/110 planes of the α-phase and equivalent (020/120) planes of the β-phase are inclined at different angles to the lamellar normal. The superposition of the two patterns gives the impression of a ring (*Figure 7d*). As with the electron diffraction, the pseudo-hexagonal 0.42 nm diffraction signal occurs between the 0.44 and 0.37 nm arcs.

The behaviour of nylons 4 8, 4 10, 4 12, 6 10, 6 12, 6 18 and 8 12 on heating is markedly different from that of nylon 6 6, as can be seen by comparing *Figures 6a* and *b* with *Figure 6c*. For all these nylons the room temperature spacings of the characteristic spacings are close to 0.44 and 0.37 nm. These values hardly change for the nylons in the present study in the temperature range 20–100°C. Beyond 100°C they move towards each other. The Brill temperature and the melting point are coincident (*Figures 6a* and *b*). In contrast, for nylon 6 6 single crystals, the Brill temperature is 220°C, well below the melting temperature of 265°C (*Figure 6c*). Other nylons found only in the α-phase at room temperature, e.g. the nylon X 4[6] and nylon Z Y[24] families, also have Brill temperatures well below their melting points.

Where the pseudo-hexagonal diffraction signal is present from ambient, it is seen to increase in spacing slowly with temperature (owing to thermal expansion of the lattice), reaching the same spacing as the strong diffraction signal at the Brill temperature, which is coincident with the melting temperature (*Figures 6a* and *b*).

Nylons 4 8 and 6 6 are similar; the spacings of the hydrogen bonds within the *ac* sheets are the same, but the direction of the amide groups within these sheets has been reversed, as shown in *Figure 8*. Therefore, since the spacings of the hydrogen bonds are identical, these two nylons might be expected to have similar properties. Certainly the melting points are similar; 253°C for nylon 4 8 and 265°C for nylon 6 6. In addition, both nylons grow in, and melt from, the pseudo-hexagonal phase. However, in nylon 4 8 this pseudo-hexagonal phase is attained, on re-heating from room temperature, only as the polymer melts, whereas Brill temperatures for nylon 6 6 have been reported in the range 170–220°C (220°C for single crystals, *Figure 6c*), well below the melting point (265°C). Furthermore, we have commonly observed nylon 4 8 single crystals in the α-, β- and pseudo-hexagonal forms at room temperature, whereas nylon 6 6 single crystals have only been reported in the α-phase. It is worthwhile to consider possible reasons for these differences, particularly since similar differences will occur in other nylon groups.

Upon heating, the alkane segments within the nylon chains become increasingly mobile; the amide groups are more constrained, because of their connecting hydrogen bonds. The alkane segments undergo restricted rotations, or librations, and the inter-sheet 0.37 nm spacing increases, indicative of the increased alkane segment motion in this direction. At the Brill temperature, the alkane segments have attained the same mobility in the inter-sheet direction as they possess within the sheets. This has led some authors to propose that the Brill transition merely represents the attainment of a 'rotator' phase for the alkane segments, but that the hydrogen bonds remain in the original sheets[25–27]. We believe, however, that this increased torsional flexibility of the alkane segments exerts a torsional force on the more rigid amide groups, a proportion of which then flip out (by ±60° or even ±120°) to form inter-sheet hydrogen bonds. These inter-sheet hydrogen bonds pin the nylon chains onto the pseudo-hexagonal lattice sites and prevent the chains from moving further apart and melting.

Irrespective of the precise model that is adopted for the pseudo-hexagonal structure (rotator phase with or without inter-sheet hydrogen bonds), it is more disordered than the α-phase. Hence it has more entropy and is favoured at higher temperatures. Similarly, in both models the initial driving force for the transition will be the same, namely, the increased mobility of the alkane segments at higher temperatures. The alkane segment mobility will depend critically upon the torsional barriers to the C–C rotations. Rotations about C–C bonds adjacent to HN–CO, OC–NH and C–C bonds have different torsional energies[26], thus it is not surprising that the Brill temperature is dependent upon the exact environment of the alkane segments. Indeed, n.m.r.[27] and molecular dynamic[28] studies on nylon 6 6 concluded that motion in the diacid alkane segment was less hindered than in the diamine segment, despite the greater length of the latter. The higher temperature required to produce the pseudo-hexagonal phase in nylon 4 8, compared with that required for nylon 6 6, may therefore be attributable, in part, to the greater rigidity of the alkane segments in nylon 4 8. Conversely, this greater rigidity will result in a higher activation energy for the transition from the pseudo-hexagonal to the α-phase on cooling. Thus, it will be easier to 'trap in' the pseudo-hexagonal phase in nylon 4 8 on cooling to room temperature, in agreement with our observations.

Although there is quite a wide range in hydrogen bond density (4 8 cf. 6 18), these nylons form a family with similar properties. We can display all the even–even nylons (nylons X Y, with both X and Y even) on a chart, with X, the number of carbon atoms in the diamine segment along one axis and Y, the number of carbon atoms in the diacid segment (including the carbons in the carbonyl groups) along the other (*Figure 9*). The seven nylons which are the subject of this study are then all grouped together, they occupy a triangle bordered by lines $X = 4$ and $X = Y - 4$, as shown (dark shading) in *Figure 9*). We do not, at present, have the other nylons in this triangle (light shading, *Figure 9*). We anticipate that they have similar properties to those in the group reported here.

CONCLUSIONS

Single crystals of the seven nylons: 4 8, 4 10, 4 12, 6 12, 6 18 and 8 12 have been crystallized from solution in 1,4-butanediol. These nylons form a family with similar properties, both at room temperature and at elevated temperatures.

The crystals are composed of chain-folded, hydrogen-bonded sheets which stack, some progressively, others alternately, to form α- and β-crystalline phases, both with different triclinic unit cells, respectively. Both crystalline phases were found (in varying proportions) in all preparations observed at room temperature. In addition, some crystals, or parts of crystals, were found in the pseudo-hexagonal phase (usually a high temperature phase) at room temperature.

The melting points of solution grown crystals of the nylons in this group decrease with decreasing linear hydrogen bond density.

On heating single crystals of the seven nylons in this group, the two strong spacings, characteristic of the even–even nylons, move together and meet at the melting point.

Chemically similar nylons may have different physical properties. Nylons 6 6 and 4 8 are identical except that the amide groups are reversed relative to the respective alkane segments. Nylon 6 6 does not exhibit any β-phase crystals and the Brill temperature is well below the melting temperature. In contrast, nylon 4 8 has both α- and β-phase crystals at room temperature and the Brill temperature is equal to the melting temperature. However, as expected from the hydrogen bond density, the melting points of these two nylons are similar.

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