On the Crystal Structure of Nylon 6

JAMES P. PARKER, *American Enka Company, Enka, North Carolina 28728*, and PAUL H. LINDENMEYER, *Seattle, Washington 98109*

Synopsis

Nylon 6 can exist in either of two stable crystal structures, the α crystal with hydrogen bonds between antiparallel chains or the γ crystal with hydrogen bonds between parallel chains. Both structures have been observed in the same highly annealed fiber, suggesting that the polymer should not be regarded as a pure compound but a multicomponent mixture. Nylon 6 can also exist in a series of metastable crystal structures which vary continuously in size, perfection, and structural parameters from a pseudohexagonal structure to either of the two stable forms. A single equatorial reflection in the wide-angle x-ray pattern (i.e., pseudohexagonal structure) will not distinguish which of the two stable forms will result upon annealing. Measurement of the 0,14,0 reflection in oriented fibers will distinguish the major trend, but it is still uncertain to what extent annealing conditions can favor one stable form over the other. The variation in the unit cell parameters as a function of annealing has been accurately measured, and the observed phenomena can be qualitatively described by postulating various balances between the basic forces which hold the crystal together (i.e., hydrogen bonding, dipole–dipole interaction, van der Waals attraction, and covalent bonding).

INTRODUCTION

Although nylon 6 has been known for well over 40 years and worldwide commercial production is in excess of 2.2 million metric tons annually, there still remains considerable confusion in the literature concerning the nature and stability of the various crystalline forms that this important material may assume. The purpose of this paper is to survey the crystal structure data reported to date and to attempt to rationalize these more or less conflicting reports, based on additional measurements of our own.

It may perhaps be asking too much to inquire what is the equilibrium crystal structure of nylon 6 since it is well known that all polymers are composed of a large number of molecular lengths. Consequently, it is quite conceivable that two or even more different crystalline phases might exist in equilibrium with each other.[1] Likewise, it is not unreasonable to expect that the unit cell parameters might vary with composition (i.e., the actual molecular lengths incorporated into the crystal). Since it is now well established that molecular fractionation occurs to a greater or lesser degree depending upon crystallization rate, one might expect changes in the unit cell parameters also to be dependent upon the conditions under which crystallization occurred.

It will be shown that all results reported in the literature fall essentially on a single curve of continuously varying structure parameters. New data have been obtained to reproduce the full range of crystal structures. This series of struc-

tures can be described phenomenologically in a simple manner, and it can be shown that one might expect such structural variations as a consequence of different possible balances between van der Waals attractions, hydrogen bonds, dipole–dipole forces, and torsion about covalent bonds.

The earliest reported crystal structure of nylon 6 was by Brill[2] in 1943. This was followed by a more precise analysis of the unit cell by Wallner[3] in 1947. The most complete crystal structure determination was probably that of Holmes, Bunn, and Smith[4] in 1955. All of these early investigators recognized the existence of alternate crystalline forms in addition to the one they determined. In particular, Bunn called the secondary structure "β" and suggested that it consisted of an alternate way of packing the hydrogen bonded sheets in an analogy to the "α" and "β" structures of nylon 66 which he had determined earlier.[21]

In 1959, Ziabicki[5] reported that the β structure was obtained exclusively when nylon 6 is spun rapidly from a melt into a dry atmosphere. He suggested that the β structure was hexagonal. He pointed out that this β structure was unstable and transformed into the α structure upon annealing or exposure to moisture. In 1959, Kinoshita[6] also reported on his investigation of a series of polyamides, including nylon 6, and concluded that there existed a basically different crystal structure which he called "γ" and which is characterized by a twisted amide group which causes a shortening of the chain. He determined the structure of nylon 77 to be of this γ type and suggested that nylon 6 would also exist in this structure after treatment with an iodine–potassium iodide solution and washing with potassium thiosulfate solution. Next Reichle and Prietzche[7] published a paper which described the β form as a monoclinic structure having opposed amide groups in adjacent hydrogen-bonded sheets (one of the alternate suggestions of Bunn) and called the γ structure hexagonal.

In 1963, Voglesong[8] published a crystal structure determination on nylon 6 fiber which had been treated with iodine. He concluded that the structure was hexagonal with statistically distributed hydrogen bonds in all three principal directions. In this same year, Roldan and Kaufman[9] summarized their experience by proposing that nylon 6 could exist as an "α" crystal,[4] an "α paracrystal" with variable unit cell parameters, a stable "β" crystal with a hexagonal structure (in drawn fibers) and unstable pseudo-hexagonal structure similar to a nematic liquid crystal which they called the "γ" crystal.

A series of papers by Japanese authors[11-14] described the transitions between the α and the γ crystal as accomplished by iodine treatment. Some authors claimed the γ crystal was hexagonal or pseudohexagonal;[15] others, that it was monoclinic;[16] and all seemed to ignore or doubt the existence of a β structure of the type suggested by Bunn, Reichle, and Ziabicki. In fact, the β crystal fell into such disrepute that when Illers[17] required a symbol for a hexagonal structure which yielded the α crystal upon annealing, he called it "$\gamma*$" to distinguish it from a hexagonal structure which annealed to the monoclinic γ crystal of Arimoto[16] or the orthorhombic structure of Bradbury and Elliot.[18]

A summary of the unit cell data in the literature is given in Table I. To facilitate comparison, all data have been converted to the monoclinic form and the axes assigned in a way to make the data directly comparable. From these data, it is clear that the reported unit cells fall into two classes: (1) in which the chain axis (b-axis) is in excess of 17 Å and the crystallographic β angle is 60° or greater, and (2) in which the b-axis is about 16.8 Å and the β angle is 60° or less.

From these data, we formed the working hypothesis that there exist at least

two basically different ways of packing nylon 6 chains into crystal structure: one in which the hydrogen bonds are between antiparallel chains which are almost completely extended and the fiber repeat distance is >17 Å; and the other in which the amide groups are twisted out of the plane of the methylene groups, shortening the chain repeat distance to about 16.8 Å and permitting hydrogen bonds to form between parallel chains.

Although Roldan and Kaufman[9] reported the existence of nylon 6 with a "paracrystalline" structure having a varying unit cell, exact data and method of preparation of samples were lacking. In addition, most of the data in the literature were obtained from laboratory-prepared films which had been drawn and/or rolled, whereas we were primarily interested in the crystal structures that might exist in filament yarns made under production conditions. Finally, there have been persistent attempts to explain the convergence of the observed equatorial reflections into a single peak as the consequence of a mixture of α and γ crystals combined with broadening due to small crystal size and degree of perfection. Thus, it seemed desirable to verify whether or not such a physical mixture of these two crystal forms could duplicate the observed x-ray diffraction.

EXPERIMENTAL

All samples were initially a regular production nylon 6 carpet yarn of 2080 denier, spun and drawn but not textured. The iodine treatment[9,11,12,16] involved soaking such yarns in 0.5% molar iodine–potassium iodide solution for 10 min and rinsing in a 7.3% by weight solution of sodium thiosulfate followed by water at 22°C.

The x-ray equipment used was a Norelco vertical diffractometer in the transmission mode. A Philips focusing monochromator was used.

The yarn specimens were hand wound in a single, tightly packed flat layer onto 0.5-mm-thick frames. The equatorial scans were made with the fiber axis perpendicular to the divergence slit. In all cases, the diffractometer scan rate was 1°/min.

TABLE I
Summary of Unit Cell Data

Author (year)	a	b	c	Crystallographic Angle β	Reported symmetry and type
Brill (1943)[2]	9.66	17.00	8.32	65°	monoclinic, α
Wallner (1948)[3]	9.45	17.08	8.02	68°	monoclinic, α
Holmes (1955)[4]	9.56	17.20	8.01	65.5°	monoclinic, α
Ziabicki (1959)[5]	9.60	17.20	9.60	60°	hexagonal, β
Ruscher (1960)[10]	9.65	17.20	8.11	66.3°	monoclinic, α
Vogelsong (1963)[8]	9.58	16.7	9.58	60°	hexagonal, γ
Bradbury (1963)[18]	9.64	16.7	9.19	58.3°	orthorhombic, γ
Ota (1964)[15]	9.62	16.6	9.35	60°	monoclinic, γ
Arimoto (1964)[16]	9.56	16.9	9.33	59°	monoclinic, γ
Illers (1972)[17]	9.66	16.68	9.20	58.3°	orthorhombic, γ
	9.68	16.68	9.14	59°	monoclinic, γ

[a] $a/2$ = Distance between hydrogen bonded chains; b = fiber repeat distance; $c \sin \beta / 2$ = distance between sheets of hydrogen bonded chains.

RESULTS

The first and perhaps one of the most significant results of our experimental measurements was the observation that a single equatorial reflection and a strong 020 meridional peak is not sufficient evidence for the existence of γ structure (i.e., for the existence of parallel hydrogen bonding). Since our measurements were all made on drawn fibers, it was possible to measure the spacing of the 0,14,0 reflection which yields an accurate value for the unit cell length along the polymer axis (see Kaji and Sakurada[19]). According to our working hypothesis, crystals with a fiber repeat distance in excess of 17 Å have hydrogen bonds between antiparallel chains, while bonding between parallel chains requires this distance to be 16.8 Å or less. Differences of this magnitude can be clearly distinguished in measurements of the 0,14,0 reflection which varied from $2\theta = 77°$ to $80°$. Figure 1 shows diffraction traces from two different nylon 6 fibers. Both have single equatorial reflections characteristic of hexagonal (or nearly hexagonal) symmetry, both have strong meridional reflections at $2\theta \cong 11°$, but one has 0,14,0 meridional reflection at $2\theta = 80°$ characteristic of the parallel hydrogen bonding of the γ crystal, while the other has an 0,14,0 reflection at $2\theta = 77.6°$ characteristic of antiparallel bonding.

The significance of this observation must be emphasized since it accounts for much of the confusion in the literature. Hexagonal symmetry in the equatorial reflections plus the existence of a strong 020 reflection cannot be taken as sufficient evidence of parallel hydrogen bonding and the γ crystal structure. Thus much of the literature which refers to the $\gamma \rightarrow \alpha$ transition and to the formation of the γ structure is open to question since it is doubtful if many investigators have measured the 0,14,0 reflection, which has measureable intensity only in oriented fibers. The existence of two different hexagonal forms is described by Illers et al.[17] on the basis of their behavior upon annealing. In agreement with these authors, we found that annealing the fiber with hexagonal structure and antiparallel hydrogen bonding yields only structures with antiparallel bonding (i.e., α crystals); but in contrast to their results, our parallel bonded structures yielded a mixture of α and γ crystals. In fact, when annealed for 5 hr in a steam autoclave at 147°C, the result (Fig. 2) shows well-formed crystals of both the α and the γ crystal structure existing in a single fiber. The peaks seen here are, from left to right, associated with the 200 planes of the α form at $2\theta = 20.2°$, the 200 planes of γ form at $21.8°$, the 002 planes of the γ form at $22.7°$, and finally the 002,202 planes of the α form at $24.0°$. The 002 peak of the γ form is seen only as a slight shoulder in Figure 1 and emphasizes how well the γ material has been developed in the material of Figure 2. In the material of Figure 1, the β angle of the unit cell is close to $60°$ and the various planes are spaced about equally. In the well-developed γ form, this angle decreases well below $60°$, and the spacings are no longer equal and the 002 peak emerges as a well-defined separate peak.

This again is a highly significant observation since it shows that these two crystal structures can exist in one and the same fiber under conditions which must be approaching equilibrium (i.e., steam annealing for 5 hr at 147°C). Clearly, both of these structures are stable, and the fact that they can exist in apparent equilibrium is a violation of the phase rule for a pure material. Thus, we must
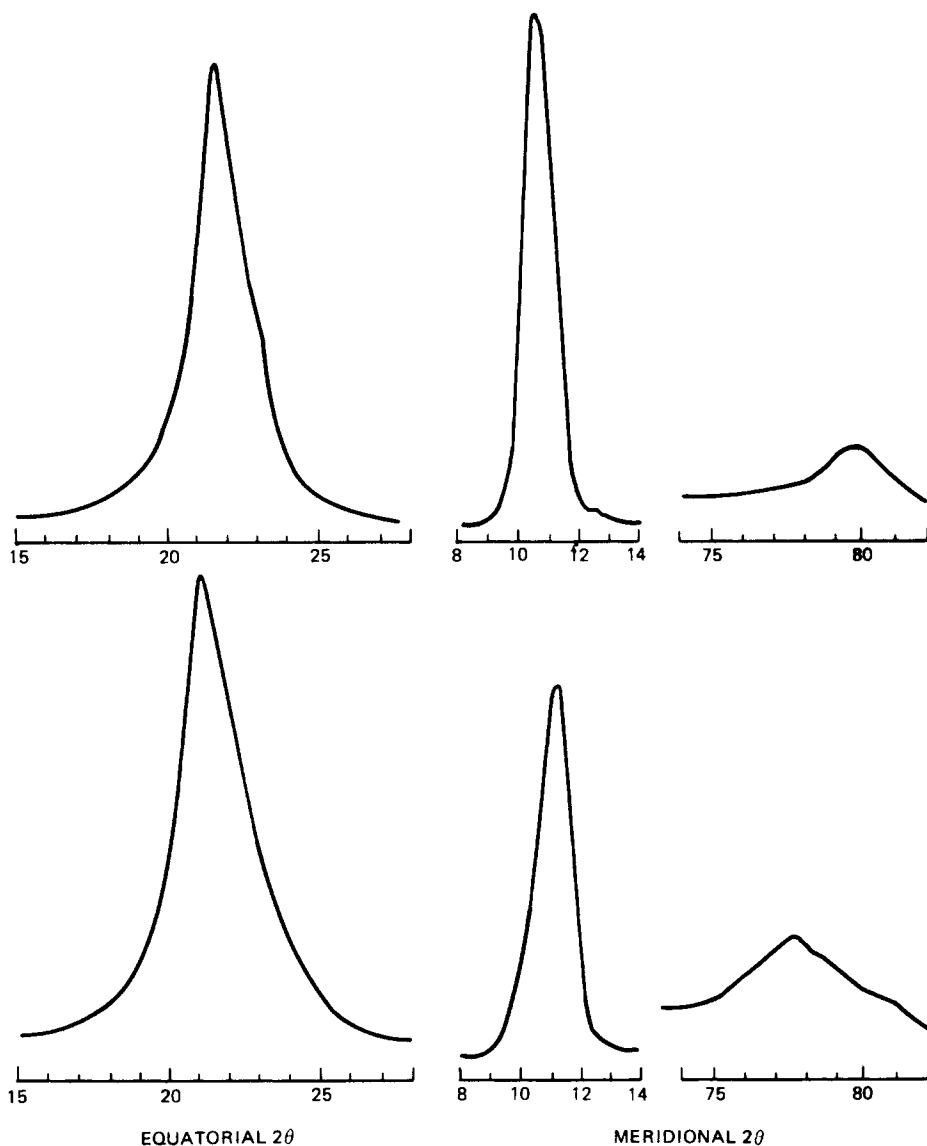
Fig. 1. Diffractometer scans of (a) iodine-treated nylon 6 fiber with parallel hydrogen bonding, (b) production nylon 6 fiber with antiparallel hydrogen bonding.

conclude that nylon 6 should not be considered as a pure material, but rather as a multicomponent alloy where the components are molecules of different lengths.[7]

It has been customary to suggest that the diffraction patterns of nylon 6 which are normally observed may be interpreted as mixtures of the two generally proposed crystalline forms. In order to test this hypothesis, we prepared physical mixtures of fibers which contained only the pure α crystal and the pure γ crystal. Figure 3 shows the results along with a typical production fiber. From this figure,
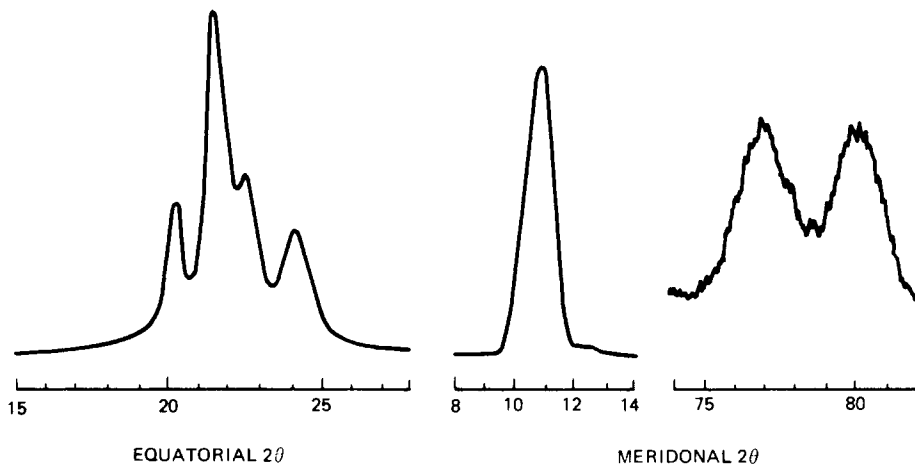
Fig. 2. Diffractometer scans of iodine-treated nylon 6 fiber after 5 hr in a steam autoclave at 147°C, showing both α and γ forms.

it is clear that the typical yarn cannot be a simple mixture of these two forms. Even if extensive line broadening is proposed as a consequence of reduced crystal size and imperfections, it is not possible to produce the diffraction profile of the production fiber from a combination of the two pure crystalline forms. This conclusion is supported by a separate experiment, using a special computer program to resolve the various peaks. In this program, it was possible to allow the position of each peak to be fixed and the peak width varied, corresponding to a situation in which only the two pure forms are present, but with varying crystal size. It also permitted a second analysis in which both the position and the width of the peaks could vary, simulating a state in which cell geometry varied as well as the crystallite size. When these programs were applied to the curve of Figure 3a, the first produced a significantly poorer fit than did the second. While this is only indirect evidence, it does reinforce our conclusion. Thus, we must seek alternate explanations.

Following the hypothesis that the various values of unit cell parameters reported in the literature (Table I) may all be essentially correct, we selected the angle between the a- and the c-axis (i.e., the crystallographic β angle) as the critical unit cell parameter and plotted the volume of the unit cell versus this parameter (Fig. 4). Roldan and Kaufman[9] have also reported β angles as low as 62°, but their data could not be included in Figure 4 because only ranges rather than actual data were given. To fill in the blank areas and to obtain data on fibers for which the fiber repeat distance (and hence the type of hydrogen bonding) could be measured, we performed the following annealing experiment.

A production yarn was dried at room temperature in a vacuum chamber for 16 hr, resulting in a moisture content of 1.0–1.5%. Samples of this yarn were annealed for 2 hr at various temperatures starting at 55°C and increasing in 15° increments up to 205°C. The 2-hr time was selected because most significant changes had occurred by this time and increasing the annealing time to 18 hr had resulted in only minor additional change. The results of this annealing on the equatorial diffractometer scan are shown in Figure 5. Additional samples were prepared: (1) by boiling the starting material in acetic acid, (2) by simulating
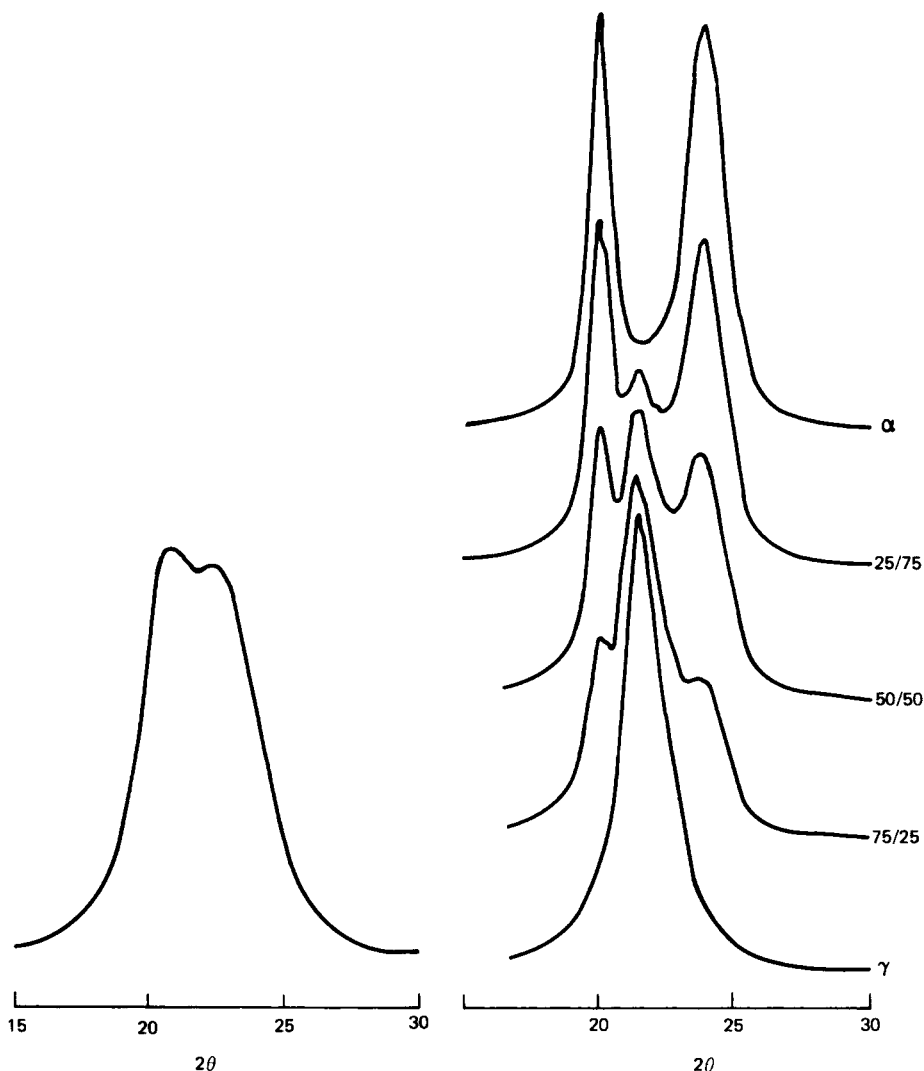
Fig. 3. Comparison of (a) typical commercial yarn with (b) yarns made of a physical mixture of fibers containing only α and γ crystal structure.

the conditions of Ziabicki, and (3) by the iodine–potassium iodide treatment described above.   Table II gives the identification of these samples.

In order to see where these several samples fall on the curve of cell volume versus β angle, the fiber repeat distance (i.e., the b-axis) was measured by meridional scan of the 0,14,0 peak and a, c, and β were determined by obtaining the best computer-calculated fit to all measureable equatorial reflections.   This latter calculation was not unequivocal and allowed for some judgement in selecting the best possible fit.   When such judgement was necessary, the values selected were those which permitted the most regular variation of a and c with the angle β.   The greatest uncertainty occurs in the region of $60° < \beta < 63°$ where few equatorial peaks are resolved.

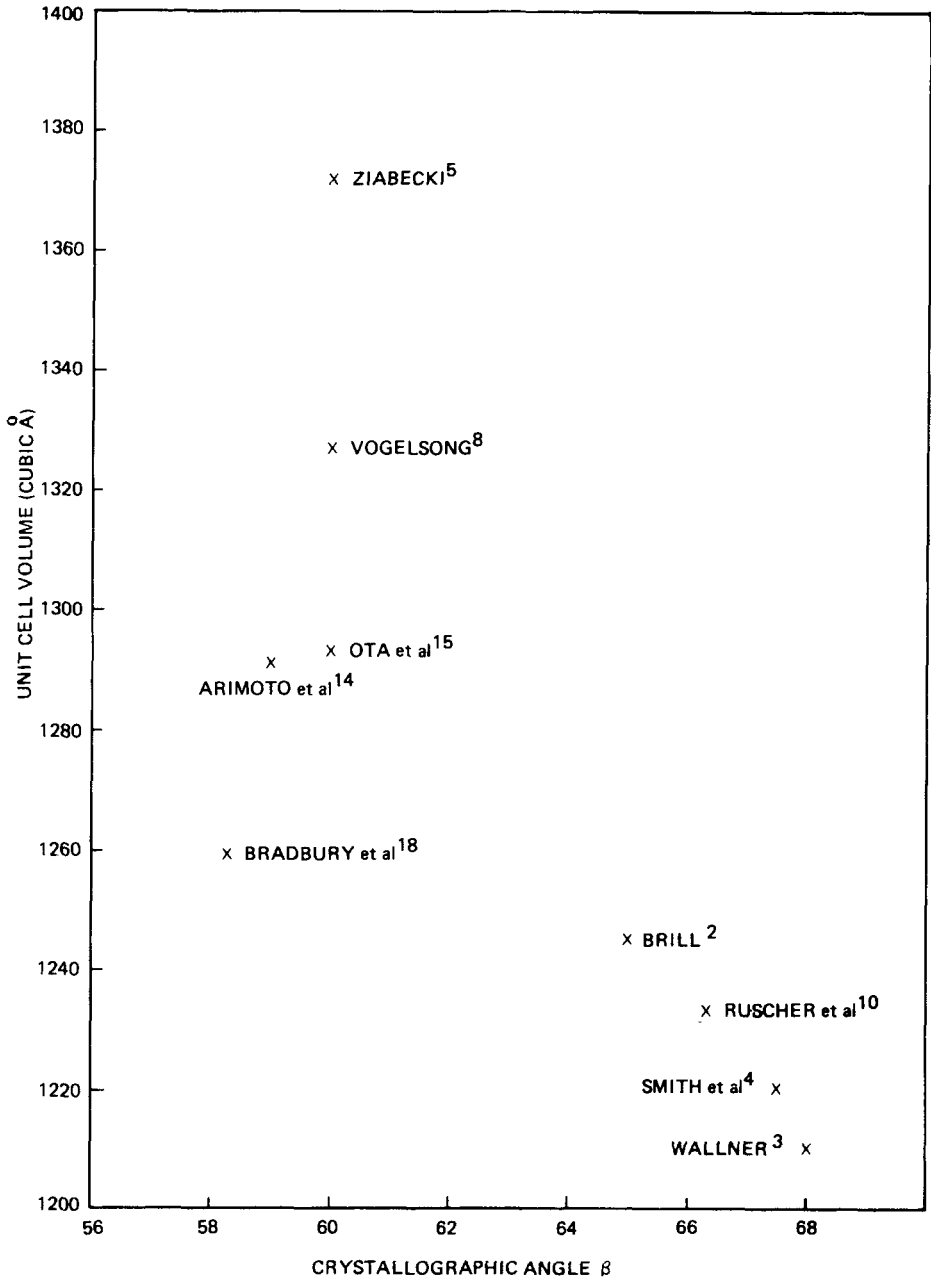When these data are combined with the literature values (Fig. 6), we obtain

Fig. 4. Reported values of unit cell volume vs. crystallographic angle β. Numbers shown refer to references listed in the bibliography.

a continuous variation in unit cell volume with β angle for crystal structures with antiparallel hydrogen bonding ($\beta > 60°$) as well as for parallel bonding ($\beta < 60°C$). It is important to note that increasing the temperature of annealing results in a steady decrease in cell volume accompanied by a gradual increase in the β angle for those samples with $\beta > 60°$ (samples a through l). Sample m shows the best α form that we have been able to produce. Sample n shows that a nearly perfect
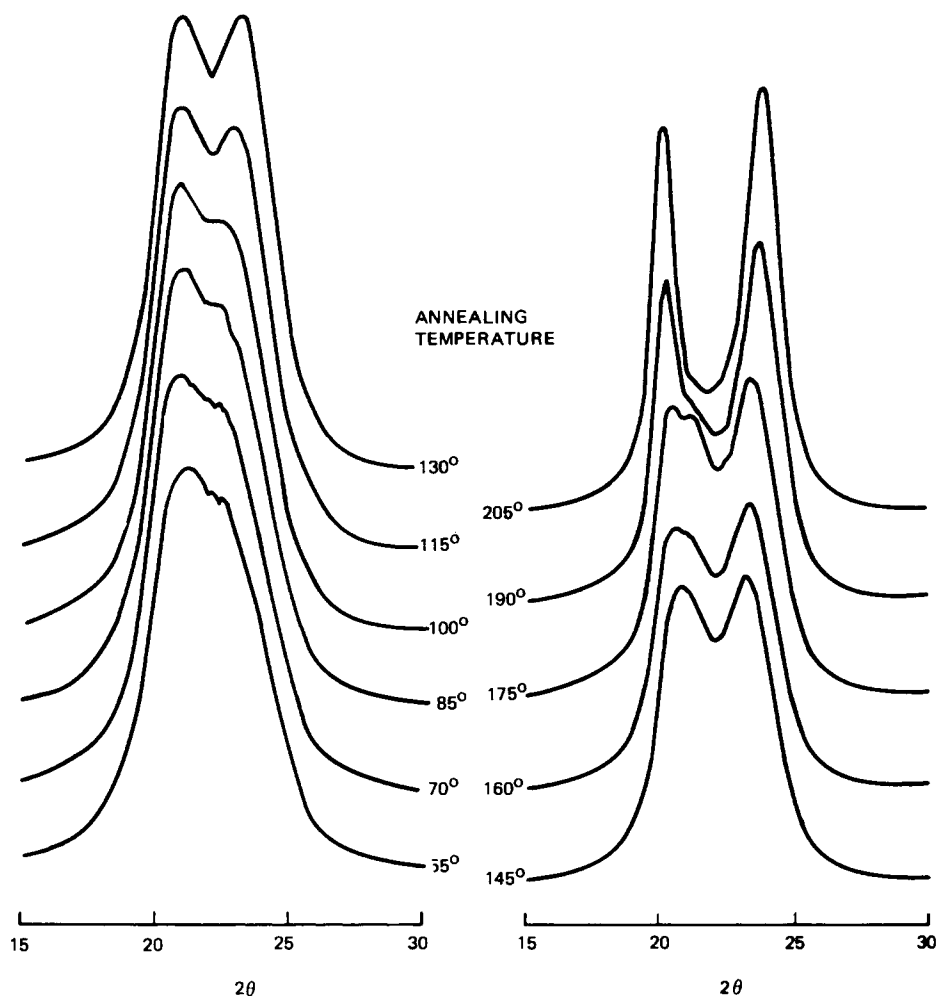
Fig. 5. Diffractometer scans of production nylon 6 as a function of annealing temperature. Scale on the right-hand set of curves is reduced by one half.

hexagonal ($\beta = 60°$) is possible, while samples o, p, and q show that the γ form also can be annealed into increasingly compact unit cells. When one approaches hexagonal symmetry ($\beta = 60°$), both antiparallel and parallel hydrogen bonding can occur resulting in a wide variation in the unit cell volume. If one takes the unit cell volume as a measure of the stability, then it is clear that the hexagonal symmetry represents an unstable structure which can anneal to the α crystal structure ($\beta > 64°$) or to the γ crystal structure with $\beta < 60°$. This interpretation of a varying β angle has been directly confirmed by measurements on single crystals of nylon 6. Following our suggestion, Geil[20] has directly measured the β angle on the electron diffraction patterns of single crystals grown from various solvents under various conditions. He has observed both α and γ crystals as well as hexagonal crystals. In addition, he finds that the β angle can vary beyond the range observed by x-ray diffraction so that γ crystals having β as low as 56.5° and α crystals with β as high as 69° have been observed.

Finally, in order to obtain a clearer picture of what is occurring on a molecular

basis, we have plotted the fiber repeat distance versus the angle in Figure 7; the distance between hydrogen bonded chains, $a/2$, in Figure 8; and the distance between sheets of hydrogen bonded chains, $\frac{1}{2} c \sin \beta$, in Figure 9. Note that both the fiber repeat distance and the separation between hydrogen bonded sheets show discontinuities at $\beta = 60°$, whereas the distance between hydrogen-bonded chains $(a/2)$ is continuous. The fiber repeat distance is larger as β increases from 60°. At high value of β, this is obviously approaching the value 17.42 Å which one calculates for a completely extended chain using the bond angles and bond distances generally accepted.[4] The maximum in the a-axis at 65° is believed to be significant even though it is quite small since it corresponds to a very sharp decrease in the intensity of the 020 meridional reflection and other irregularities in the diffraction patterns.

With these data, it now becomes possible to explain in a rational manner the nomenclature that has been suggested in the literature. Clearly, crystal structures having parallel hydrogen bonding and $\beta \leq 60°$ correspond to the γ crystal structure. The symmetry may vary from pseudohexagonal[9–12] or monoclinic[16] to orthorhombic.[18] The single crystal electron data[20] showed that the extreme $\beta = 56.5°$ was essentially orthorhombic, but intermediate values of β were clearly associated with monoclinic symmetry. Equally clear, the structure with $\beta \geq 64°$ must be associated with the α crystal.[4] This leaves the hexagonal structure with antiparallel bonding to be associated with the β crystal[4,5] or the γ^* form of Illers[17] and the region of $60° \leq \beta \leq 64°$ for the β structure[8] of the "paracrystal" of Roldan.[10] Since these latter structures are (1) unstable and (2) closely associated with the α crystal, it is questionable whether the terms β and/or γ^* need be retained.

DISCUSSION

Having measured what has occurred phenomenologically, the next step is to suggest forces to explain why such changes occur. Our procedure will be to as-

TABLE II
Sample Treatment Conditions

| Sample	Preparation
a	starting material
b	annealed at 55°C
c	annealed at 70°C
d	annealed at 85°C
e	annealed at 100°C
f	annealed at 115°C
g	annealed at 130°C
h	annealed at 145°C
i	annealed at 160°C
j	annealed at 175°C
k	annealed at 190°C
l	annealed at 205°C
m	boiled in acetic acid for 15 min
n	Ziabicki conditions (approx.)
o	I–KI treatment
p	sample o after autoclaving at 100°C for 60 min
q	sample o after autoclaving at 147°C for 300 min
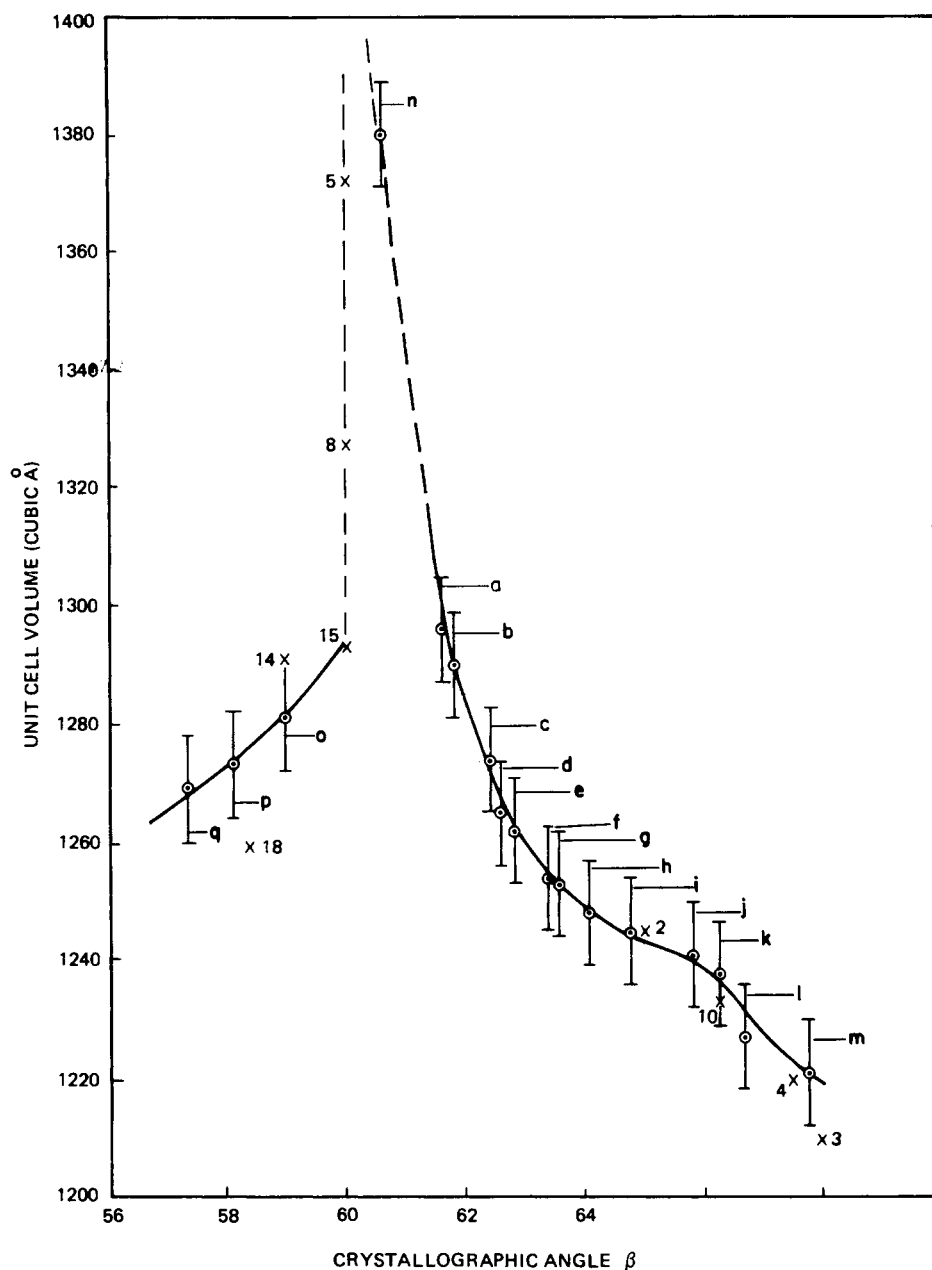
Fig. 6. Unit cell volume vs. crystallographic angle β. Numbers shown refer to references in the bibliography. Bars indicate the standard deviation of the laboratory results of the present work. Dashed portion of the curve reflects the difficulty in determining the position of the peak.

sume that the crystal structure results from a balance of the following forces in a manner which minimizes the energy of the crystal. Four forces will be considered: (1) the force required to twist a carbon–carbon bond about its minimum energy conformation, (2) the force required to position one dipole moment with respect to another, (3) the force required to change the direction or separation
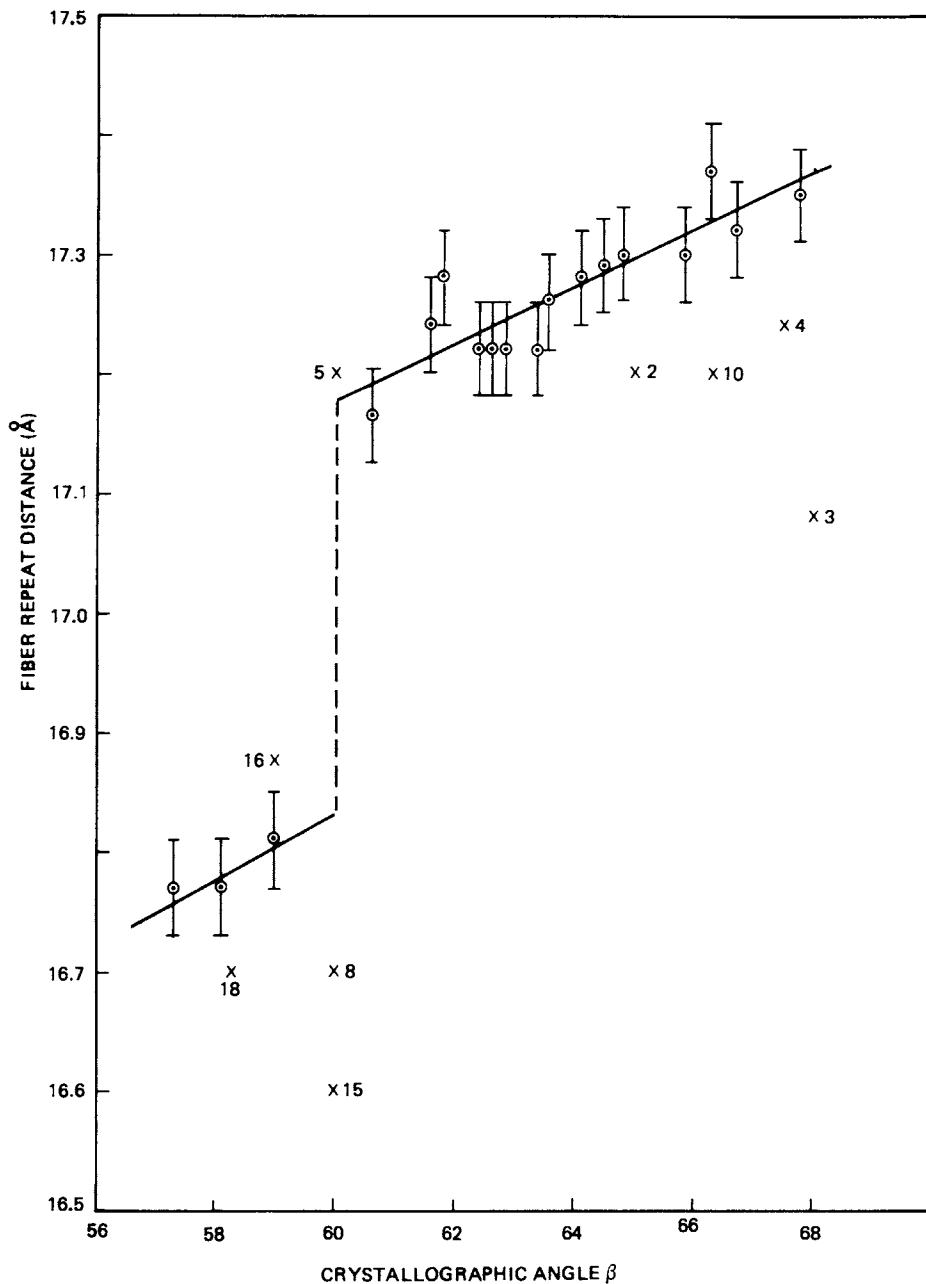
Fig. 7. Fiber repeat distance vs. crystallographic angle β.

distance in a hydrogen bond, and (4) the van der Waals forces between molecules. If these were the only forces involved, there would be one and only one set of crystal structure parameters which minimize the energy. However, since hydrogen bonds can form between either parallel or antiparallel chains, it is possible that two sets of parameters exist which might have nearly equal energies and which are separated by such a high kinetic barrier that interconversion is not feasible.
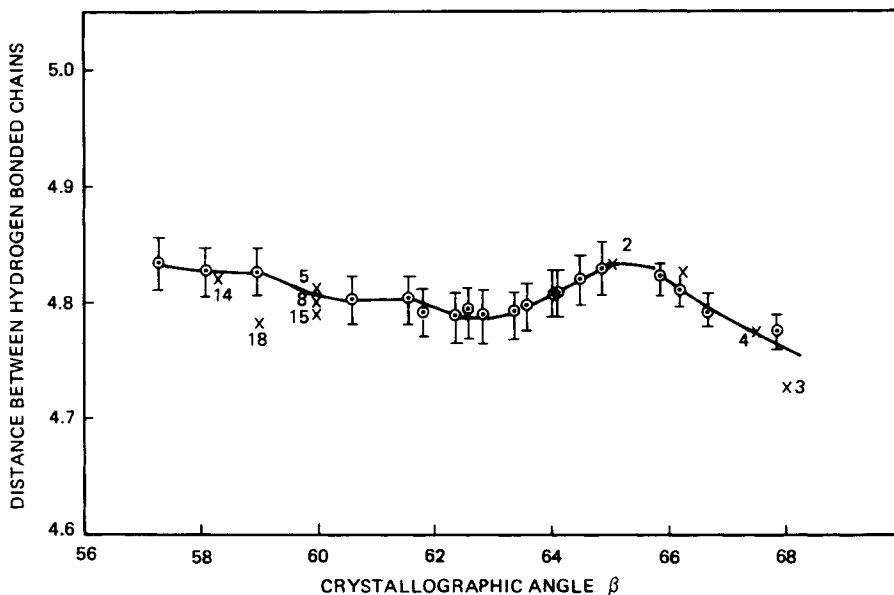
Fig. 8. Distance between hydrogen-bonded chains ($a/2$) vs. crystallographic angle β.

Furthermore, many other forces can come into play in determining the crystal structure. For example, stress along the polymer chain can influence the structure by making it more difficult to twist the amide groups as required in the γ crystal structure. By far the most important additional force is the interaction of a crystal with its neighboring crystals or amorphous regions. The extent of these interactions will be dependent upon (1) the molecular chain length, (2) the fold period, and (3) the size of the crystal and other variations in molecular arrangements. These cannot be exactly evaluated, but may combine to allow a nearly continuous range of crystal structure parameters in a manner analogous to the variation in structure parameters with composition in a multicomponent alloy.

Since we cannot exactly evaluate these interactions, we will make the assumption that (1) they vary inversely with crystal size, and (2) their principal influence is to control the separation of the hydrogen-bonded sheets. Since Figure 9 clearly shows that the distance between hydrogen-bonded sheets is by far the most important variable in changing the unit cell volume, we shall consider this variable to be controlled by the interaction of the crystal with its neighbors and describe the changes in structure parameter in terms of a balance of forces with this distance as an independent variable.

When nylon 6 first crystallizes under the conditions which prevail in modern high-speed spinning, it does so in the form of very small, very imperfect crystals. These crystals are pseudohexagonal since they generally have only a single or, at best, a partially resolved equatorial reflection. This work shows that such crystals can develop into either α crystals or γ crystals depending upon whether they have antiparallel or parallel hydrogen bonding. How these crystals develop during subsequent processing is still a subject of considerable concern since it is highly desirable to ascertain how much is predetermined by initial solidification and how much can be influenced by subsequent processing steps.

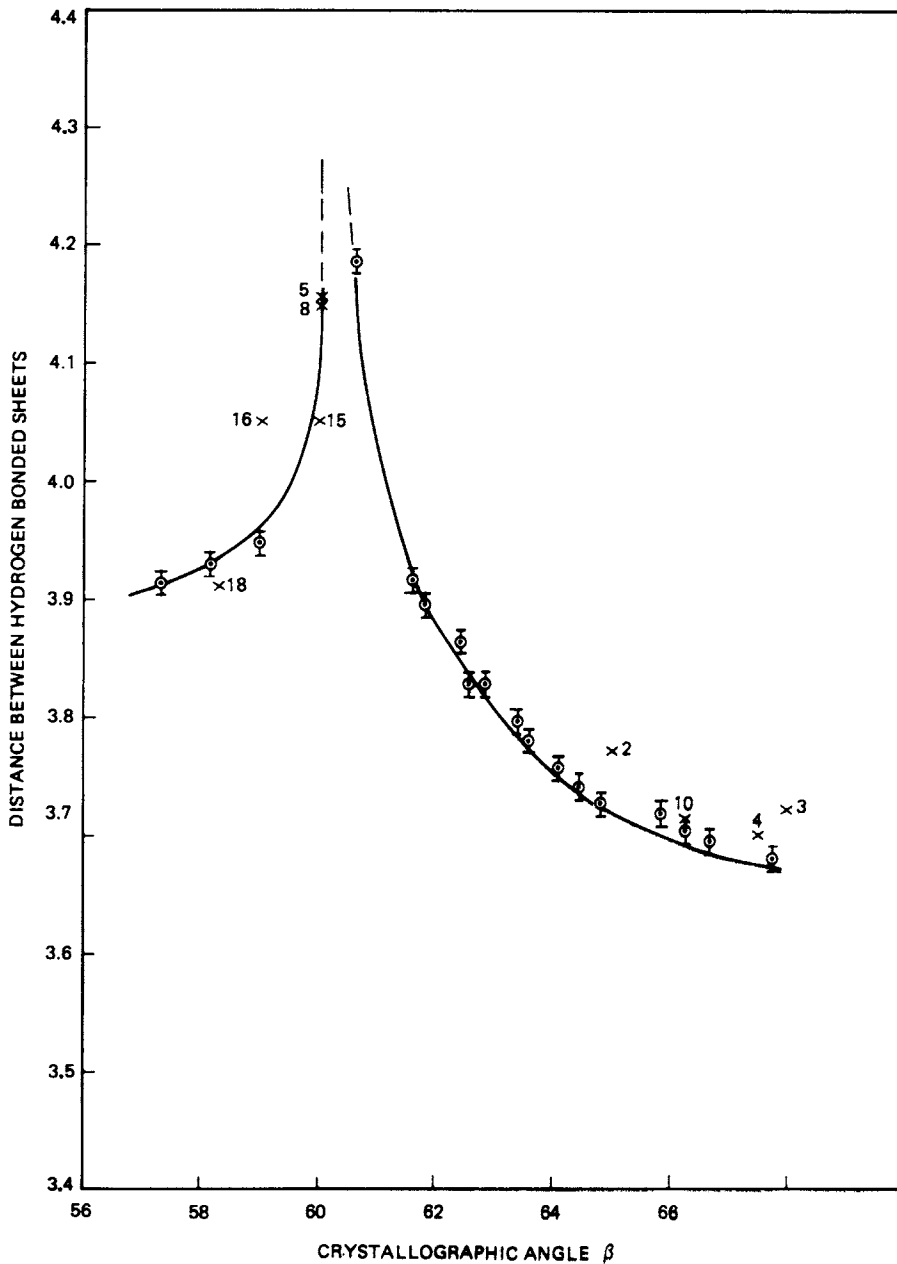It is known from infrared spectroscopy[22] that all possible hydrogen bonds are

Fig. 9. Distance between hydrogen-bonded sheets ($c \sin \beta/2$) vs. crystallographic angle β.

formed even in a polyamide melt. Consequently, when nylon 6 is quenched rapidly from the melt, it is reasonable to assume that any small crystals initially formed might be bound by chains having hydrogen bonds formed in the other two principal directions. Thus, the initial, very small crystals would have a spacing between sheets of hydrogen-bonded chains very nearly equal to the distance between hydrogen bond chains, and the crystal would have a pseudo-hexagonal symmetry (i.e., $\beta \sim 60°$).

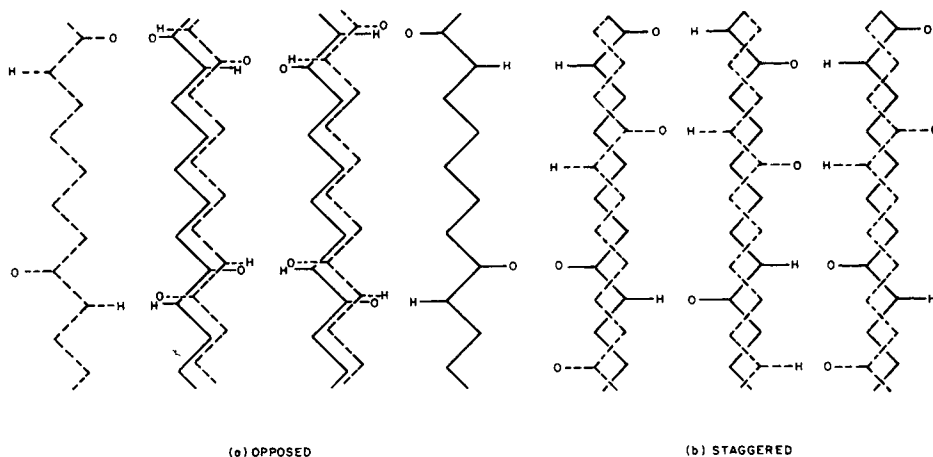(a) OPPOSED   (b) STAGGERED

Fig. 10. Stacking of hydrogen-bonded sheets with amide groups (a) opposed and (b) staggered.

Let us select such a small crystal and postulate what might happen to the balances of forces as the crystal grows larger and the distance between the sheets of hydrogen-bonded chains decreases. First of all, let us assume that the hydrogen bonds in our crystal are between antiparallel chains. In order to form the strongest hydrogen bonds between antiparallel chains, the interchain distance would theoretically be 4.77 Å and the H-C=C bonds would be linear. In order to form the minimum energy packing, the methylene chain would require a 4.79 Å interchain distance and the plane of the methylene groups would make an angle of 12° with the line joining their centers as in monoclinic polyethylene. To completely stretch out the molecule (i.e., all bonds in their minimum energy trans conformation) and at the same time to maintain the hydrogen bonds linear would require the methylene groups in adjacent chains to be coplanar which results in a higher packing energy.

If only a single hydrogen-bonded sheet is considered, then clearly the best compromise is to twist the amide groups (since the energy minimum about the transconformation is rather flat) and permit the interchain distance to remain only slightly greater than that which minimizes the hydrogen bond energy (Fig. 8). Twisting the amide group has the effect of shortening the fiber repeat distance. Such a shortening is observed in Figure 7 where the fiber repeat distance is less than the value of 17.42 calculated from the bond angles and bond lengths generally accepted.[4] Such a twisting of the amide group also has the effect of rotating the plane of the methylene chain in a manner that more clearly approximate the arrangements in paraffin or the monoclinic polyethylene structure. However, the methylene chain on either side of the amide group is displaced on opposite sides of the plane defined by the hydrogen bonds, hence the hydrogen-bonded sheet is in effect a corrugated sheet. We see from Figure 8 that the distance between hydrogen bond chains soon becomes quite close to the corresponding distance in polyethylene (i.e., 4.79 Å).

Now, as the crystal grows larger, this balance changes, the effect of adjacent regions decreases, and the sheets of hydrogen-bonded chains come closer together. The influence of the van der Waals forces between sheets increases, tending to remove the twist, iron out the corrugations, and increase the distance

between hydrogen-bonded chains. The accompanying increase in fiber repeat distance and in interchain distance is observed in Figures 7 and 8. The hydrogen bond can be weakened in two ways. One, it can be weakened by increasing the distance which also increases the interchain distance, or it can weaken by rotation out of the plane which would permit the interchain distance to decrease. We believe that the maximum in the interchain distance, although it is small and close to the limit of experimental error, is nevertheless real and marks a significant change in the packing since it also corresponds to the marked decrease in the intensity of the 020 reflection.

The change that occurs in the vicinity of $\beta = 64\text{--}65°$ involves more than just a straightening of the chains and an apparent increased chain separation. The rapid decrease in the intensity of the 020 reflection in this region indicates a significant change in the way in which the sheets are packing. When the distance between sheets is large, the dipole–dipole interactions dominate the arrangement. Such forces can minimize their energy when the center of positive charge in one sheet is aligned directly over the center of negative charge in the other. Thus, dipole–dipole interactions can minimize their energy when the amide groups in adjacent sheets are exactly opposed. However, this is a very unfavorable arrangement for packing the methylene groups when the sheets come closer together. Thus, as the distance between hydrogen-bonded sheets decreases, there comes a point where the total energy can be minimized by shifting the dipole–dipole interactions from an exactly opposed Figure 10a to a staggered arrangement Figure 10b (the α crystal arrangement) in order to accommodate a better packing of the methylene groups. This staggered arrangement of amide groups results in the decrease in intensity of the 020 reflection.

The final change that occurs as β increases beyond 65° is a continued straightening of the chain and weakening of the hydrogen bond by shifting it out of the plane of the two amide groups which it connects. In the α crystal, it is estimated that this shift is approximately 7°. This final change is caused by the increased dominance of the van der Waals forces between sheets as the distances are decreased over the hydrogen bonds which are weakened by twisting out of the plane.

In the γ crystal, the balance of forces is primarily between the van der Waals forces and the twisting of the amide groups out of the plane. The hydrogen bonds always remain in their minimum energy conformation, and increased methylene packing results in a shortening of the chain by increasing the twist rather than the lengthening as in the α crystal. Along this line, we might note that in nylons in which the number of methylene groups between the amide groups is greater than six, the dominance of the van der Waals forces over the hydrogen bonds is such that the α form seldom exists. The form usually observed is the γ form where the van der Waals forces compete with twisting and hydrogen bonds retaining full strength exist. The opposite is true for the nylons with shorter methylene chains. Here, the α form persists since the van der Waals attraction of the methylene groups is not sufficient to distort the hydrogen bonds. Only in nylon 6 is the ratio of methylene to hydrogen bonds such that the α and γ forms have nearly the same total energy so that they can exist under conditions near equilibrium.

It is recognized that although we think that we now have a much better understanding of the crystal structures of nylon 6 and the nature of some of the

structural changes which occur, we are still a long way from a complete understanding of this very interesting and unique material. We have said nothing about its melting behavior or the degree of crystallinity or how the various morphologic changes correlate with the above. Such discussion must await further publication. We hope that what we have said here will aid in clearing up some of the confusion that has existed in the literature regarding crystal structure.

References

1. P. H. Lindenmeyer, *Polym. J.* **3**, 507 (1972).
2. R. Brill, *Z. Phys. Chem.*, **B-53**, 61 (1943).
3. L. G. Wallner, *Monatsh. Chem.*, **79**, 279 (1948).
4. D. R. Holmes, C. W. Bunn, and D. J. Smith, *J. Polym. Sci.*, **17**, 159 (1955).
5. A. Ziabicki, *Kolloid-Z.*, **167**, 132 (1959).
6. Y. Kinoshita, *Makromol. Chem.*, **33**, 1 (1959).
7. A. Reichle and A. Prietzch, *Angew. Chem.*, **74**, 562 (1962).
8. D. C. Vogelsong, *J. Polym. Sci.*, **A-1**, 1055 (1963).
9. G. Roldan and H. S. Kaufman, *J. Polym. Sci.* **B-1**, 603 (1963).
10. C. Ruscher and H. J. Schröder, *Faserforsch. Text. Tech.*, **11**, 165 (1960).
11. S. Ueda and T. Kimura, *Chem. High Polym., Tokyo*, **15**, (1958).
12. M. Tsuruda, H. Arimoto, and M. Ishibashi, *Chem. High Polym., Tokyo*, **15**, 619 (1959).
13. Y. Kawaguchi, O. Yoshizaki, and E. Nagai, *Chem. High Polym., Tokyo*, **20**, 337 (1963).
14. H. Arimoto, *Chem. High Polym., Tokyo*, **19**, 204 (1962).
15. T. Ota, O. Yoskizaki, and E. Nagai, *J. Polym. Sci.*, **A-2**, 4865 (1964).
16. H. Arimoto, *J. Polym. Sci.* **A-2**, 2283 (1964); H. Arimoto, M. Ishibashi, M. Hirai, and Y. Chatani, *J. Polym. Sci.*, **A-3**, 317 (1965).
17. H. K. Illers, H. Haberkorn, and P. Simak, *Makromol. Chem.*, **158**, 285 (1972).
18. E. M. Bradbury and A. Elliott, *Polymer*, **4**, 47 (1963); E. M. Bradbury, L. Brower, A. Elliott, and D. A. D. Parry, *Polymer*, **6**, 465 (1965).
19. K. Kaji and I. Sakurada, *J. Polym. Sci. A-2*, **12**, 1491 (1974).
20. P. H. Geil, private communication.
21. C. W. Bunn and E. V. Garner, *Proc. Roy. Soc. A*, **189**, 39 (1947).
22. A. Miyake, *J. Polym. Sci.*, **44**, 223 (1960).
23. M. Kyotani and S. Mitsuhaski, *Kobunski Kagaku*, **28**, 211 (1971).
24. M. Kyotani and S. Mitsuhashi, *J. Polym. Sci. A-2*, **10**, 1497 (1972).