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Nylon 65 Has a Unique Structure with Two Directions of Hydrogen Bonds

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ABSTRACT: A new type of polyamide structure has been found for nylon 65 and it is reported here. The structure and morphology of nylon 65 lamellar crystals have been investigated using transmission electron microscopy, selected-area electron diffraction, and X-ray diffraction. Additional data have been obtained from uniaxially oriented fibers. The deduced unit cell parameters (a = 4.60 Å, b = 30.95 Å, c = 8.62 Å, $\alpha = \beta = 90°$, and $\gamma = 114°$) and the space group symmetry indicate a different structure for nylon 65 than the conventional α and γ-forms of nylons. Each molecule is linked to its four neighbors by a network of hydrogen bonds made by amide groups in two different orientations. Structural modeling has been carried out using the linked-atom least-squares (LALS) methodology. The results obtained point to a particular conformation for the glutaryl units which play a decisive role in establishing such a unique structure. The temperature-induced structural changes have also been studied. A pseudohexagonal packing is found at 190 °C. Modifications are believed to occur without changes in the hydrogen bond system, in a way that is similar to that found in nylon 66. Fiber diffraction patterns of nylon 66 at 220 °C are also presented in order to confirm such conclusion.

Introduction

Nylons can be synthesized by condensation of amino acids (nylons *n*) or diamines and dibasic acids (nylons *m,n*). However, only two basic structures have been reported at low temperature, in spite of the differences in the disposition of amide groups (i.e., nylon 6[1] and nylon 66[2]) and in the methylene content of the repeat units (i.e., nylon 4 and nylon 12). The first one is the so-called α-form, in which the molecules are packed in either a monoclinic unit cell (nylon 6) or a triclinic unit cell (nylon 66). Basically, the structure consists of hydrogen-bonded sheets with fully extended chains. In nylon 66, the sheets are displaced along the unique hydrogen bond direction and also staggered in the chain axis direction. The second structure, the γ-form,[3] corresponds to a pseudohexagonal form and it is observed when the amide groups are tilted ca. 60° off the sheet plane. As a consequence, a characteristic shortening in the chain axis repeat is noticed when compared with the values of the extended conformation. However, hydrogen bonds remain in a single direction. The γ-structure is considered to be a less ordered phase than the α-form. It is characteristic of nylons with a high methylene content in their chemical repeat units (nylons 11 or 12) or nylons for which linear hydrogen bonds between adjacent chains cannot be established when an extended conformation is considered (even–odd, odd–even, and odd–odd nylons). In many even or even–even nylons, the α-form can be converted to the γ-form (or vice versa) or both can coexist in various proportions. Transformations can be engineered by solvent or swelling agents,[4] rates of fiber spinning,[5] temperature,[6] or a combination of all three.

Structural changes in the lattice parameters during heating have recently been studied for different nylons.[7–11] In general, the two basic equatorial spacings characteristic of the α-form (ca. 4.40 and 3.80 Å) merge into a single one indicative of a pseudohexagonal modification and presumably related to a γ-form. Different explanations for this phenomenon, often called the Brill transition, have been given: (a) anisotropy of the thermal expansion,[1] (b) the development of a three-dimensional network of hydrogen bonds between the chains, induced by rotational molecular jumps of 60° at elevated temperatures,[7,12,13] and (c) a transition involving a greater mobility of the methylene groups, while hydrogen bonds remain arranged in a single direction.[14,15] Structural investigations at elevated temperature and NMR measurements carried out on nylon 66 support the last possibility instead of a three-dimensional network of hydrogen bonds. However, a complete understanding of the Brill transition does not yet exist, since different problems remain. For example, the transition temperature to a pseudohexagonal phase is not constant for a specific polyamide since it clearly depends on the thermal history of the sample.[10] A pseudohexagonal phase can also be observed for some even nylons in quenched samples, and it has been interpreted as a frozen state arising from the high-temperature modification.[8] However, such a state is not stable since it reverts quickly to the α-modification when crystals are heated above their T_g.

In recent years, our laboratory has carried out a systematic effort aimed at investigating polyamides with structures different from conventional ones. Thus new structures with three,[16–20] two,[21,22] or one[23–25] hydrogen bond directions have been found in polyamides where an isolated methylene group is placed between two amide units. The structure of these nylons strongly depends on the conformational preferences of glycine ($-NHCH_2CO-$), methylenediamine ($-NHCH_2NH-$), and malonyl ($-COCH_2CO-$) residues. Moreover, different crystallographic studies on model compounds support these new structures[26–30] and also reveal that polymethylene segments may be in a folded conformation which induces a rotation between adjacent amide planes (glutaryl,[31] succinyl,[29] and 6-aminocaproyl[30] residues) or just a shortening in the chain axis repeat (adipoyl[29] residues). The conformational preferences "in vacuo" for some model molecules (glutaramide[31] and succinamide[32] derivatives) have also been studied using *ab initio* quantum mechanical calculations. The results,

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in agreement with the solid-state experiments, indicate that an *all-trans* conformation for polymethylene segments is not always energetically favored. In this sense, we decided to study the crystalline structure of nylon 65 since it is composed of glutaramide units and a new structure might be expected. It is also worth noting the similarity between the chemical repeat units of nylon 65 and nylon 66.

Experimental Section

Synthesis and Characterization. Nylon 65 was synthesized by interfacial polycondensation of 1,6-diaminohexane and glutaryl dichloride. Organic solvent (toluene, carbon tetrachloride, or methylene dichloride) and proton acceptor (NaOH, Na_2CO_3, or diamine excess) were optimized in order to increase the molecular weight of the polymer. Approximately 30 mmol of the dichloride dissolved in 150 mL of the organic solvent was added dropwise to a stirred solution of 30 mmol of 1,6-diaminohexane and 120 mequiv of proton acceptor in 150 mL of water. After addition was complete, stirring was continued for 30 min. The polymer which precipitated was isolated by filtration and washed successively with water, ethanol and ethyl ether before drying in a vacuum desiccator at 60 °C.

The intrinsic viscosity of the polymer was determined by measurements with a Cannon-Ubbelohde microviscometer in dichloroacetic acid solutions at 25 ± 0.1 °C. The density of the powder sample was measured at 25 °C by the flotation method in mixtures of ethanol and carbon tetrachloride. The chemical constitution of the polymer was ascertained by infrared and NMR spectroscopy and elemental analysis. The infrared absorption spectrum was recorded from potassium bromide pellets with a Perkin-Elmer 783 spectrophotometer in the 4000–500 cm^{-1} range. NMR spectra were registered from polymer solutions in deuterated trifluoroacetic acid using a Bruker AMX-300 spectrometer operating at 300.1 MHz for ^1H NMR and at 75.5 MHz for ^{13}C NMR.

Thermal behavior was investigated with a Perkin-Elmer DSC-4 equipped with a TADS data station at a heating rate of 20 °C/min in a nitrogen atmosphere. The instrument was calibrated for temperature (T) and heat of fusion (ΔH) using an indium standard ($T_m = 429.5$ K, $\Delta H_m = 3.267$ kJ/mol). The expected accuracy is 1–2 K for T and ±3% for ΔH. A baseline was always run and subtracted to avoid the effects of the changing environment.

Structural Methods. Crystallization experiments were carried out isothermally from dilute solutions (0.05–0.1% (w/v)) in polar polyfunctional alcohols such as 1,4-butanediol and glycerin. The polymer was dissolved in the 160–190 °C range, and the solutions were transferred to constant-temperature baths in the 70–140 °C interval for 2–5 h. The crystals were recovered by centrifugation and were repeatedly washed with 1-butanol.

For electron microscopy, the crystals were deposited on carbon-coated grids which were then shadowed with Pt–carbon at an angle of 15°. A Philips EM-301 electron microscope operating at either 80 or 100 kV for bright field and electron diffraction modes, respectively, was used throughout this work. Electron diffraction diagrams were recorded by the selected-area method on Kodak Tri-X films. The patterns were internally calibrated with gold ($d_{111} = 2.35$ Å).

X-ray diagrams were recorded under vacuum at room temperature, and calcite ($d_B = 3.035$ Å) was used for calibration. A modified Statton camera (W. R. Warhus, Wilmington, DE) with Ni-filtered CuKα radiation of wavelength 1.542 Å was used for these experiments. Patterns were recorded from polymer powders, fibers, or mats of single crystals which were prepared by slow filtration of a crystal suspension on a glass filter. Fiber patterns were also registered as a function of temperature by using a temperature-controlled chamber provided by the manufacturer.

Structural modeling was achieved with the CERIUS program and the LALS methodology. Calculations were run on a HP-340 computer.

Table 1. Synthesis and Viscosimetric Data of Nylon 65

sample	organic solvent	base	yield (%)	[η] (dL/g)
1	CH_2Cl_2	HMD[a]	45	0.54
2	CCl_4	HMD[a]	60	0.65
3	$C_6H_5CH_3$	HMD[a]	53	0.66
4	CH_2Cl_2	NaOH	43	0.55
5	CCl_4	NaOH	59	0.61
6	$C_6H_5CH_3$	NaOH	43	0.75
7	CH_2Cl_2	Na_2CO_3	31	0.57
8	CCl_4	Na_2CO_3	65	0.58
9	$C_6H_5CH_3$	Na_2CO_3	68	0.68

[a] HMD: 1,6-hexamethylenediamine.

Results and Discussion

Synthesis and Characterization. The results obtained in the synthesis of nylon 65 are reported in Table 1. Sample 6, obtained using toluene as organic solvent and sodium hydroxide as proton acceptor, gave the highest molecular weight and was selected for posterior studies. Anal.: Calcd for $C_{11}H_{20}N_2O_2$: C, 62.26; H, 9.43; N, 13.20. Found: C, 62.12; H, 9.57; N, 13.10. The measured intrinsic viscosity (0.75 dL/g) corresponds to a molecular weight of about 16600 (DP 79) if the viscosimetric equation of nylon 66[33] is applied for calculation.

The infrared spectrum of nylon 65 shows characteristic amide and methylene absorption bands: 3312 (amide A), 3082 (amide B), 2933 and 2859 (C–H), 1638 (amide I), 1546 cm^{-1} (amide II). Furthermore the region between 800 and 500 cm^{-1} contains two peaks specific for the known nylon polymorphism,[34] the amide V and VI modes at 688 and 590 cm^{-1}, respectively, seen for α crystals. The former peak is not seen for γ crystals, while the latter peak shifts to ca. 630 cm^{-1}. The chemical shifts of the intense signals observed in the ^1H and ^{13}C NMR spectra are in full agreement with the anticipated chemical composition: ^1H-NMR (300.1 MHz, TFA-*d*): δ 1.49 (4H, m, $NHCH_2CH_2C\mathit{H_2}$), 1.73 (4H, m, $NHCH_2C\mathit{H_2}$), 2.20 (2H, m, $COCH_2C\mathit{H_2}$), 2.78 (4H, t, $COCH_2$), 3.53 (4H, t, $NHC\mathit{H_2}$). ^{13}C-NMR (75.5 MHz, TFA-*d*): δ 23.11 ($COCH_2CH_2$), 27.86 ($NHCH_2CH_2CH_2$), 29.74 ($NHCH_2CH_2$), 34.12 ($COCH_2$), 43.78 ($NHCH_2$), 179.48 (CONH). Furthermore, no sign of branching or irregularities are detected in the NMR spectra.

Differential Scanning Calorimetry. Figure 1 shows a sequence of four scans performed with a solution-crystallized sample (1,4-butanediol at 80 °C). In the first run, the sample was heated (20 °C/min) through fusion, and left in the melt for 2–3 min, and was cooled (20 °C/min) to observe crystallization from the melt (run 2). A second heating (run 3) and a second cooling (run 4) were done to check the reproducibility of the transitions and get data for the melt-crystallized samples. Double melting peaks are seen for either solution-crystallized or melt-crystallized samples, a common observation in thermal studies of nylons.[35] Scans, registered at different heating rates (Figure 2) from the solution-crystallized sample, are in agreement with the usual explanation for the double endotherm. Thus, the effect is the result of a recrystallization process on heating affecting the population of smaller crystals with a lower melting point. When the heating rate is increased, the recrystallization is hindered and so the higher temperature peak, associated with the more perfect crystals, becomes less prominent. However, the total heat of fusion is independent of heating rate, in agreement with results reported on nylon 66.[36] Table 2 summarizes the melting points measured at the different heating rates which are compatible with the

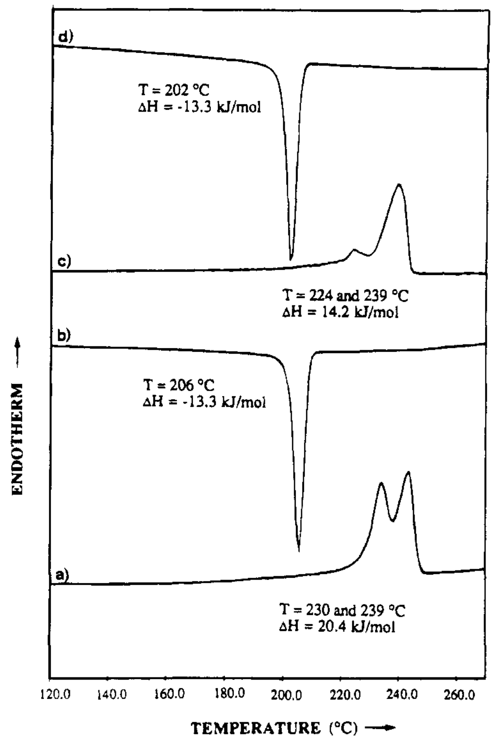

Figure 1. Sequence of four DSC traces for solution-crystallized nylon 65: run a, heating of the original sample; run b, cooling; run c, reheating; run d, recooling after the second heating. In all cases, the rate was 20 °C/min.

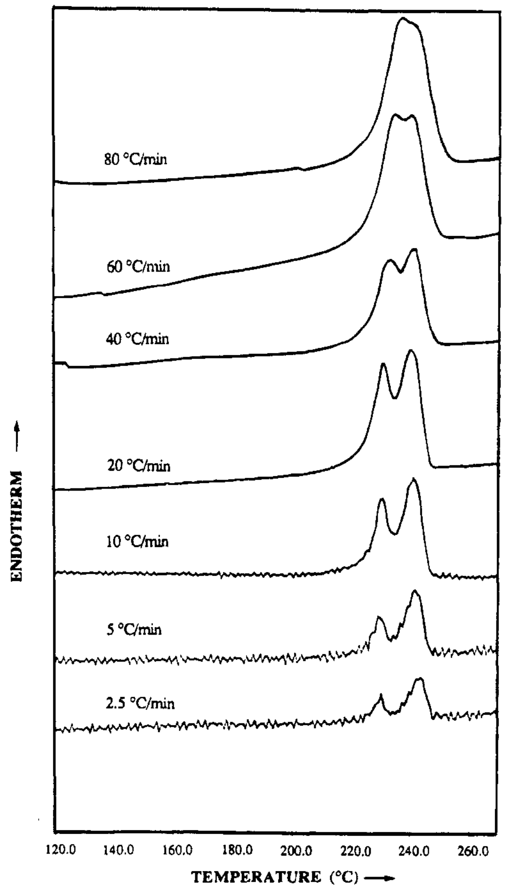

Figure 2. Thermograms obtained with scanning rates ranging from 2.5 to 80 °C/min. Note that the proportion of the lowest melting peak increases at the highest heating rates.

Table 2. Melting Peaks for Nylon 65 Obtained at Different Scanning Rates

heating rate (°C/min)	melting point (°C)	
2.5	230	243
5.0	229	241
10.0	230	241
20.0	230	239
40.0	233	240
60.0	234	240
80.0	236[a]	

[a] Single peak with shoulder.

Table 3. Measured and Calculated X-ray Diffraction Spacings d_B (Å) for Different Nylon 65 Samples: Powder Recovered from Synthesis, Mat of Sedimented Crystals Obtained from 1,4-Butanediol Solution, and Annealed Fiber

index[a]	calcd	powder[b]	crystal mat[b]	annealed fiber[b]
lamellar thickness	60		60[c] s, M	
020	14.1	13.6 vs	13.9 vs, M	14.1 vs, off-M
040	7.1	6.8 s	7.0 s, M	7.05 s, off-M
060	4.71	4.7 w	4.70 w, M	4.70 m off-M
002	4.31	4.32 vs	4.32 vs, E	4.32 vs, E
$1\bar{2}1$	4.03	3.96 m	4.0 w	
101	3.78	3.71 s	3.75 vs, off-E	3.75 s, E
103	2.37			2.37 w, E
$1,\overline{12},1$	2.44			2.35 m, M
$1,\overline{13},1$	2.28			

[a] On the basis of a monoclinic cell: $a = 4.60$ Å, $b = 30.95$ Å, $c = 8.62$ Å, $\alpha = \beta = 90°$, $\gamma = 114°$. [b] Abbreviations denote intensities or orientation: vs, very strong; s, strong; m, medium; w, weak. M, meridional; E, equatorial; off-M, off-meridional; off-E, off-equatorial. [c] Observed only in low angle X-ray patterns.

literature data reported[37] for nylon 65 (241 °C) and also compare well with the data reported[37] for the isomer compound: nylon 56 (223–225 and 251–258 °C). The melting temperature is lower than expected when compared with similar even–even nylons (i.e., 265 °C for nylon 66), suggesting a different structure or differences in chain mobility. No endothermic peak was detected near the Brill transition temperature (ca. 190 °C, as will be discussed below), in disagreement with some nylon 66 measurements which consider the Brill transition as a first-order transition.[38]

The DSC traces shown in Figure 1 indicate thermal stability, since the transition observed on heating is reproducible. Comparison between Figures 1a and 1c indicates a greater reorganization during heating for the melt-crystallized samples or a preferential crystallization from the melt in the high-temperature state. In order to evaluate the crystallinity of nylon 65 we estimate their equilibrium heat of fusion (ΔH_f^{eq}) as a first approximation. An ΔH_f^{eq} of 40 kJ/mol was calculated using the reported[39] group contributions of the amide (2.0 kJ/mol) and the methylene (4.0 kJ/mol) groups. Thus crystallinities around 51 and 41% were evaluated for the solution and melt-crystallized samples, respectively.

X-ray Diffraction Data. Diffraction spacings generally attributed to an α-form (4.32 and 3.75 Å) are found (Table 3) in powder samples of nylon 65 obtained directly from the polymerization medium after purification. This is a striking feature since a γ-form should be expected as indicated by Kinoshita[3] for even–odd nylons. Structures based on an *all-trans* conformation would either have only 50% of hydrogen bonds with optimum geometry (Figure 3a) or hydrogen bond distances and angles far from the optimum ($d(\mathrm{H}\cdots\mathrm{O})$ = 2.3–2.4 Å and ∠NHO = 130–140°) (Figure 3b). Since both possibilities appear to be energetically unfavored

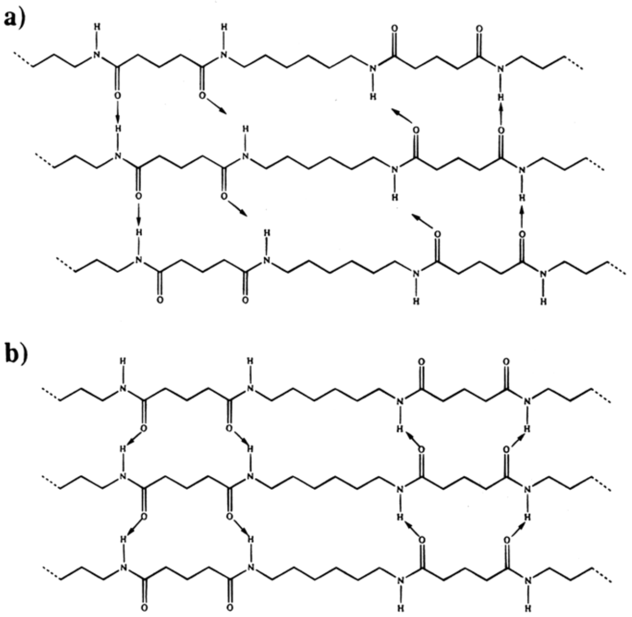

Figure 3. Schematic representation of two possible arrangements of hydrogen bonds in an extended conformation. (a) Only 50% of the NH and CO groups face correctly in order to establish hydrogen bonds. (b) All hydrogen bonds are established between CO and NH groups which are shifted one bond along the chain direction. Such organization is compatible with a conventional γ-form.

and in addition infrared spectroscopy data indicate a strong and unique kind of hydrogen bond, we decided to study in more detail the crystalline structure of nylon 65.

Figure 4a shows the diffraction pattern of a fiber obtained from the melt. In this case, a single equatorial spacing at 4.25 Å is characteristic, which suggests a pseudohexagonal packing. Meridional reflections related to the chain axis repeat (13.7, 7.0, and 4.7 Å) are also observed. Both features suggest a poorly ordered γ-form structure. The pattern changes drastically when the sample is annealed at 100 °C (Figure 4b). Then the $0k0$ reflections appear at about 24° off the meridian, suggesting a triclinic or monoclinic (α or $\gamma \neq 90°$) unit cell. Moreover, the equatorial arc is now split into two reflections at the same spacings as in the powder samples. A clear and diffuse meridional arc at about 2.35 Å is also observed. Diffraction in this region is attributed to the zigzag nature of the methylene chain and should appear even when the samples are poorly oriented.

Wide- and low-angle X-ray diffraction patterns of sedimented mat crystals (obtained from 1-butanol solutions at 80 °C) are shown in Figure 5. The diagrams show poor orientation but some features may be inferred:

(a) The more intense reflections correspond to the chain packing spacings (4.32 and 3.75 Å) observed in the fiber pattern. While the former spacing has an equatorial orientation, the second one appears practically disoriented or slightly off the equator. These observations may indicate that the molecular chains are tilted to the crystal surface and correspond to a situation which should be expected from a triclinic or a monoclinic (α or $\gamma \neq 90°$) structure that collapses on sedimentation.

(b) An approximate meridional orientation is observed for the $0k0$ spacings.

(c) An arched reflection is observed on the meridian (along the mat normal) in the low-angle diffraction region. This spacing arises from the stacking of lamellae 60 Å thick, as explained in the next section.

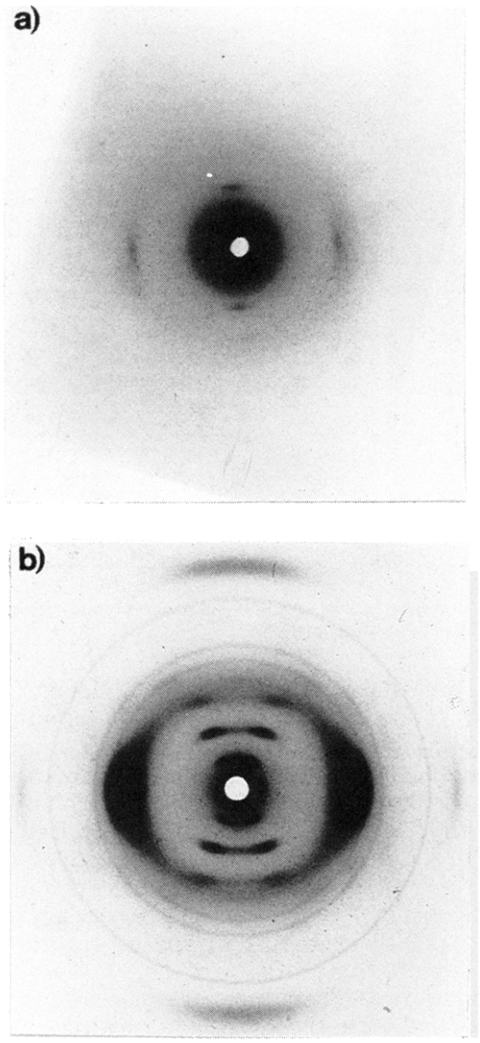

Figure 4. X-ray diffraction patterns of oriented fibers of nylon 65. (a) Fibers obtained directly from the melt show meridional reflections and only one equatorial arc at 4.25 Å. (b) When the fibers are annealed at 100 °C for 1 h, the equatorial reflection is split into two reflections at 4.31 and 3.75 Å. An off-meridional orientation is observed for the $0k0$ reflections, which correspond to the main chain direction. The weak rings probably correspond to a low molecular weight impurity.

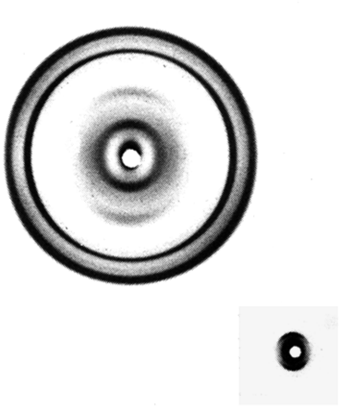

Figure 5. Wide-angle X-ray diffraction pattern from a mat of sedimented crystals of nylon 65. The $0k0$ reflections have a meridional orientation, whereas the 002 reflection appears on the equator. A meridional reflection (60 Å) related to the lamellar thickness is present in the low-angle pattern (inset).

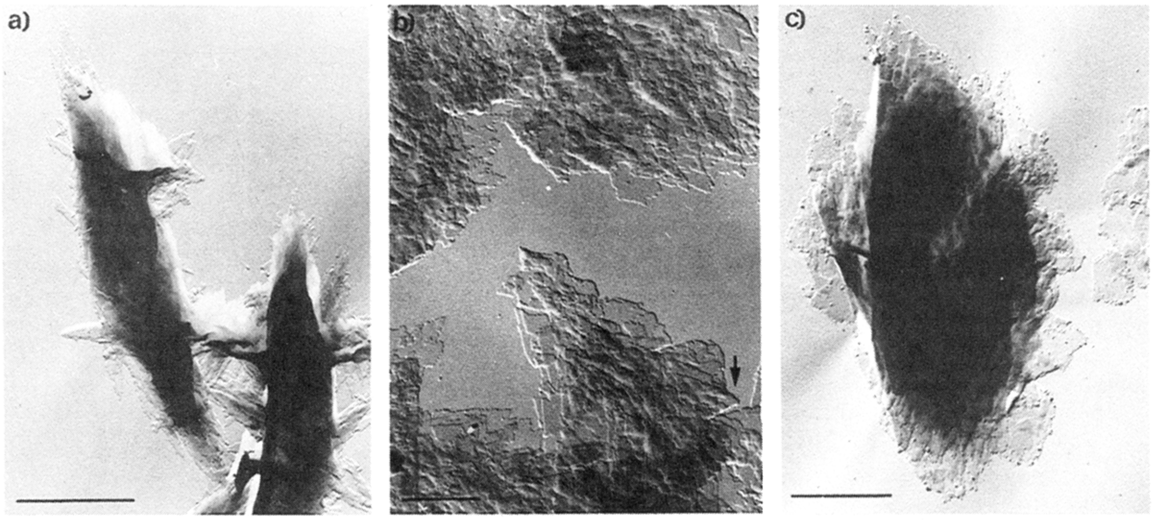

Figure 6. Transmission electron micrographs of nylon 65 crystals, illustrating the influence of crystallization conditions on morphology: (a) sheaves obtained from 1,4-butanediol at 80 °C. (b) lamellae with irregular edges prepared from glycerin at 80 °C [note the characteristic serrated edges and the occasional fractures (see arrow)] (c) crystals prepared from glycerin at 140 °C. Upon preparation, the crystals probably form curved aggregates which collapse onto the film used for electron microscopy observation. Scale bar = 1 μm.

Electron Microscopy. Crystals suitable for electron microscopy were obtained by isothermal crystallization from dilute solutions in 1,4-butanediol or glycerin. Their morphology varies depending on the conditions used for the preparation of the samples. Thus long (ca. 5 μm) and thick sheaves with small lath-shaped protrusions were obtained from 1,4-butanediol at 80 °C (Figure 6a). Wider crystals were obtained when crystallization was conducted in glycerin solutions. Irregular lamellae, which frequently overgrow in one or two directions (Figure 6b), are characteristic of the 80 °C crystallization temperature. Their edges are generally irregular, in agreement with the absence of hydrogen-bonded sheets in this polymer, as discussed below. Fractures with fibrillar molecular links were detected in some cases. Fibrils are seen to bridge the two edges of the crack in an extended orientation parallel to one growth direction. They correspond to groups of molecules that have been pulled out during cleavage of the lamella. Crystallization at 140 °C renders larger lamellae with serrated edges. They often appear to be rolled and then flattened (Figure 6c). In all cases, the individual lamellae are about 60 Å thick as estimated from their shadows in the micrographs and in agreement with the low-angle X-ray diffraction measurements.

Electron diffraction patterns from either kind of crystals have the same features. However, the crystals prepared from glycerin at 140 °C give the best oriented pattern (Figure 7), since monocrystals of adequate dimensions can be selected for diffraction. The two prominent reflections are spaced at 4.31 and 3.74 Å and lie at an angle of 64° to each other. They compare well with the equatorial or quasiequatorial reflections observed in both fiber and mat patterns, indicating that molecular chains are folded as a consequence of their molecular weight and the reduced lamellar thickness. No evidence of a twinned structure has been detected in the electron diffraction patterns, in contrast to the results usually found in nylons. On the other hand, the pattern exhibits an *mm* symmetry until practically 1 Å resolution. The following conclusions may be inferred from these observations:

(a) A monoclinic unit cell is the only possibility compatible with the symmetry of the electron diffraction pattern and the nonmeridional $0k0$ reflections observed in the fiber diffraction pattern.

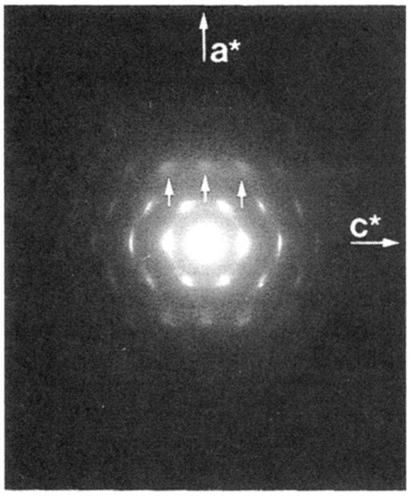

Figure 7. Selected-area diffraction pattern of nylon 65 crystals prepared from glycerin at 140 °C. Arrows indicate $h2l$ reflections.

(b) In Figure 7 it is apparent that the $00l$ reflections are sharp and clearly visible up to the 008 reflection. On the other hand, the $h0l$ reflections become diffuse as h increases. In fact, the reflections with $h \geq 3$ cannot be observed. Such observations probably indicate that the chains are inclined with respect to the lamellar surface in the a direction, which corresponds to $\gamma \neq 90°$. The presence in the electron diffraction pattern of some $h2l$ reflections gives also support to this view (Figure 7 and Table 4).

(c) Indexing of diffraction data leads unambiguously to the following unit cell parameters: $a = 4.60$ Å, $b = 30.95$ Å, $c = 8.62$ Å, $\alpha = \beta = 90°$ and $\gamma = 114°$. A shortening of about 0.4 Å/amide group with respect to an extended conformation may be calculated taking into account that the expected b parameter for two repeat units should be 32.5 Å.

(d) The systematic absences observed for the $h00$ and $00l$ reflections with h and l odd indicate a centered unit cell. Moreover the expected density (1.26 g/cm^3) is comparable with the experimental value (1.14 g/cm^3) if

Table 4. Measured and Calculated Electron Diffraction Spacings d_B (Å) for Nylon 65

index[a]	calcd	measd[b]
002	4.31	4.31 vs
101	3.78	3.74 s
103	2.37	2.36 s
004	2.16	2.17 s
200	2.10	2.08 w
202	1.89	1.88 w
105	1.60	1.62 m
204	1.50	1.52 vw
006	1.44	1.45 m
107	1.18	1.20 vw
008	1.08	1.09 vw
109	0.93	0.96 vw
$2\bar{2}0$	2.21	2.22 vw
$2\bar{2}2$	1.97	2.00 vw

[a] On the basis of a monoclinic cell: $a = 4.60$ Å, $b = 30.95$ Å, $c = 8.62$ Å, $\alpha = \beta = 90°$, $\gamma = 114°$. [b] Abbreviations denote intensities: vs. very strong; s, strong, m, medium; w, weak; vw, very weak.

we consider that the presence of amorphous material may decrease the density by about 10%, as is usually found in polyamides.

(e) A crystalline structure characterized by only one hydrogen bond direction does not seem to be compatible with the available data and the absence of molecular polarity, since hydrogen bonds must be established along the unique axis *c*. Both the short chain separation distance (4.31 Å) and the double value of the *c* parameter cannot be explained. On the contrary, the experimental data fit well when hydrogen bonds are established along both diagonals of the unit cell.

Structural Modeling. The results reported cannot be explained with the conventional α- or γ-structures. In particular the shortening of the chain repeat unit, the symmetry of the electron diffraction pattern and the energetically unfavorable hydrogen bond geometry are in clear disagreement with the α-form, whereas the chain packing spacings (4.32, 3.75 Å) and the nonmeridional 0*k*0 reflections are also incompatible with a γ-form.

The linked-atom least-squares (LALS) method[40] was used to build and refine a suitable model. The description of a generic residue of nylon 65 is given in Figure 8. Standard bond and angles for polyamides were used to build the repeating unit and were fixed throughout the whole modeling process. The torsional angles ω_i and ν_i were kept in the *trans* conformation as is usual in polyamides and so only the four torsional angles next to the amide groups (φ_i and ψ_i) and the positional parameters which fix the chain in the unit cell were allowed to vary in order to define the chain conformation and packing. The models were refined using as constraints the unit cell dimensions and the optimum hydrogen bond geometry. X-ray and electron diffraction data were only used to test and to improve the quality of the models.

The model which fits better the experimental results is based on the particular conformation of the glutaramide unit ($\psi_1 = \psi_2 \approx 150$ or $-150°$) recently proposed for nylon 1,5.[24] In fact, quantum mechanical calculations on glutaramide analogues[31] indicate that an *all-trans* conformation, which results in a parallel orientation of carbonyl groups, is energetically unfavored and consequently the C−O directions tend to rotate. An unfavorable parallel orientation between the carbonyl groups[24,31] would also appear if the glutaryl units had a γ-conformation ($\psi_1 = -\psi_2 \approx +120$ or $-120°$).

Table 5. Conformational Parameters and Hydrogen Bond Geometry for the Model of Nylon 65

molecular symmetry	2/*b*
space group	*B*112/*b*
torsional angles (deg)	
φ_1, φ'_2	+110.0
φ_2, φ'_1	−110.0
ψ_1, ψ_2	+150.0
ψ'_1, ψ'_2	−150.0
ω_i, ω'_i, ν_i, ν'_i	180.0
hydrogen bond geometry	
d(H···O) (Å)	1.79
d(H···O) (Å)	2.79
∠NHO (deg)	171

On the other hand, the diamine moiety adopts an $s^-t_4s^+$ conformation (Table 5) similar to that found in the γ-form of nylons. The molecular chains have a center of symmetry in the middle of the diamine unit and a binary axis perpendicular to the chain direction through the central carbon of the glutaramide unit. This molecular symmetry (2/*b*) has the consequence that equivalent torsional angles in consecutive repeat units are equal, but with opposite signs. Furthermore, the expected adirectional configuration of the polymer chain is preserved.

The space group *B*112/*b* is compatible with molecular symmetry, the systematic absences on X-ray patterns (i.e., reflections 0*k*0 for k = odd), and also the *mm* symmetry of the *h*0*l* electron diffraction pattern. The model appears to be stereochemically suitable and shows no significant contacts. Two hydrogen bond directions are generated because of the ca. 52° rotation induced by every glutaryl residue. This rotation is recuperative since consecutive glutaryl units have opposite torsional angles. A shift between the hydrogen-bonded chains (due to $\gamma \neq 90°$) allows all hydrogen bonds to be established with lengths and angles within the standard range (Table 5).

Molecular drawings of lateral and equatorial projections of the molecular arrangement are shown in Figure 9. The model has not been refined against diffraction data because of the reduced number of diffraction intensities available. Electron and X-ray diffraction patterns were simulated with the CERIUS program (produced by Molecular Simulation, Inc.) (Figure 10) and shows a relatively good agreement with the experimental results. The principal discrepancy arises from the low experimental intensity of the 060 reflection. However, we have to consider that we have kept all the ethylene torsional angles (ν_i) fixed at 180°. Although this is the usual value postulated for polymethylene segments, some experimental data[30] point out that they may indeed deviate slightly from 180°. On the other hand, the refining of all ν_i torsional angles does not make sense, taking into account the reduced number of available data and the excessive number of degrees of freedom that will be generated.

The model presented here for nylon 65 is similar to that suggested by us for n,3 nylons, since both have two hydrogen bond directions and similar unit cells.[22,27] However, there is an essential difference: in the malonamide derivatives (nylons *n*,3), the two carbonyl groups are mutually oriented at about 120°. The central molecule in the unit cell (similar to that shown in Figure 9c) has the two malonamide carbonyl groups oriented toward the wide side of the unit cell, whereas in nylon 65 the two glutaramide carbonyl groups are oriented toward the short side of the unit cell, forming an angle of about 50° only.

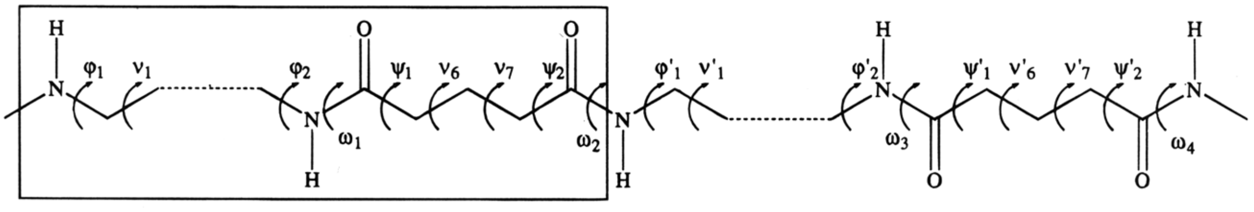

Figure 8. Representation of a nylon 65 backbone showing definition of torsional angles.

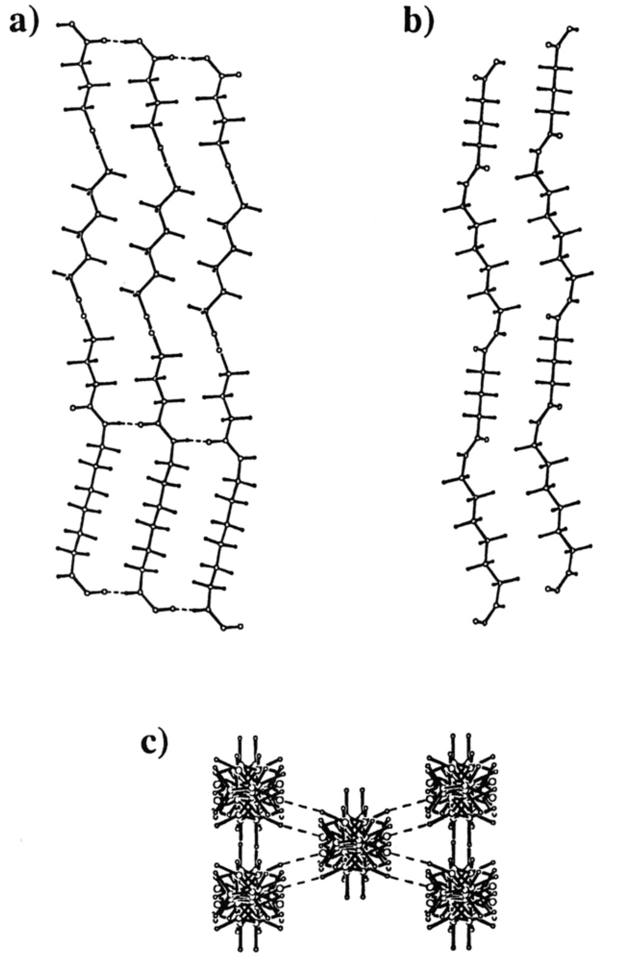

Figure 9. (a) Side view of three chains which are hydrogen bonded along the [$\bar{1}$01] direction. (b) *ab* projection of the unit cell, in this case the glide symmetry is manifested (c) Equatorial projection of the unit cell. Note that hydrogen bonds (indicated by dashed lines) are established along both diagonals of the unit cell.

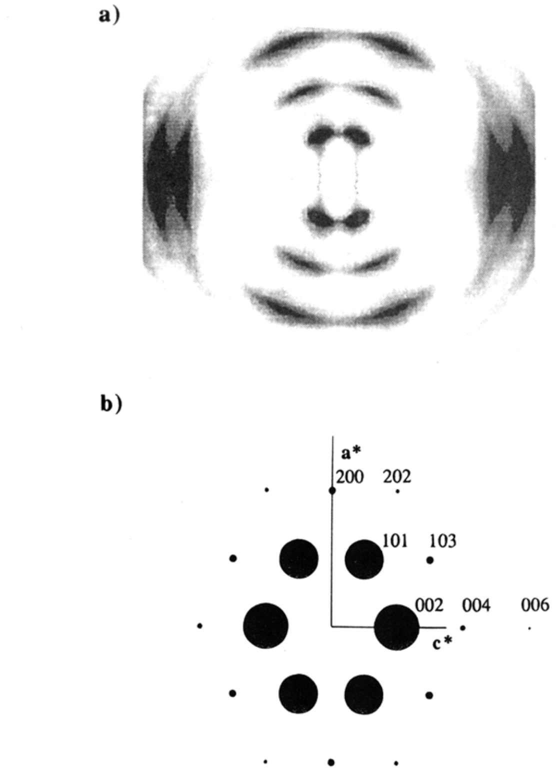

Figure 10. Simulated X-ray pattern (a) and electron diffraction pattern (b) obtained with the CERIUS program from a model optimized with the help of the LALS program.

Brill Transition. The temperature dependence of the X-ray fiber pattern has been studied from 25 to 220 °C, as shown in Figure 11 for three representative temperatures. We have found changes in spacings with temperature, as with other nylons. These changes can be summarized as follows: (a) The two strong equatorial reflections gradually merge into one peak as the temperature is increased. A single spot at 4.25 Å is observed at ca. 190 °C (about 40−50 °C before melting). (b) The 0*k*0 reflections always appear off meridian, but their deviation angle shifts gradually from 24 to 20°. On the other hand, the *b* parameter, which can be measured from the layer line spacings, slightly decreases with temperature. (c) The meridional reflection around 2.35 Å becomes weak and diffuse at elevated temperatures. We have also observed such behavior in nylon 66 fibers. As this reflection arises from the zigzag of the methylene groups, it may be inferred that they have a librational motion under these conditions.[41] (d) A nonequatorial reflection, indexed as 121, appears near the Brill transition temperature (Figure 11c). This is a striking fact since this reflection has not been observed in fibers at room temperature (Figure 11a).

A unit cell of parameters $a = 5.23$ Å, $b = 30.55$ Å, $c = 8.50$ Å, $\alpha = \beta = 90°$ and $\gamma = 110°$ can be deduced for the 190−220 °C sample (Table 6). The resulting pseudohexagonal packing is compatible with the low-temperature model based on the two hydrogen-bonding directions. Slight modifications of the φ_i and ψ_i torsional angles (φ_1 from 110 to 101° and ψ_1 from 150 to 142°) can produce both (a) ~60° rotation angle between the C−O directions of the glutaryl unit, which justifies the pseudohexagonal packing, and (b) a shortening of the *b* parameter. The influence of temperature on the structure of nylon 65 (and many other polyamides) may be thus explained assuming that the hydrogen-bonded amides are relatively immobile at all temperatures below 220 °C, as indicated by Wendolowski *et al.*[41] for nylon 66, whereas the methylene groups become increasingly mobile. At the methylene level, the Brill transition is thus similar to the high-temperature transition of paraffins to the rotator phase,[42] which in nylons takes place in a matrix of rather rigid hydrogen-bonded amide groups.

A Note on Nylon 66. The results presented here as well as those found in the *n*,3 nylons[22,27] indicate the presence of two directions of hydrogen bonding in the

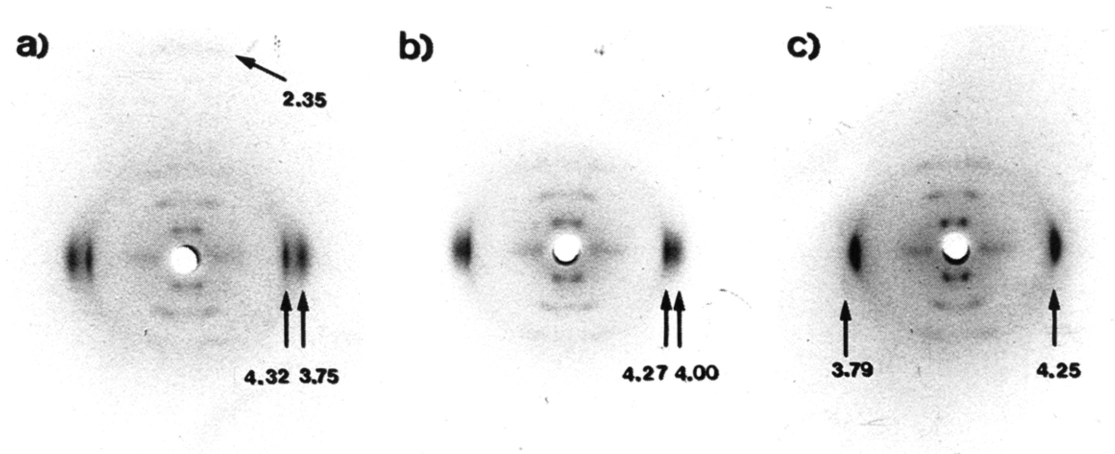

Figure 11. X-ray diffraction patterns of an annealed fiber of nylon 65. The patterns were taken at different temperatures: (a) 25, (b) 100, and (c) 190 °C. Note that the two strong equatorial reflections gradually merge into one at 4.25 Å.

Table 6. Measured and Calculated X-ray Diffraction Spacings d_B (Å) for the High-Temperature (190 °C) Structure of Nylon 65

index[a]	calcd	measd[b]
020	14.35	14.29 s, off-M
040	7.18	7.13 m, off-M
060	4.78	4.79 w, off-M
002, 101, $\bar{1}01$	4.25	4.25 vs, E
121	3.79	3.79 vw, off-M

[a] On the basis of a monoclinic cell: $a = 5.23$ Å, $b = 30.55$ Å, $c = 8.50$ Å, $\alpha = \beta = 90°$, $\gamma = 110°$. [b] Abbreviations denote intensities: vs. very strong; s, strong, m, medium; w, weak; vw, very weak. M, meridional; E, equatorial; off-M, off-meridional.

Table 7. Unit Cell Parameters and Calculated Spacings (Å) for the High-Temperature Form of Nylon 66

	ref 14	ref 15	this work
temp (°C)	>190	170	220
a (Å)	4.91	5.0	
b (Å)	5.87	5.9	
c (Å)	16.50	16.23	16.33 ± 0.15
α (deg)	55.7	56.7	
β (deg)	80.7	80.6	
γ (deg)	60.1	59.9	
100, 010, 110	4.20	4.27	4.20
210, $\bar{1}10$, 120	2.42	2.47	2.42
001	13.4	13.4	13.7
002	6.72	6.70	6.71
112	4.44	4.49	4.41
$\bar{1}03$	3.35	3.36	3.38
017	2.31	2.27	2.27

crystals of such nylons. In the case of nylon 66, it has been argued[7,13] that a three-dimensional network of hydrogen bonds might also be present at elevated temperatures. This idea has recently been advanced by other investigators.[11] On the other hand, Colclough and Baker,[15] through a detailed analysis of the X-ray fiber patterns, and Hirschinger *et al.*,[14] through solid-state NMR, concluded that such a three-dimensional network of hydrogen bonds could not exist. In view of these conflicting opinions, we decided to reinvestigate this question. We obtained a diffraction pattern from an oriented fiber of nylon 66 at 220 °C. The spacings of the most prominent spots are given in Table 7. It can be seen that they agree with the values given by other authors[14,15] within experimental error. In particular, the layer line spacing allows a direct determination of the c parameter, which had been found to be longer for solution-crystallized samples.[38] Thus our results support the conclusion of Colclough and Baker[15] and of Hirschinger *et al.*[14] in the sense that the structure of nylon 66 above the Brill transition appears to be similar to that found at room temperature in parallel sheets of hydrogen-bonded molecules. The change in the dimensions of the triclinic unit cell and, particularly, the shortening of the c value have been attributed to changes in the ethylene torsion angles[15] and to the librational motion of the methylene groups,[14] as we have also suggested above for nylon 65.

For the sake of completeness, we have tried to fit the observed diffraction spacings to a monoclinic unit cell, similar to the one described here for nylon 65 or to those found in n,3 nylons,[22] but we did not find any adequate cell, in agreement with the results reported by Colclough and Baker.[15] A monoclinic unit cell would allow the formation of hydrogen bonds in two directions. Such organization of hydrogen bonds is not possible in a triclinic cell such as the one given in Table 7 without an extensive molecular distortion. Thus we conclude that either a two- or three-dimensional hydrogen-bonded network is not present in nylon 66 above the Brill transition.

Conclusions

The results presented in this paper can be summarized as follows:

1. The melting behavior of nylon 65 shows the characteristic pattern associated with reorganization during heating of different populations of lamellar crystals.

2. We have crystallized nylon 65 in the form of chain-folded lamellae about 60 Å thick.

3. From X-ray and electron diffraction patterns, we have determined unambiguously that the crystal structure of nylon 65 at room temperature is monoclinic, with unit cell dimensions $a = 4.60$ Å, $b = 30.95$ Å, $c = 8.62$ Å, $\alpha = \beta = 90°$ and $\gamma = 114°$.

4. The experimental evidence indicates that nylon 65 has a structure different from the conventional α- and γ-forms of nylons. A new model based on two hydrogen bond directions has been built. It is compatible with all packing constraints and achieves a correct hydrogen bond stereochemistry. The resulting structure is defined by a $B112/b$ space group.

5. A particular conformation for the glutaryl units, characterized by a rotation angle about 52° between the two carbonyl directions, stabilizes the network of two hydrogen bond directions.

6. At high temperature, nylon 65 acquires a pseudohexagonal packing. The two strong reflections characteristic of the low-temperature samples gradually come together on heating and merge at 190 °C (Brill transition). The structural changes can be explained by thermal vibrations of the methylene groups without modifying the hydrogen bond network.

7. Diffraction analysis from oriented fibers of nylon 66 strongly suggests that its organization in hydrogen-bonded sheets is maintained above the Brill transition. No additional hydrogen bond orientations appear.

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