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Morphology and Structure of Nylon 68 Single Crystals

M. J. Hill* and E. D. T. Atkins

H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, U.K.

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ABSTRACT: The structure and morphology of nylon 68 single crystals were studied by transmission electron microscopy. There are two crystal phases. A monoclinic phase with $a = 0.960 \pm 0.005$ nm, $b = 0.826 \pm 0.005$ nm, and $\gamma = 115 \pm 1°$, when viewed along the chain axis, c, is the usual form for crystals cooled slowly from the crystallization temperature. This lattice is the same, within experimental error, as that of monoclinic crystals of nylon 46, a polymer which has the same chain structure, but with amide groups more closely spaced. Nylon 68 crystals quenched into nonsolvent from the crystallization temperature are found in a pseudohexagonal phase which has parameters $a = b = 0.97$ nm and $\gamma = 120°$. When monoclinic crystals are heated, they transform, gradually, into the pseudohexagonal phase; the transformation is complete at 203 °C, and melting takes place at 234 °C. The crystals grow from solution in the pseudohexagonal phase which is stable at high temperatures; they usually revert to the monoclinic phase on cooling, but the pseudohexagonal phase can be obtained at room temperature by quenching to below the glass transition temperature. Monoclinic nylon 46 single crystals were examined on heating. They transformed to the pseudohexagonal structure at 245 °C, before melting took place at 295 °C.

Introduction

In recent studies on nylon 46 chain-folded single crystals,[1] it was shown that the chain folded with the amide group in the hairpin fold, with a conformation similar to that of the β-bend in proteins.[2] It is of interest to establish whether nylon 68 behaves like nylon 46. Both have successive amide groups equally spaced and with opposite polarity, as illustrated in Figure 1 for nylon 68. Nylon 46 has the same structure, but with two less methylene groups in each alkane segment. We know of no previous reports concerning nylon 68 single crystals, although Slichter has reported studies on nylon 68 fibers;[3] his results are discussed later in this paper.

We have grown single crystals of nylon 68 from solution in butanediol and have examined them in the transmission electron microscope (TEM), both in real space and in diffraction mode. We have found that crystals of nylon 68 cluster together somewhat differently from those of nylon 46, but the crystal structures are similar, both have monoclinic unit cells at room temperature. We report the changes in crystal structure on heating both nylon 68 and nylon 46 (previously unpublished) and show that single crystals of both nylons gradually transform from monoclinic to pseudohexagonal on heating. Brill first observed this type of behavior in nylon 66.[4] Both nylon 46 and nylon 68 reach a "Brill" temperature before melting. The pseudohexagonal crystal phase can also be captured by rapidly quenching crystals from the growth temperature into cold nonsolvent.

Experimental Section

Single Crystals Preparation. A solution of nylon 68 in 1,4-butanediol (0.025% w/v) was prepared by continuously stirring under reflux conditions for 1 h at 190 °C. This solution was slowly cooled to room temperature and then seeded by holding at 170 °C for 20 min. The solution was then cooled to the isothermal crystallization temperature. The optimum crystallization conditions were found to be 120−125 °C for 36 h.

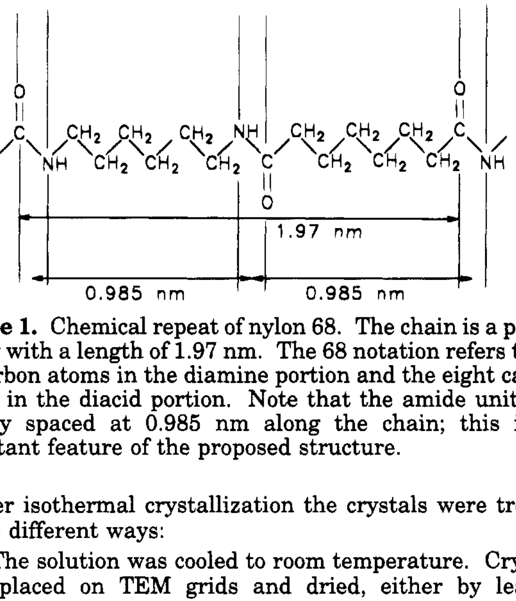

Figure 1. Chemical repeat of nylon 68. The chain is a planar zigzag with a length of 1.97 nm. The 68 notation refers to the six carbon atoms in the diamine portion and the eight carbon atoms in the diacid portion. Note that the amide units are equally spaced at 0.985 nm along the chain; this is an important feature of the proposed structure.

After isothermal crystallization the crystals were treated in two different ways:

(i) The solution was cooled to room temperature. Crystals were placed on TEM grids and dried, either by leaving overnight in the laboratory or in a vacuum oven.

(ii) The solution was "quenched" from the crystallization temperature into acetone at room temperature. The quenching method was unusual (it is first described in ref 5). After the full crystallization time the crystals, suspended in the solvent, butanediol, were poured into a Buchner funnel. The solvent was sucked rapidly through filter paper using a water vacuum. At the same time cold acetone was poured into the funnel and sucked through the filter paper with the excess solvent. This process gave rise to very rapid quenching from the crystallization temperature into cold nonsolvent.

After filtration the crystals were removed from the filter paper and resuspended in acetone. The crystal suspension was placed on carbon-coated TEM grids and allowed to air dry, in the laboratory, at room temperature.

Examination of Single Crystals. (i) Thermal Analysis. Samples of 1−2 mg were heated at 10 °C/min in a DSC 7, flushed with nitrogen, to investigate the glass transition temperature and the melting point.

(ii) Electron Microscopy. Samples were examined, both in real space and in diffraction mode, using a Philips 301 TEM operating at 80 kV. Some crystals were shadowed; others were lightly decorated with gold to calibrate the diffraction patterns. Some crystals were heated to melting in a hot stage. The

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* Author to whom correspondence should be addressed.

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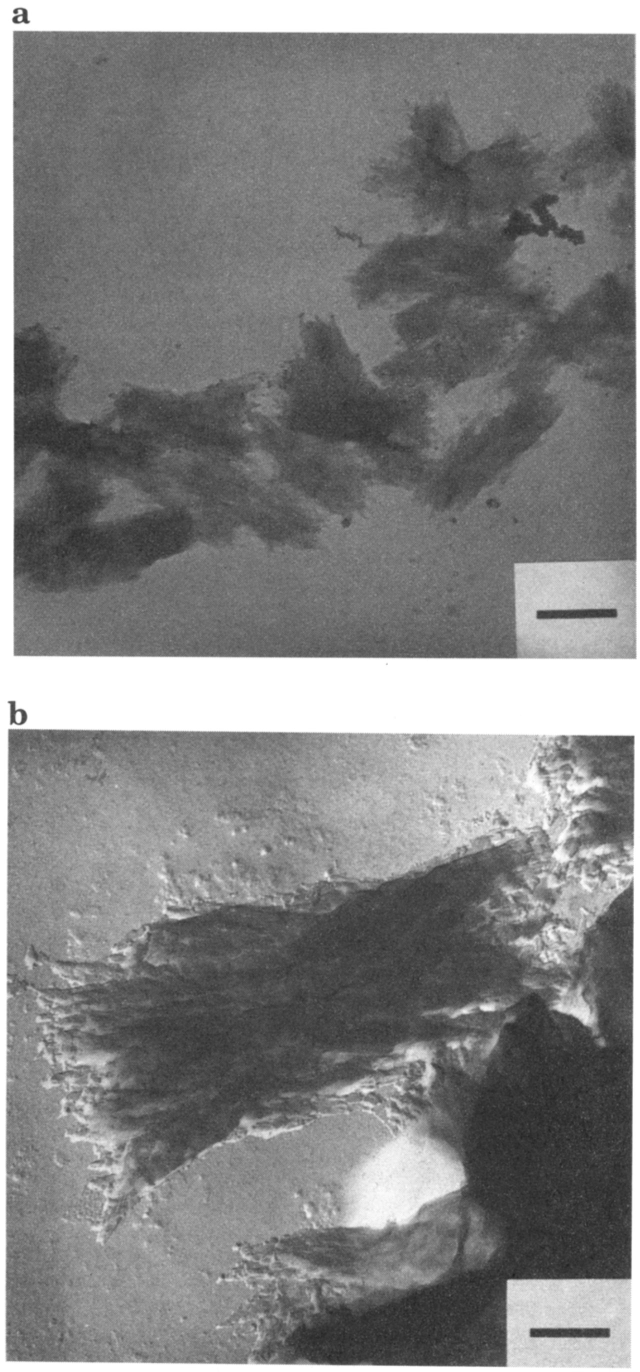

Figure 2. Transmission electron micrographs of nylon 68 crystals grown from butanediol. The scale bar represents 1 μm. (a) Quenched from the seeding temperature (170 °C) to 100 °C and held at that temperature overnight. (b) Quenched from the seeding temperature (170 °C) to 125 °C and held at that temperature for 36 h. The crystals were shadowed with platinum–palladium after drying on the carbon film. These crystals are at the edge of a thick crystal cluster (dark material, bottom right).

temperature of this hot stage could be controlled to within 2 °C; relative measurements were accurate to 2 °C and absolute measurements to within 5 °C. The hot stage was calibrated by observing the melting of polymer samples which had been previously characterized by DSC.

Results

Thermal Analysis. Heating nylon 68 crystals at 10 °C/min in the DSC revealed a broad glass transition just below 50 °C and melting at 234 °C. We recorded a broad glass transition at just over 50 °C for nylon 46 (higher than the literature value of 43 °C[6]).

Table 1. Electron Diffraction Spacings of the Nylon 68 Monoclinic and Pseudohexagonal Phases and Cell Parameters of Monoclinic Nylons 68 and 46 and Pseudohexagonal Nylon 68

a. Nylon 68 Monoclinic Phase

	measd spacing (nm)	strength	index	calcd spacing (nm)
1	0.435	very strong	20	0.435
2	0.376	strong	02	0.375
3	0.374	medium	22	0.372
4	0.237	very very weak	22	0.240
5	0.236	weak	42 and twin	0.235
6	0.188	very weak	04	0.188

b. Nylon 68 Pseudohexagonal Phase

measd spacing (nm)	intensity	index	calcd spacing (nm)
0.420	strong	20	0.420
0.243	weak	22	0.242
0.210	very weak	40	0.210

c. Cell Parameters

a (nm)	*b* (nm)	*c* (nm)	*γ*, deg
	Monoclinic Nylon 68		
0.960	0.826	1.97	115
	Monoclinic Nylon 46		
0.960	0.826	1.47	115
	Pseudohexagonal Nylon 68 (and for Nylon 46)		
0.970	0.970		120

Appearance of Single Crystals. Typical single crystals, prepared from butanediol, are shown in Figure 2. Figure 2a shows small crystals grown at low crystallization temperature (100 °C), and Figure 2b shows larger crystals, grown at 125 °C. We were unable to obtain isolated single crystals but always found approximately rectangular aggregates of lathe-shaped multilayers. We have not obtained rectangular groupings before in the other even nylons that we have studied. Nylons 46,[1] 4,[7] and 8[5] grew from butanediol as lathe-shaped multilayers, but the aggregates give the general appearance of ribbons. There are, in the literature, records of crystals of even-numbered nylons in groupings more like those that we see for nylon 68, particularly where other solvents have been used (see, for instance, ref 8). Nylon 68 crystals, fast quenched from the crystallization temperature into cold acetone, are of the same appearance as those hot filtered in the usual way, as are those allowed to cool in butanediol.

Electron Diffraction. Although the appearance of the single crystal aggregates is rather different from those of other even nylons, the electron diffraction patterns are very similar. Electron diffraction patterns obtained from the edges of aggregates of unquenched crystals reveal that the polyamide chains run normal to the crystal surfaces. There are two strong diffraction signals, at 0.435 and 0.375 nm. These two strong diffraction signals are characteristic of many low even nylons[1,5,7,9–12] and represent the projected interchain distance within a hydrogen-bonded sheet (actual value 0.48 nm) and the intersheet distance, respectively. In the best nylon 68 diffraction patterns six reciprocal lattice signals can be seen and these are listed in Table 1a. Nylon 68 crystals are usually twinned, a feature also observed in nylon 46 crystals.[1] The electron diffraction pattern of unquenched nylon 68 single crystals is shown in Figure 3a and sketched in Figure 3b (to show the positions of the weaker reflections, not visible in the print). The azimuthal orientation of the electron diffraction pattern can be correlated with the real space image of the diffracting nylon 68 crystal, enabling us

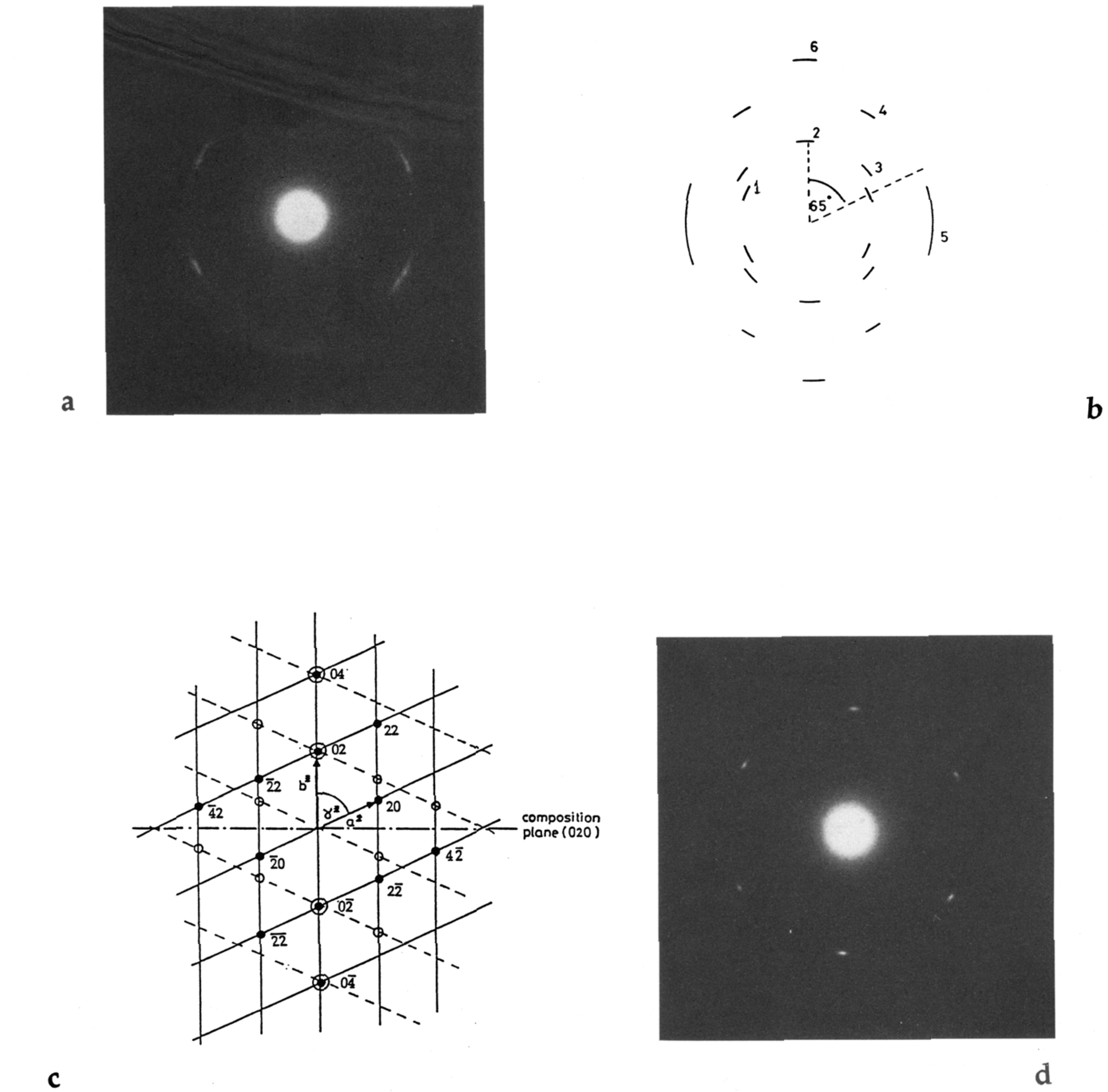

Figure 3. (a) Electron diffraction obtained from unquenched (monoclinic) nylon 68 single crystals. Only the strongest diffraction signals, 1, 2, and 3 in Table 1a, are visible on the print. (b) Sketch of the diffraction pattern to show weaker reflections not visible on the print. The numbers refer to Table 1a. (c) Drawing of the *hk*0 reciprocal net for unquenched nylon 68 single crystals. The filled circles index on a reciprocal lattice with $a^* = 2.30$ nm^{-1}, $b^* = 2.67$ nm^{-1}, and $\gamma^* = 65°$ or, in real space, $a = 0.480$ nm, $b = 0.413$ nm, and $\gamma = 115°$. It can be shown (see text) that *a* and *b* need to be doubled to obtain the true unit cell. The reflections are twinned about the (010) composition plane, and the twinned reflections are indicated by the open circles. (d) Electron diffraction obtained from quenched (pseudohexagonal) nylon 68 single crystals. Only the strongest diffraction signals, spaced at 0.420 nm, are visible on the print.

to establish that the hydrogen-bonded sheets run parallel to the long axis of the crystal. This is also the case in other even nylons (46,[1] 4,[7] and 8[5]).

The electron diffraction pattern shown in parts a and b of Figure 3 is typical of those we obtained from all the nylon 68 crystals which we prepared, except for those quenched from the crystallization temperature. The projection of the unit cell for unquenched nylon 68 crystals is shown in Figure 3c. The *ab* projection of the nylon 68 unit cell (really the *hk*0 reciprocal net) is, within experimental error, the same as that of the nylon 46 unit, for which $a = 0.960 \pm 0.005$ nm, $b = 0.826 \pm 0.005$ nm, and $\gamma = 115 \pm 1°$.[1] All the same diffraction signals can be seen from our preparations of nylons 46 and 68, however, the diffaction signals listed as 2 and 3 are less sharp from our crystals of nylon 68, compared with those of our crystals of nylon 46, increasing the uncertainties in the lattice dimensions of the nylon 68. We are not certain why some diffraction signals are less sharp than others; this may well be a result of some disorder in the way in which of the hydrogen-bonded sheets pack.

In the *ab* plane the unit cell spacings have been doubled from those measured directly from the diffraction pattern. In nylon 46 this doubling was established from the X-ray data. We do not have X-ray data for nylon 68 single crystals. However, it is still clear that the spacings have to be doubled. Along *b* it is because, as in other even nylons,[1,5-7,9-12] the hydrogen-bonded sheets shear in order to pack together most effectively. The shear can be either alternately up and down (as in nylons 46[1] and 6[12]) or progressive, each in the same direction with respect to the last (as in nylon 66).[9-12] Because in nylon 68 the chains run normal to the crystal surfaces, we know that the shear must be alternating, not progressive, so the b spacing is 0.826 nm, rather than 0.413 nm. Along a the hydrogen-bonding pattern gives rise to the doubling of the lattice (see below). We cannot obtain any information about the spacing along the chain direction from electron diffraction of untilted nylon 68 single crystals. However, we predict (by extrapolation from nylon 46) that the c spacing will be 1.97 nm. So, for this c spacing, the whole unit cell would have parameters $a = 0.960 \pm 0.005$ nm, $b = 0.826 \pm 0.005$ nm, $c = 1.97$ nm, and $\gamma = 115 \pm 1°$.

On examining nylon 68 crystals quenched from the crystallization temperature into cold acetone, we found a hexagonal electron diffraction pattern, with strong diffraction signals at 0.420 nm and two weaker sets of additional signals; these are listed in Table 1b. A hexagonal pattern is shown in Figure 3d. This structure is similar to that found on quenching nylon 8 crystals in the same way.[5] The hexagonal net has parameters $a = b = 0.970$ nm and $\gamma = 120°$. We have kept the dimensions a and b commensurate with those of the monoclinic cell because the two structures are closely related (see below). Only detailed three-dimensional modeling of the hydrogen bond linkages can show if the actual values of a and b are submultiples, or even multiples, of these values. Just as we found for nylon 8,[5] the hexagonal structure transforms to the usual room temperature monoclinic on modest heating (e.g., at 65 °C).

Changes on Heating Monoclinic Nylon 68 Crystals. On heating monoclinic crystals in the electron microscope hot stage, we found changes in spacing with temperature. The two strong diffraction signals moved together, finally meeting at 203 °C, at a spacing of 0.42 nm. Thus 203 °C can be termed the "Brill" temperature for nylon 68. The actual recorded spacings are shown in Figure 4a, and their ratio is shown in Figure 4b. Note that this 0.42-nm hexagonal signal is the same as was observed on quenching from the crystallization temperature into nonsolvent.

We have previously reported similar effects in nylon8[5] and nylon 4[7] single crystals. In those polymers the strong diffraction signals moved together on heating but did not meet before the crystals melted. We now add the behavior of nylon 46 on heating, not reported in our previous paper dealing with crystals of that polymer. The observed spacings for nylon 46 are shown in Figure 5a, as a function of temperature, and their ratio is shown, as a function of temperature, in Figure 5b. For nylon 46 the "Brill" temperature, at which the spacings come together, occurs at 245 °C. There is a curious plateau in the nylon 46 data, between 185 and 240 °C, not found in nylons 4,[7] 8,[5] or 68. The final, high temperature, spacing was measured as 0.418 nm, compared with 0.420 nm for nylon 68. However, these values are equal, within the errors of the experiment.

Discussion

Comparison of Nylon 68 and Nylon 46 Single Crystals. It is clear from the foregoing experimental results that nylon 68 is similar to nylon 46. In both cases the single crystals from butanediol grow with the chains normal to the crystal faces. They are found in a monoclinic phase (except after drastic quenching) and are usually twinned. The ab projections ($hk0$ reciprocal nets) of the two unit cells are the same, within the experimental errors. The important temperatures for nylons 46 and 68 are compared in Table 2. The glass transition temperatures for the two nylons are close, although that of nylon 68 is lower; many nylons have glass transition temperatures at about 50 °C.[13] Other

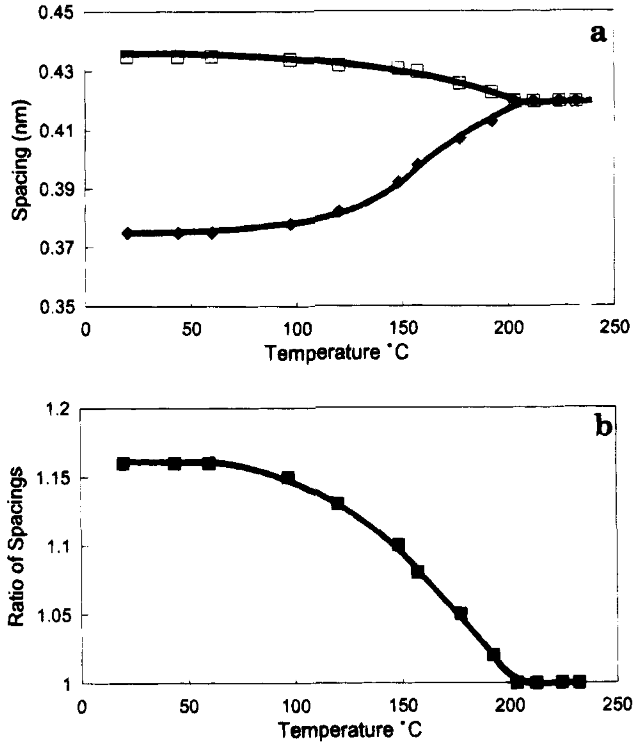

Figure 4. Changes in spacing of the two prominent electron diffraction signals on heating isothermally crystallized nylon 68 crystals of the monoclinic phase: (a) the actual spacings; (b) their ratio.

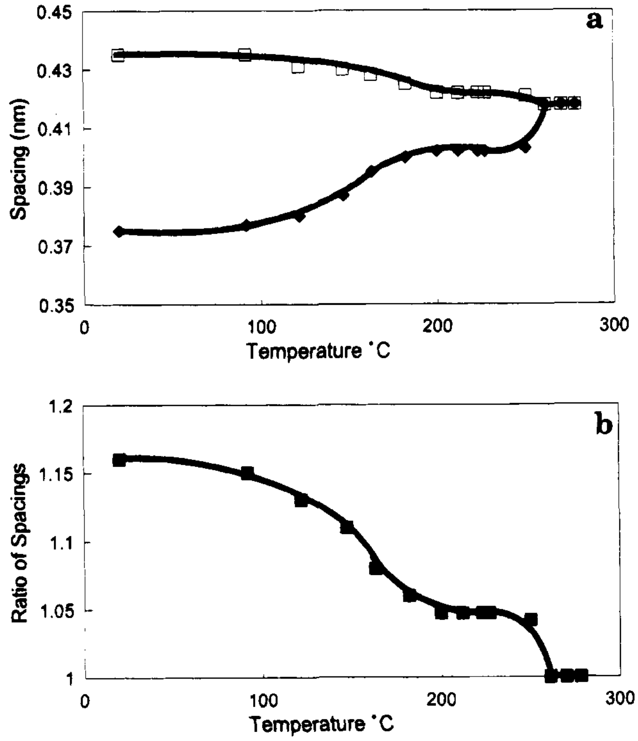

Figure 5. Changes in spacing of the two prominent electron diffraction signals on heating isothermally crystallized nylon 46 crystals of the monoclinic phase: (a) the actual spacings; (b) their ratio.

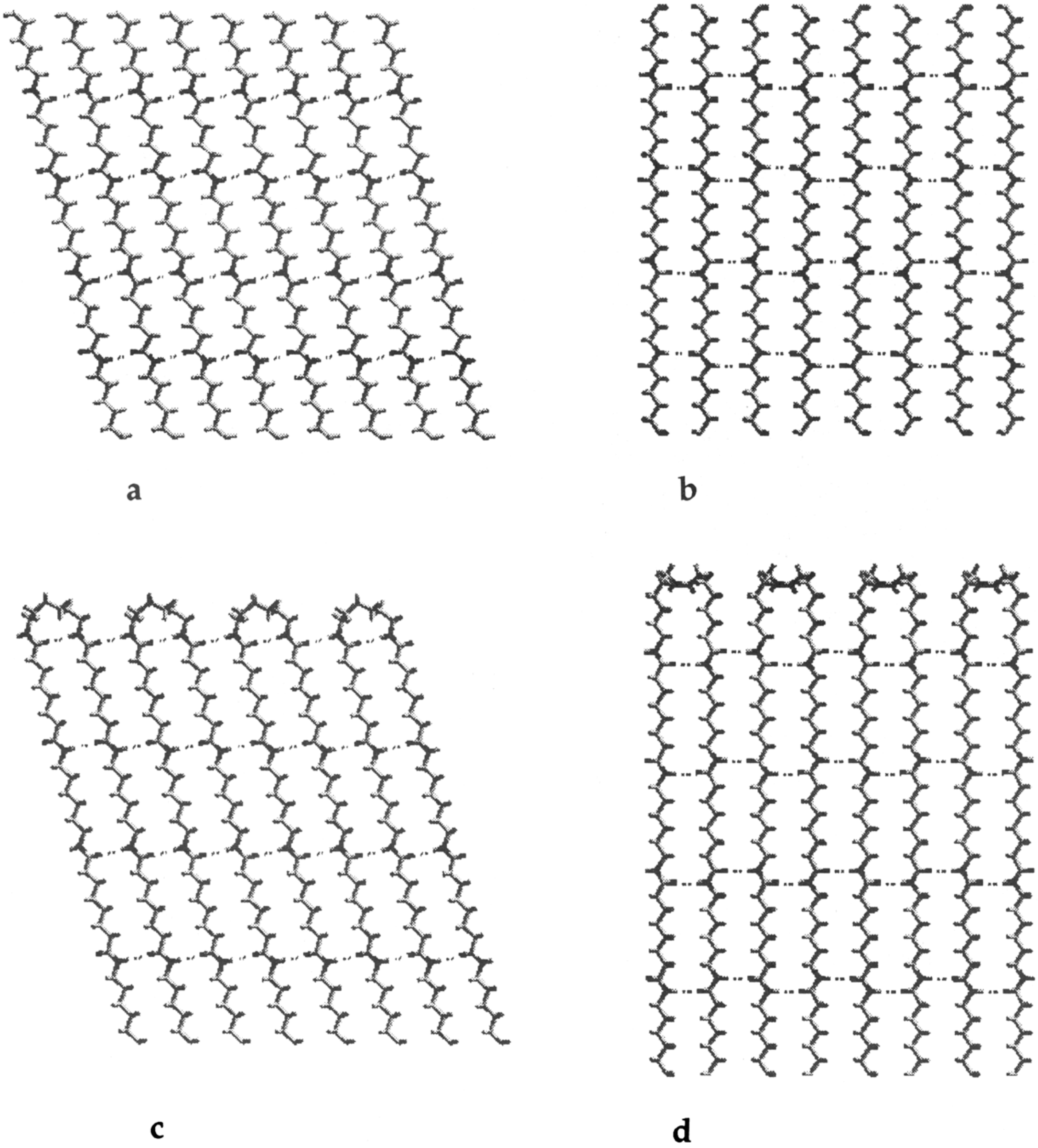

Figure 6. Details of the chain-folded, hydrogen-bonded sheets of various nylons. (a) Nylon 66, showing the progressive hydrogen-bonding pattern. (b) Nylon 6, showing the alternating hydrogen-bonding pattern. (c) A possible structure for nylon 68 with progressive hydrogen bonding. One fold surface is shown. Note that the fold is in the alkane part of the chain. (d) A possible structure for nylon 68 with alternating hydrogen bonding. One fold surface is shown. Note that this structure is only possibe if there is an amide unit in each fold. Also note that the hydrogen bond pattern here is not the same as that in b.

key temperatures are lower for nylon 68 than for nylon 46, as would be expected because the hydrogen bonds are less frequent in nylon 68.

Table 2. Characteristic Temperatures for Nylons 68 and 46 (°C)

nylon	highest crystallizn	optimum seeding	T_g	Brill	T_m
68	125	170	about 48	203	234
46	160	195	about 53	245	295

Comparison with Other Even Nylons. We are involved in studies of single crystals of a series of even nylons. Nylon 46 was the subject of a recent paper,[1] and we have studied nylons 4[7] and 8[5] since. Over the years there has been a great deal of work on nylon 66, including work on single crystals (e.g., refs 4 and 9–11). In all these nylons the requirement that the hydrogen bonds between adjacent chains should be linear is a crucial feature in determining the crystal structure adopted by single crystals. In nylon 66 single crystals the hydrogen bonds can only be linear if the chains in the sheet progressively shear in each hydrogen-bonded sheet. As a consequence the chains must run oblique to the crystal surfaces,[1,3] as is observed experimentally.[9–11] A hydrogen-bonded sheet of nylon 66 is shown in Figure 6a. The unit cell is triclinic because of the progressive shear in the hydrogen bond plane coupled with the progressive shear between hydrogen-bonded sheets.[9] On the other hand, nylons 4, 6, and 8 can only form linear hydrogen bonds, with the chains shearing alternately up and down within a hydrogen-bonded sheet. This, coupled with the alternating up and down shear between adjacent hydrogen-bonded sheets, gives rise to monoclinic unit cells with chains normal to the crystal surfaces.[5,7,12] A hydrogen-bonded sheet of nylon 6 is shown in Figure 6b.

Because of the equal spacing of the amide units along the chain (Figure 1), both the progressive linear hydrogen bond pattern and an alternating pattern should be possible for nylon 68 and nylon 46. The hydrogen-bonded sheets for both possible structures of nylon 68 are drawn in parts c and d of Figure 6 (the alternating pattern is slightly different from that of nylon 6, compare parts b and d of Figures 6). In single crystals it is the alternating pattern (the structure of Figure 6d) that is observed in both nylon 68 and nylon 46.[1] This structure can only be achieved, with adjacent reentry chain folding, if there is an amide in the fold (as argued in detail, for nylon 46, in ref 1). In contrast, the progressive pattern can only be achieved if the fold is in an alkane segment (see Figure 6c). Note, from Figure 6d, that because the hydrogen bonds move alternately up and down between adjacent chains in the monoclinic structure that is observed, we have to double the unit cell size along a.

Comparison with Nylon 68 Fibers. In a paper dealing with a number of aliphatic polyamides,[3] Slichter reported a fiber pattern for nylon 68. He observed a pattern composed of two elements superimposed. One gave every indication of being from a structure like that of nylon 66, with progressive hydrogen bonding, as shown in Figure 6c. The other had "amide groups in planes normal to the molecular axes". We believe, as did Slichter, that these fibers contained a combination of the two possible structures, sketched in parts c and d of Figure 6. In Slichter's fibers the progressive structure was predominant; however, we have not seen any crystals of the progressive structure (Figure 6c) in our nylon 68 single crystal preparations.

Behavior at High Temperatures. Nylon 68 crystals crystallized from butanediol are usually found in the monoclinic phase at room temperature, but we have found a pseudohexagonal phase both on quenching nylon 68 from the crystallization temperature to below the glass transition temperature (nylon 8 behaves in a similar way[5]) and on heating the monoclinic phase to 203 °C and above. In nylon 68 the two phases, monoclinic and pseudohexagonal, are quite similar in structure, the angle γ has only to change from 115° to 120°, a from 0.960 to 0.970 nm, and b from 0.826 to 0.970 nm.

It seems that for nylon 68 single crystals the higher density monoclinic crystal form is more stable at room temperature. However, the pseudohexagonal structure is the stable form at high temperatures, and the monoclinic crystals move toward it on heating. We believe that the crystals grow in the high-temperature, pseudohexagonal structure, and this can be "frozen in" by quenching rapidly from the crystallization temperature to below the glass transition temperature; that is why the pseudohexagonal form is obtained on quenching very drastically from the crystallization temperature into nonsolvent at room temperature. However, as soon as the crystals are heated above T_g (about 48 °C), they revert to the monoclinic structure which is more stable at low temperatures. On further heating the alkane segments begin to move about, the hydrogen-bonds rearrange, flipping ±60° out of the original sheets,[14] and the structure shifts back toward the high-temperature pseudohexagonal phase. Ramesh et al.[11] have recently shown that nylon 66 grows from the bulk in a pseudohexagonal phase but transforms to the triclinic form (as Figure 6a), stable at low temperatures, on cooling.

We have now observed a movement, with temperature, from monoclinic to pseudohexagonal structures for a number of even nylons (4, 8, 46, and 68), and a related change from triclinic to pseudohexagonal has been seen in nylon 66.[4,11] For some nylons, as here in nylons 46 and 68 and in nylon 66, the change is fully accomplished; for others (nylons 4 and 8) it is not completed before melting.

Conclusions

(1) Nylon 68 single crystals have a high-temperature pseudohexagonal phase and a low-temperature monoclinic phase (like nylons 8 and 4). We also report here, for the first time, the high-temperature pseudohexagonal phase for nylon 46.

(2) The quenching experiments indicate that nylon 68 crystals actually grow in the pseudohexagonal phase and can be frozen into that phase by quenching to below T_g. Crystals quenched into the pseudohexagonal phase revert to monoclinic on heating above T_g.

(3) The $hk0$ reciprocal net of the monoclinic phase on nylon 68 is, within experimental error, the same as that of nylon 46.

(4) In nylon 68 single crystals the chains run normal to the crystal faces. This means that the hydrogen bond pattern must be of the alternating type (as nylon 46) not the progressive type (as nylon 66). This is only possible if each fold contains an amide group.

(5) In nylon 68, and in nylon 46, the strong reflections gradually come together on heating; a "Brill" temperature, at which the transformation of the monoclinic phase into the pseudohexagonal phase is complete, has been recorded for both. The "Brill" temperature is 203 °C for nylon 68 and 245 °C for nylon 46.

(6) The whole behavior on nylon 68 is very like that of nylon 46 but transposed to lower temperatures. This is no surprise because the structures of the two polymer chains are the same except that the hydrogen bonds are spaced more widely in nylon 68.

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