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Synthesis and Characterization of the Two Crystal Forms of Nylon 2/12

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ABSTRACT: The alternating copolyamide poly(glycyl-12-aminododecanoic acid) (nylon 2/12), was prepared by polycondensation of the "dimer" glycyl-12-aminododecanoic acid pentachlorophenyl ester and subsequently studied by calorimetry, X-ray diffraction, and electron microscopy. Two crystal forms reminiscent of those characteristic of polypeptides and nylons, respectively, were found for nylon 2/12. Form I is made of fully extended chains arranged in hydrogen-bonded sheets which are staggered in a layered structure similar to the α-form of nylons. Form II consists of a hexagonal array of 6-fold helices intermolecularly linked in a crystal lattice of $a = 0.479$ nm and $c = 1.88$ nm with features close to the peculiar polyglycine II crystal form. Evidence differentiating form II from the common γ-form of nylon-12 was provided by a comparative electron microscopy study carried out on single crystals of the two nylons in each respective form. Nylon 2/12 melts at 232 °C and crystallizes, both from the melt and from solution, mainly in form II, which was found to be by far the predominant crystal structure adopted by this polymer.

Introduction

The crystal structure known as Polyglycine II (PGII) consists of a hexagonal array of 3-fold helices interlinked by a three-dimensional network of hydrogen bonds. In this structure, a rotation angle of 120° is fixed by every glycyl residue so that each chain is systematically H-bonded to its six neighbors.[1] It has been assumed for years that the occurrence of such a structure was restricted to certain polypeptides and fibrous proteins.[2] Recently, Puiggalí et al.[3] demonstrated that nylon 2/3, poly(glycyl-β-alanine), was able to crystallize in a structure similar to PGII, a finding that represented a departure from the traditional behavior displayed by non-polypeptidic polyamides. In the last few years, the crystal structure of other copolyamides 2/*n* has been examined.[4,5] A crystal dimorphism involving a helical structure (form II) related to the PGII crystal form and a layered structure (form I) similar to the fully extended α-form typical of nylons, has been observed in every case. Form II consists of a hexagonal lattice of $a = 0.479$ nm and a c parameter with a value depending on the number of methylenes contained in the repeating unit. Modeling studies carried out on the model compound $CH_3CO—(Gly\text{-}\beta\text{-}Ala)_2—NHCH_2CH_2CH_3$ established that all interatomic bonds except those joined to methylene contained in the glycyl residue were in a *trans* conformation.[6] On the other hand, results from the modeling analysis of nylon 2/3 revealed that a statistical distribution of up and down chains is the most probable arrangement for the crystal structure of this nylon in form II.[7] A common model with the polymethylene chain of the ω-amino acid unit in conformation $ST_{n-2}\bar{S}$ and the glycine unit arranged like in PGII, has been recently proposed for the whole series of nylons 2/*n*.[8] In this model, the polymer chain is arranged in either a 6-fold or a 3-fold helix according to whether the number of carbons contained in the ω-amino acid is even or odd.

None of these copolyamides was found to crystallize in the γ-form, another crystal model commonly adopted by nylons, a fact that is rather surprising given the closer proximity of this form to the PGII structure. Chains in the γ-form are packed in a hexagonal or nearly hexagonal array of 2-fold helices with CONH groups alternatively tilted by ±60° with respect to the *all-trans* polymethylene plane and with hydrogen bonds running along a unique direction within the crystal.[9] Although this is the most widely accepted model for the γ-form, other arrangements differing in the scheme followed by hydrogen bonds have been also proposed.[10–12]

It is well-known that nylon 12 shows a strong tendency to crystallize in the γ-form, with the fully extended α-form only appearing under rather particular crystallization conditions.[13] In order to explore if the insertion of glycine in a nylon 12 chain has the same influence on conformation as observed for other lower nylons previously studied by us, the synthesis of nylon 2/12 has been carried out and its crystal structure examined by means of differential scanning calorimetry (DSC), X-ray diffraction, and electron microscopy. Nylon 2/12 has the lowest concentration of amide groups among the 2/*n* nylons synthesized to date, being in this regard comparable to nylon 7. Such a feature attaches additional interest to the study of nylon 2/12 since a decrease in the melting point of the copolyamide is expected to occur when the length of the ω-amino acid unit is increased. By following this approach, new nylons with a crystal structure similar to PGII and susceptible to be processed by the usual methods could be attained. This aim is considered of priority given the potential applications as biodegradable materials that have been claimed for glycine-containing nylons.[14]

Since the side-by-side packing of the chains in the PGII crystal is similar to that taking place in the γ-form, the unoriented diffraction diagrams of these two structures along the chain axis are practically undistinguishable. Discrimination between these two forms should be made on the basis of diffraction data related to the periodicity of the structure along the chain axis. However, none of the 2/*n* copolyamides studied so far could be stretched in fibers suitable for X-ray analysis and it has turned out to be the case for nylon 2/12 too. In order to obtain experimental evidence confirming the occurrence of form II in nylon 2/12, a comparative study on the γ-form of the nylon 12 has been included in this work.

Experimental Section

All chemicals were ACS grade or higher and were used as received. Solvents were purified and dried by appropriate

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standard methods.[15] 12-Aminododecanoic acid was prepared from commercial lauryl lactam by hydrolysis in refluxing hydrochloric acid. Nylon-12 with a molecular weight of 20 000 was purchased from Aldrich Co. (Germany) and was used as received. The synthesis of the monomer, glycyl-12-aminododecanoic pentachlorophenyl ester hydrobromide, was performed by applying methods commonly used in the synthesis of peptides. This compound was purified by recrystallization from acetic acid–ethyl ether and its structure assessed by infrared spectroscopy and elemental analysis (Found: C, 51.99; N, 4.18; H, 5.03. Calcd for $C_{20}H_{28}O_3N_2Cl_5Br$: C, 51.33; N, 4.28; H, 5.04).

Polymerizations were conducted at room temperature in a dimethyl sulfoxide solution containing triethylamine, for a period of 5 days. The polymer was precipitated from the reaction mixture by adding ethyl ether and recovered by centrifugation as a white powder with a melting point of 225 °C. After heating at 190 °C for 1 h under a nitrogen atmosphere, the polymer was subjected to fractionation in formic acid by gradual addition of ethanol. After drying under vacuum, the product showed an infrared spectrum consistent with the constitution expected for poly(glycyl-12-aminododecanoic acid). Calcd for $C_{14}H_{26}O_2N_2$: C, 66.14; H, 10.23; N, 11.02. Found: C, 64.03; H, 10.31; N, 10.52. It should be noted that a full concordance between calculated and experimental data may be attained by assuming a content of about 1 mol of water per two formula repeating units of the polymer.

Intrinsic viscosities were measured in dichloroacetic acid in a Cannon-Fenske viscometer at a temperature of 25.0 ± 0.1 °C. Infrared spectra from samples in KBr disks were registered on a Perkin-Elmer 783 instrument. GPC analyses were carried out on a Waters Associates apparatus fitted with a differential refractometer detector and using chloroform as the mobile phase. In order to render the polyamide soluble in the eluent, it was subjected to trifluoroacetylation according to the method reported by Schulz.[16] Trifluoroacetylated samples were run in a Polymer Laboratories columns set with an exclusion range of 10^3–10^4 nm and calibration was made by using polystyrene standards. Density measurements were made by the flotation method in mixtures of water and 25% potassium iodide aqueous solution. Crystallization and melting experiments were performed on a Perkin-Elmer DSC4 instrument calibrated with indium, at heating and cooling rates of ±10 °C/min, respectively. X-ray diffraction diagrams were obtained in a modified Statton Camera (W. H. Warhus, Willmington, DE) using nickel-filtered Cu Kα radiation of wavelength 0.1542 nm and were internally calibrated with calcite.

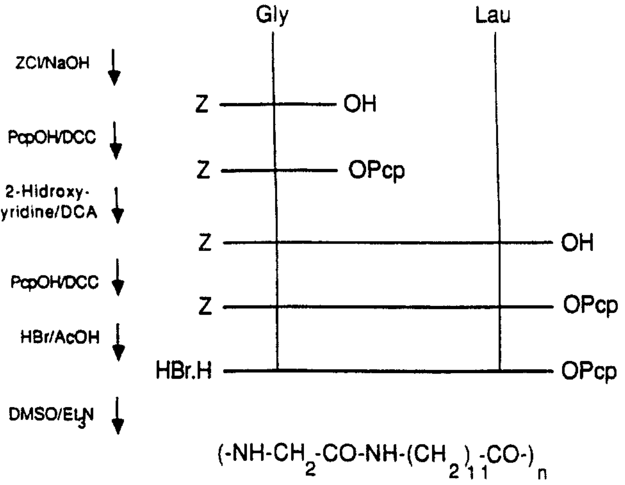
Samples to be studied by electron microscopy were prepared as both monocrystals and oriented films. Single crystals were obtained by crystallization from dilute solutions of the polymer either in formic acid–butanol mixtures or in pure glycerine. Sedimented crystals were recovered from mother solutions by centrifugation, repeatedly washed with butanol, and deposited on carbon-coated grids. Grids to be observed in the bright field were shadowed with Pt–carbon at an angle of 15°. Oriented ultrathin films suitable for electron diffraction examination were obtained by epitaxial crystallization on either benzoic acid or hydroquinone by following the technique described by Wittmann and Lotz.[17] Highly birefringent zones of these films were selected under the polarizing microscope and deposited on grids, as usual. A Philips EM-301 microscope operating at 80 or 100 kV for bright field and electron diffraction, respectively, was used in this work. Electron diffraction diagrams were recorded in the selected area mode and were internally calibrated with gold (d_{111} = 0.235 nm).

Structural modeling was performed by the LALS (link-atom-least-squares) methodology[18] with angles and bond distances fixed at the values experimentally observed for the oligopeptide model.[6] Only the torsional angles and the parameters defining the position of the chain in the unit cell were refined against stereochemical criteria.

Results

Synthesis. Nylon 2/12 has been prepared from glycine and 12-aminododecanoic acid by following the methodology previously applied by us for the preparation of other 2/*n* copolyamides.[3-5] Reactions implied in the synthesis are depicted in Scheme 1 where the following abbreviations have been used: Z = benzyloxycarbonyl; Pcp = pentachlorophenyl; DCC = 1,3-dicyclohexylcarbodiimide; DCA = dichloroacetic acid; DMSO = dimethyl sulfoxide; LAU = 12-aminododecanoic acid.

Scheme 1



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Although every intermediate was isolated and conveniently purified, only the compound pentachlorophenyl glycyl-12-aminododecanoate hydrobromide to be used as monomer in the polycondensation was fully characterized. Polymerization reactions were performed in DMSO with triethylamine as the proton acceptor. The infrared spectrum of the polymer showed absorptions at 3280, 3084, 1632, 1554, and 720 cm^{-1} corresponding respectively to the A, B, I, II, and V bands characteristic of polyamides, as well as a weak absorption around 1780 cm^{-1} arising from pentachlorophenyl ester end groups. The last indicates that polycondensation has not progressed as far as expected, a fact that was corroborated by the low limiting viscosity number (0.19 dL/g) found for the resulting polymer. Different reaction conditions were tested in order to increase the polymerization degree, but no significant improvement could be achieved. A noticeable increase in molecular weight was attained however when the polymer was heated in the solid state at 190 °C. After such treatment, the 1780 cm^{-1} band disappeared in the infrared spectrum (Figure 1) and the intrinsic viscosity reached a value of 0.72 dL/g. This value could be further increased to 0.77 dL/g by precipitating the polymer from formic acid by gradual addition of ethanol. Such a viscosity number would correspond to a molecular weight of about 8500 (DP ~ 35) if the viscosimetric equation of nylon 11[19] were applied for calculation; a value nearly doubled would result if the equation for nylon 66[20] were used instead. The GPC analysis of the polymer, performed as described in the Experimental Section, gave a molecular weight of 7000, in good concordance with the value estimated by viscosimetric measurements.

DSC Measurements. A comparative study on the thermal properties of nylons 1,*n*; *n*,3; and 2/*n* including some preliminary data on nylon 2/12 has been recently published by Xenopoulos et *al.*[21] These authors report temperatures of 55 and 230 °C for the T_g and T_m of this nylon and estimate a crystallinity between 23% and 36% depending on the manner in which samples were crystallized.

As depicted in Figure 2, DSC traces of nylon 2/12 contain well-defined peaks corresponding to both melting and

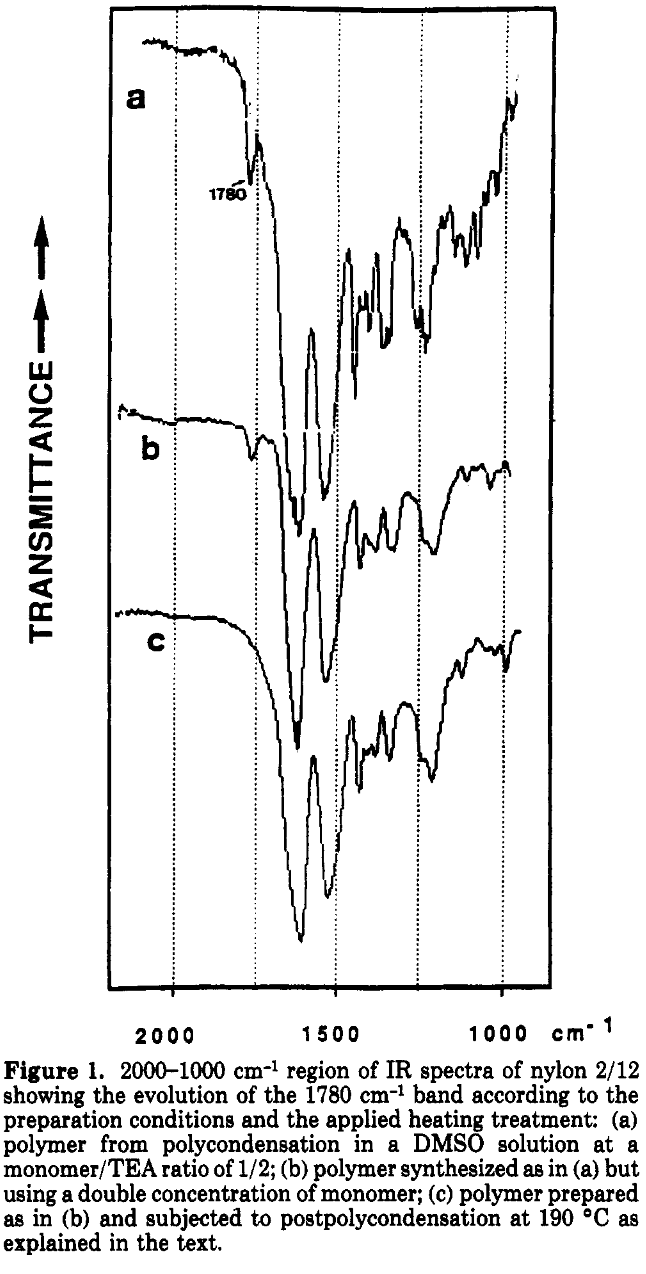


Figure 1. 2000–1000 cm^{-1} region of IR spectra of nylon 2/12 showing the evolution of the 1780 cm^{-1} band according to the preparation conditions and the applied heating treatment: (a) polymer from polycondensation in a DMSO solution at a monomer/TEA ratio of 1/2; (b) polymer synthesized as in (a) but using a double concentration of monomer; (c) polymer prepared as in (b) and subjected to postpolycondensation at 190 °C as explained in the text.

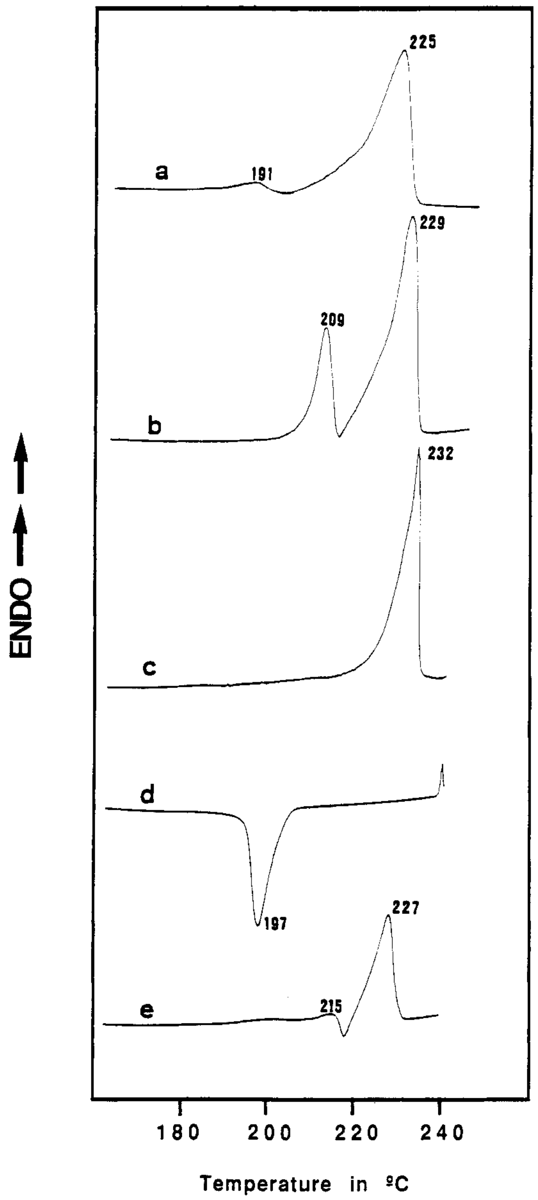


Figure 2. DSC traces of the following samples of nylon 2/12: (a) polymer coming directly from polycondensation; (b) postpolycondensated polymer; (c) film prepared by casting in formic acid; (d) cooling curve of the sample molten in (c); (e) heating curve of the sample crystallized in (d).

crystallization transitions. The thermogram recorded from the polymer coming directly from polycondensation exhibited a main endothermic peak around 225 °C preceded by a minor one at 191 °C. After the heating treatment applied to postpolycondensate, the lower melting point was moved to higher temperatures and its enthalpy increased greatly. Both effects became intensified when either the temperature or the time of application of the heating treatment was increased. Conversely, a sample prepared by casting the untreated polymer in formic acid gave a thermogram containing a single endotherm at 232 °C. This led us to discard the low molecular weight species as being responsible for the weak peak present in thermograms of Nylon 2/12 coming directly from polymerization. On the other side, a unique crystallization peak was invariably observed in the cooling curve of molten nylon 2/12, whatever was the history of the sample. Heating traces of the molten polymer reproduced the melting peak at near 230 °C, which was preceded by a small exotherm indicative of cold crystallization.

In order to gain insight into the origin of the double melting exhibited by nylon 2/12, a sample of this polymer which had been subjected to postpolycondensation was annealed at different temperatures gradually increasing from 192 to 214 °C. The corresponding DSC curves registered after each treatment at the indicated temperatures are reproduced in Figure 3. It was observed that the lower temperature melting peak moved up as the temperature of the treatment increased to finally overlap with the higher melting peak, whose position remained essentially unchanged. Such evolution of the endotherm with annealing is common in polyamides and it is currently interpreted as the result of a recrystallization process affecting the population of smaller crystallites whose melting point is lower.[22,23] We have observed also that DSC scans registered at increasing heating rates show a significant increase in the heat of fusion associated with the low-temperature endotherm while the total amount of energy absorbed by the sample remains approximately constant. Such evolution of the heat of fusion with the heating rate is considered as additional evidence for recrystallization as the interpretation of the observed double melting effect.[24] However, this interpretation is not devoid of controversy, in particular when nylons displaying crystal dimorphism are concerned.[25] In such cases, the double endotherm may be related to the respective melting of the two crystal forms and the

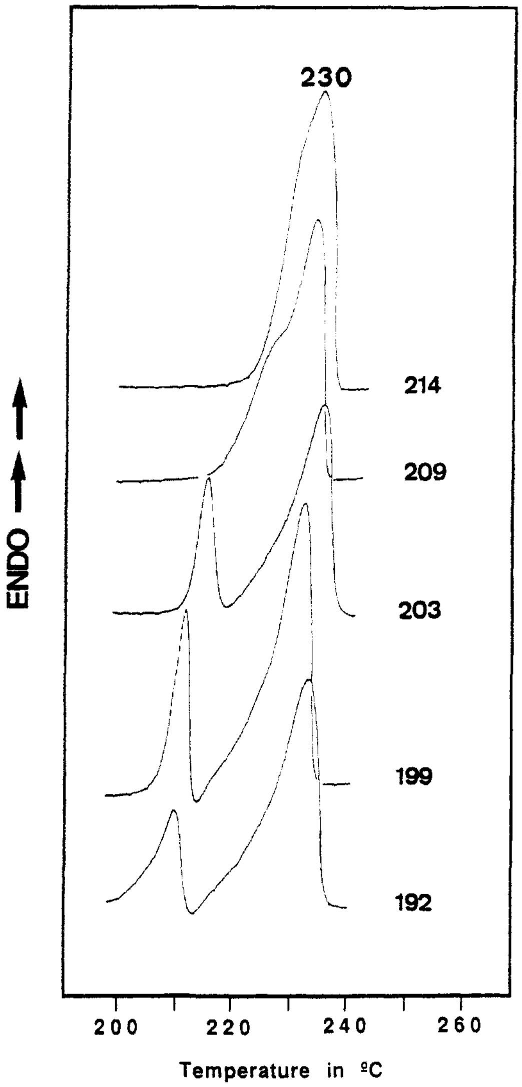


Figure 3. DSC heating curves of a nylon 2/12 sample coming from postpolycondensation and subjected to annealing at the indicated temperatures for a period of 15 min.

displacement of the peaks associated with a crystal transition taking place at heating. Since it turns out to be the case of nylon 2/12, samples of this nylon that had been subjected to annealing were then analyzed by X-ray diffraction. Results coming from this analysis will be described in the next section.

X-ray Diffraction. The X-ray diffractogram shown in Figure 4a was recorded from a sample of nylon 2/12 that had been subjected to postpolycondensation and then fractionated in formic acid–ethanol. The pattern displays a noticeable anisotropy, indicating that the sample, which was obtained as thin flakes by centrifugation, became spontaneously oriented upon recovering. Two intense reflections orthogonally oriented to each other and corresponding to Bragg spacings of 0.415 and 1.85 nm, respectively, dominate this diagram. All other reflections appearing in the wide range region are weak with the exception of a medium intense one that is equatorially oriented with a spacing 0.24 nm (Table 1). According to antecedents on other glycine-containing copolyamides,[3–5] the pattern is made to correspond to the crystal form II of nylon 2/12 consisting of a hexagonal array of helical chains with $a = 0.479$ nm and a residue translation height of 1.88 nm. The calculated density for this structure is 1.128 g/mL, in good agreement with the value of 1.09 g/mL which has been experimentally observed.

The diagram shown in Figure 4b was obtained from a sample subjected to stretching while crystallizing from the melt. All the spacings contained in the diagram of the precipitated polymer (Figure 4a) are included in this one with the only difference concerning the 0.37 nm reflection which appears now markedly reinforced. In addition, a sharp reflection with a spacing of 0.44 nm is present on the equator. Since these two spacings are characteristic of the α-form of nylons,[26] the diagram therefore is interpreted as arising from nylon 2/12 crystallized in form II but contaminated with a minor amount of form I, which incidentally appears well oriented.

Once the two crystal forms of nylon 2/12 have been identified, an X-ray analysis of samples differing in their origin or thermal history was undertaken. Diffractograms consisting exclusively of form II were recorded when the polymer was recovered from solution whereas a mixture of forms I and II were found in samples prepared by crystallization of the melt or by casting from an ethanol–phenol solution. Moreover, form II is the only phase present in the sample submitted to the annealing process depicted in Figure 3 at any stage of the applied treatment. It may be thus concluded that the endothermic peak appearing at 210–220 °C in thermograms of nylon 2/12 should be attributed to the melting of a second population of small crystallites in form II, rather than to the presence of form I.

On the other hand, a comparative inspection of the medium–low angle region (1.5–3.0 nm) of X-ray diagrams recorded from samples crystallized under different conditions revealed differences which are worthy of comment. Whereas the ring at 1.85–1.90 nm appears well outlined in diagrams from samples crystallized from solution, a diffuse ring embracing a broad range of spacings from 1.7 to 1.9 nm was observed in diagrams of samples crystallized from the melt. The broadness of this reflection is indicative of the degree of disorder that takes place in nylon 2/12 that has been rapidly crystallized. It may be related either to the occurrence of crystals with a thickness even smaller than 4 nm containing less than two residues or to a spreading of the residue heights resulting from an uneven puckering of the chains.

Electron Microscopy. Crystallization of nylon 2/12 from a 0.1% solution in glycerine at 170 °C yielded large rounded platelets as those shown in Figure 5a. Conversely, hexagonal-shaped crystals were formed when crystallization was conducted in a mixture of formic acid–butanol (1:2) at 98.5 °C (Figure 5b). Both types of morphologies display abundant screw dislocations and are composed of lamellae with a thickness of about 4 nm, as estimated from their shadows in electron micrographs. Electron diffraction from either of these two kinds of crystals rendered identical patterns consisting of a hexagonal array of reflections with a basic spacing at 0.415 nm. Such a pattern is the expected one arising from a hexagonal structure of $a = 0.479$ nm which is oriented with the c axis normal to the basal plane of the crystal. Therefore, it may be reasonably concluded that nylon 2/12 crystals prepared from solution by both methods are in form II. X-ray diffraction of sediments of these crystals provided slightly oriented diffractograms which confirm the existence of such form. In addition to the characteristic spacings arising from form II, these diagrams exhibit meridional reflections corresponding to higher orders of the lamellar thickness, which is in turn detected as a sharp reflection in the low–medium angle region with a spacing of 3.8 nm. All X-ray and electron diffraction spacings observed for nylon 2/12 samples in form II with their corresponding indexes are collected in Table 1.

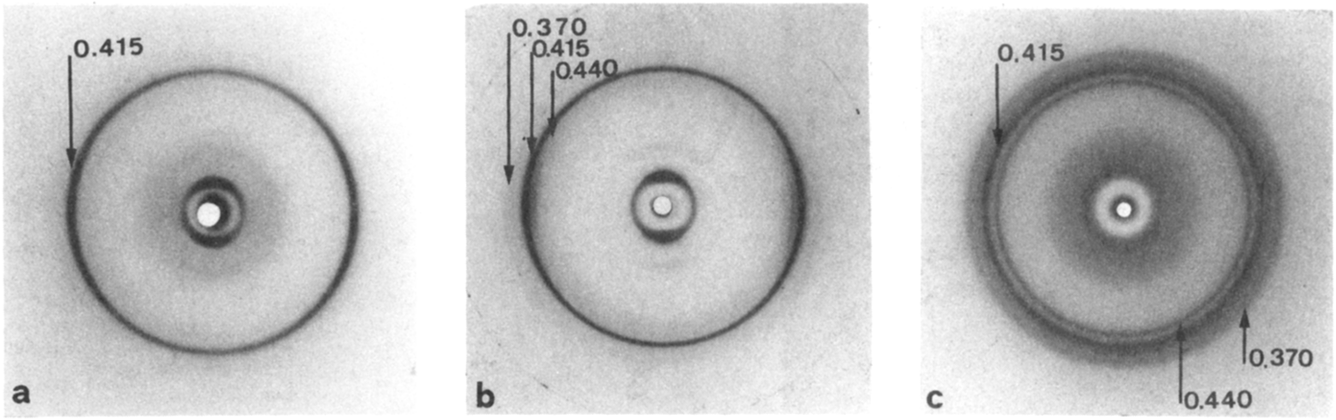


Figure 4. X-rays of nylon 2/12: (a) powder precipitated from formic acid; (b) sample stretched from the melt (oriented reflections at 0.44 and 0.37 nm are due to form I); (c) powder X-ray diagram of nylon 12 precipitated from formic acid by adding butanol. The sharp rings observed at higher angles correspond to calcite (0.303 nm) used for calibration.

Table 1. Observed and Calculated Spacings (nm) for Form II of Nylon 2/12

obsd[a]	intensities[b]	calcd[c]	indexing
		Meridional	
3.80	m	3.76	003
1.85	vs	1.88	006
0.90		0.94	0,0,12
0.465	w	0.470	0,0,24
0.370	vw	0.376	0,0,30
0.310	w	0.313	0,0,36
		Equatorial[d]	
0.415	vs	0.415	100
0.240	m	0.239	110
0.207	vw	0.207	200
		Off-Meridional	
0.374	w	0.377	1,0,12
0.332	w	0.341	1,0,18
0.219	w	0.224	1,1,18
0.196	w	0.197	2,0,18

[a] Average values of spacings observed in X-ray diagrams from samples including films, powders, and mats of crystals. [b] Relative values estimated visually: vs = very strong; m = medium; w = weak; vw = very weak. [c] Assignments made on the basis of a hexagonal lattice with $a_0 = 0.479$ nm and $c_0 = 11.28$ nm; alternatively, a subcell with $c_0 = 3.76$ nm could be used for indexing. Meridional reflections may be made to correspond also to the lamellar thickness with a spacing of 3.76 nm and its even orders with the exception of the sixth one. [d] Observed also in electron diffraction diagrams produced by single crystals.

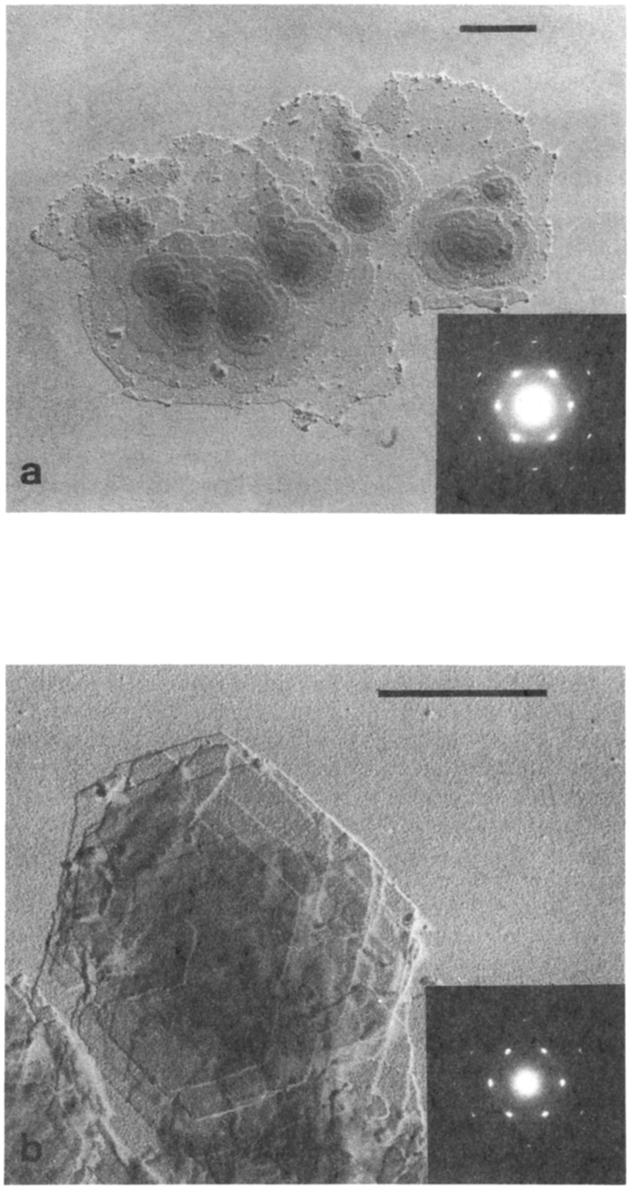


Figure 5. Lamellar crystals of nylon 2/12 and their corresponding electron diffraction diagrams: (a) crystallized from glycerine at 170 °C; (b) crystallized from formic acid–butanol (1:2) at 98.5 °C. The bar denotes 1 μm in both cases.

Epitaxial crystallization on organic substrates has proved to be a valuable method to obtain oriented films of nylons suitable for examination by electron diffraction. Two substrates, benzoic acid and hydroquinone, have been used in this work to grow epitaxial films of nylon 2/12. As has been found for other 2/*n* copolyamides previously studied by this methodology, crystallization of the polymer in the extended conformation is highly favored. As expected, the crystallites became oriented with chains lying on the film plane, although the crystallographical plane in contact with the substrate surface was different in each case. The diagram shown in Figure 6a was recorded from a film grown onto hydroquinone. The presence of equatorial reflections with spacings at 0.44 and 0.24 nm indicates that more than one reciprocal plane must be contained in this diagram. This is consistent with the uneven distribution of spacings found for *hk*8 reflections aligned along the layer line at 0.25 nm. A spacing of 0.123 nm becomes accurately defined by the meridional streak indexed as *h*,*k*,16. Such a distance clearly corresponds to the average rise per interatomic bond along the backbone and demonstrates that chains are in a fully or nearly fully extended conformation. Diagrams arising from form I lying on a different *hkl* plane were obtained from films grown onto benzoic acid. They contain additional spacings

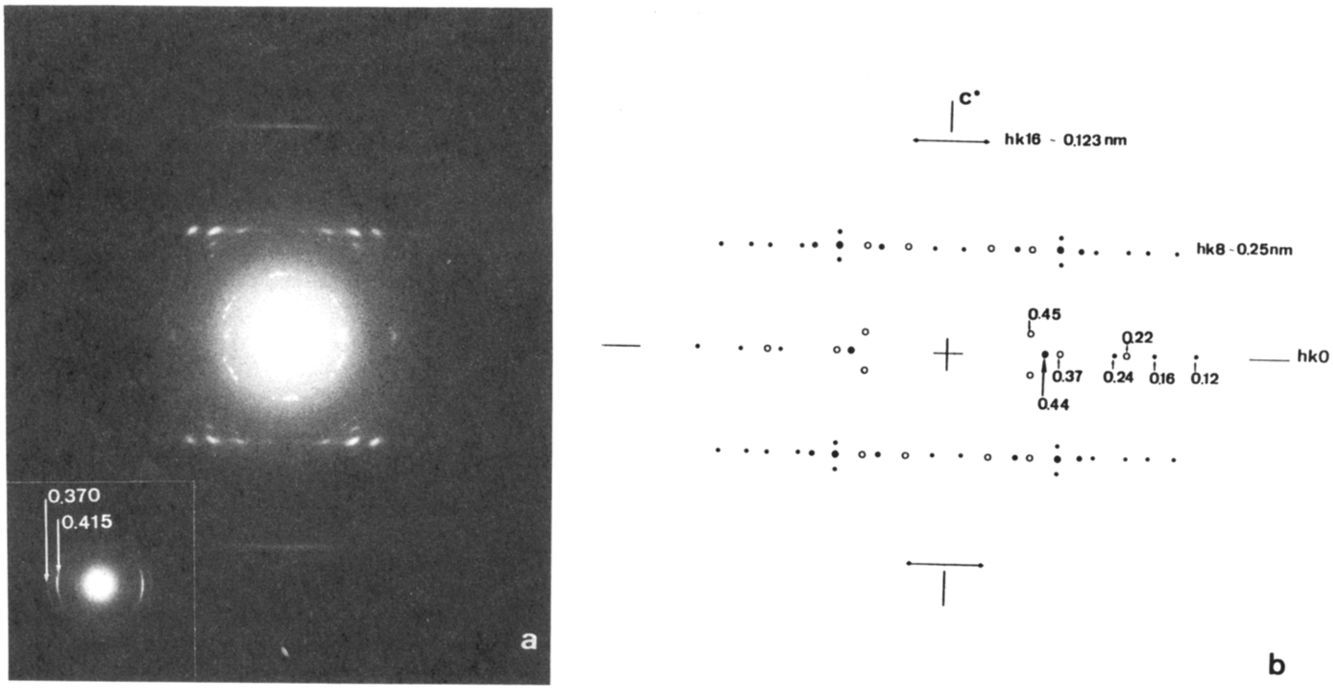


Figure 6. (a) Electron diffraction diagram obtained from a film of nylon 2/12 in form I, which was grown onto hydroquinone. The lattice is oriented with the chain axis lying on the film plane and along the vertical. The grainy hexagonal pattern observed with a Bragg spacing of 0.415 nm arises from form II, which is oriented with chains standing perpendicular to the film plane. Inset: Inner zone of a diagram produced by a film of nylon 2/12 grown onto benzoic acid. The 0.37 nm intersheet spacing characteristic of form I is brought out on the equator. (b) Schematic representation of reflections contained in the electron diffraction diagram shown in (a) (filled circles). Empty circles represent reflections which are observed in diagrams from films grown onto benzoic acid. Only the most significant spacings with regard to the geometry of the lattice have been labeled. Reflections arising from form II have not been included.

of form I, in particular the characteristic 0.37 nm reflection related to the intersheet distance. A composed scheme including the most significant reflections recorded from both types of films is depicted in Figure 6b. The detailed analysis of these diffraction data allows us to conclude that the crystal model for nylon 2/12 in form I consists of a layered structure similar to the familiar α-form of nylons. In this model, hydrogen-bonded sheets are shifted along the *a* direction by a distance of about *a*/6 and are packed side-by-side in a staggered fashion.

Nylon 12. A sample of nylon 12 prepared by precipitation of the polymer from formic acid by adding ethanol gave the X-ray diagram shown in Figure 4c. The pattern contains the reflections characteristic of the two crystal forms known for this nylon, the γ-form (0.415 nm) and α-form (0.445 and 0.370 nm), the former appearing as the predominant structure. Nylon 2/12 prepared under similar conditions was made exclusively of form II (Figure 4a). On the other hand, films of nylon 12 prepared by casting from phenol–ethanol consisted of the pure α-form, whereas those of nylon 2/12 obtained in the same manner were made of a mixture of forms I and II. Crystallization of nylon 12 from formic acid–butanol at 98.5 °C, which were the conditions used for growing the hexagonal platelets of nylon 2/12 shown in Figure 5b, yielded the lathlike crystals displayed in Figure 7. Selected area diffraction from these crystals gave diagrams consisting of a hexagonal array of reflections with a basic spacing at 0.415 nm. This pattern exhibits *mmm* symmetry indicative of the γ-form with the intense pair of reflections at 0.24 nm placed on the 2-fold axis, which is aligned parallel to the preferent growth direction of the lamella. Such symmetry contrasts with the 6/*mmm* symmetry displayed by electron diffraction patterns produced by crystals of nylon 2/12 in form II (Figure 5). Such differences between the γ-form and form II in both morphology and diffraction symmetry are in agreement with what should be expected for the arrangement adopted by hydrogen bonds in each of these structures.

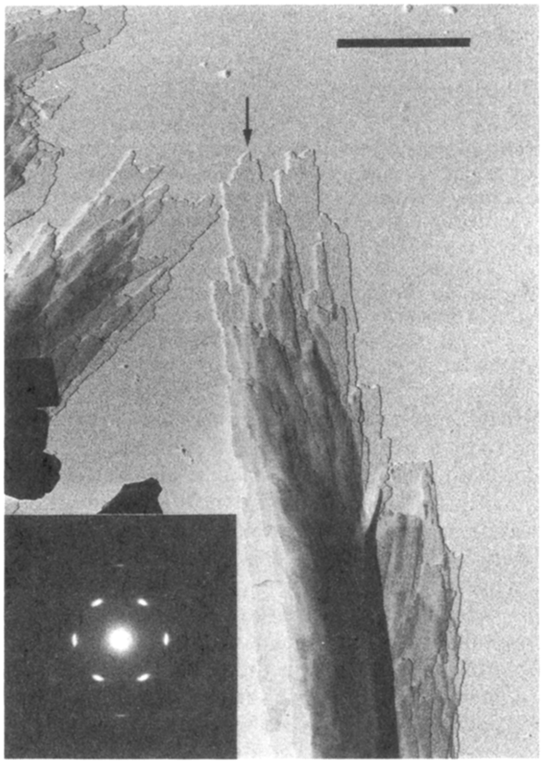
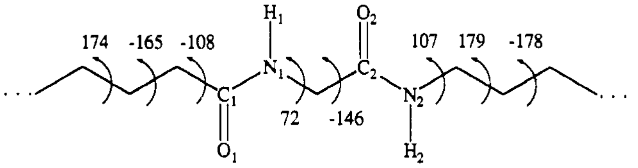


Figure 7. Lamellar crystals of nylon 12 grown from formic acid–butanol (1:2) at 98.5 °C. The bar denotes 1 μm. Inset: Electron diffraction diagram of the arrowed crystal which has been placed in a corresponding orientation. Note how the 2-fold symmetry of this pattern compares with the 6-fold symmetry displayed by diagrams arising from form II of nylon 2/12 (Figure 5).

Table 2. Distances and Angles for Hydrogen Bonds between Parallel and Antiparallel Chains of the Alternating Copolymer 2/12 in Form II

	distances (nm)		angles (deg)	
parallel	H1⋯O1	0.186	N1—H1—O1	157.6
	H2⋯O2	0.178	N2—H2—O2	161.1
	N1⋯O1	0.282		
	N2⋯O2	0.274		
antiparallel	H1⋯O2	0.186	N1—H1—O2	147.8
	H2⋯O1	0.165	N2—H2—O1	166.0
	N1⋯O2	0.277		
	N2⋯O1	0.264		

Crystal Model of Form II. Following the stereochemical outlines previously adopted for establishing the PGII crystal structure of nylon 2/6,[8] a model consisting of a hexagonal array of 6-fold left-handed helices with an asymmetric unit length of 1.88 nm has been built for form II of nylon 2/12 by using the LALS program. The resulting structure has a repeating period along the chain of 11.28 nm and an interchain distance of 0.479 nm. The conformation adopted by the polymer in this structure may be envisaged as intermediate between these occurring in PGII and the γ-form of nylons. The torsion angles ψ and φ about the CC$^\alpha$ and NC$^\alpha$ bonds contained in the glycine residue of the left-handed helix have values of −146 and +71°, which turn out to be very close to those of the 3-fold helix of polyglycine described by Crick and Rich.[1] Conversely, the polymethylene segment assumes a conformational arrangement $ST_{10}\bar{S}$ similar to that found in nylon 12 in the γ-form. Distances and angles calculated for hydrogen bonds set between neighboring chains have the values given in Table 2; all these values fall within the permissible range whether the arrangement followed for the chains in the lattice is parallel or antiparallel. The two versions of the model corresponding to the two possible orientations are drawn in Figures 8 and 9.



Discussion

Polycondensation in solutions of glycyl-ω-amino acids activated as pentachlorophenyl esters has proved to be a useful method to prepare a number of alternating 2/n copolyamides.[3-5] However, molecular weights of the resulting polymers were rather low, as inferred from their intrinsic viscosities which ranged in the interval 0.15–0.35 dL/g. In the preparation of nylon 2/12, we have found that a significant increase of the polymer size may be attained by subjecting the reaction product to subsequent heating in the solid state at a temperature near but below the melting point. This type of treatment had been previously used successfully by us in the synthesis of the regular terpolyamide 3/5/7.[27] The increase in molecular weight is thought to be due to the reaction taking place between those remaining amine and active ester end groups located near each other. Since the applied temperature is well above the T_g, the mobility of the chain ends is increased and therefore the probability of reaction favored. The convenience for carrying out the polycondensation in two stages, first in solution at room temperature and then in the solid state at high temperature, is easily understandable because, by this means, most of the pentachlorophenyl released in the first step may be removed so that further interaction of this compound with the formed polyamide is avoided. With the application of such a treatment, the active ester polycondensation method gains additional interest as a general route for the synthesis of 2/n nylons.

In full agreement with all other 2/n copolyamides previously studied by us, nylon 2/12 displays a crystal dimorphism involving a helical structure (form II) with features close to those of PGII, as well as a layered structure (form I) similar to the familiar α-form of nylons (form I). As it happens with the other lower members of the series, form II is by far the structure preferentially adopted by nylon 2/12, although the capability to give the extended form under certain conditions is still not completely repressed. Nevertheless, the case of nylon 2/12 is noteworthy because the influence of glycine on conformation is still retained in spite of the low specific weight that the α-amino acid has in the constitution of the copolyamide.

The model proposed for form II has been constructed by following the stereochemical criteria adopted in the modeling of nylon 2/6.[8] In this model, each 6-fold helix is linked to its six neighbors by a tridimensional network of hydrogen bonds made by amide groups. A helix with a pitch of 11.28 nm results for nylon 2/12 according to the length of the polymethylene segment contained in this nylon. Since no asymmetric carbon exists in the molecule, models built with either left-handed or right-handed helices are equally stable, although, as anticipated by Rich and Crick[1] for polyglycine II, chains within a given crystallite must have the same sense in order to enable the formation of all hydrogen bonds. On the other hand, no substantial modifications were observed in the conformational parameters when the lattice was generated with chains arranged either parallel or antiparallel. Nevertheless, the occurrence of thin lamellae of nylon 2/12 requiring chain folding, gives strong support to a structure based on an up-and-down arrangement. Furthermore, it should be noted that a hexagonal array of directional chains implies both kinds of neighboring interactions, parallel and antiparallel. Consequently, a unit cell based on a statistical average of two chains in opposite orientation, each one having an occupancy of one-half, is regarded as the most plausible model for the crystal structure in form II.

Lamellae of nylon 2/12 are grown from solution in form II with a thickness of 3.8–4.0 nm, as measured by both X-ray diffraction and electron microscopy. This height corresponds to twice the chemical repeat distance, implying practically the absence of any amorphous component. They display more or less well-shaped hexagonal morphologies and yield diffraction patterns consistent with the hexagonal structure determined for this form. It is certainly striking that only about one-third of the repeating period of the 6-fold helix can be accommodated within the height of such crystals provided that chain axes are perpendicular to their basal planes. This is a peculiar situation difficult to reconcile with the 6/mmm symmery exhibited by the diffraction patterns obtained from such crystals. Nylons 2/6[4] and 2/11[5] crystallized in helical form, which have been previously studied by us, are affected by a similar conflict. Lamellae able to crystallize with a thickness less than the chain crystallographical repeat have been described also for poly(ether ketone)s,[29] although in this case no diffraction data from single crystals were reported.

The topological restriction imposed by a lamellar thickness that is much shorter than the length of the structural repeating unit of the 6-fold helix gives rise to the question of what precise segment of the molecule is

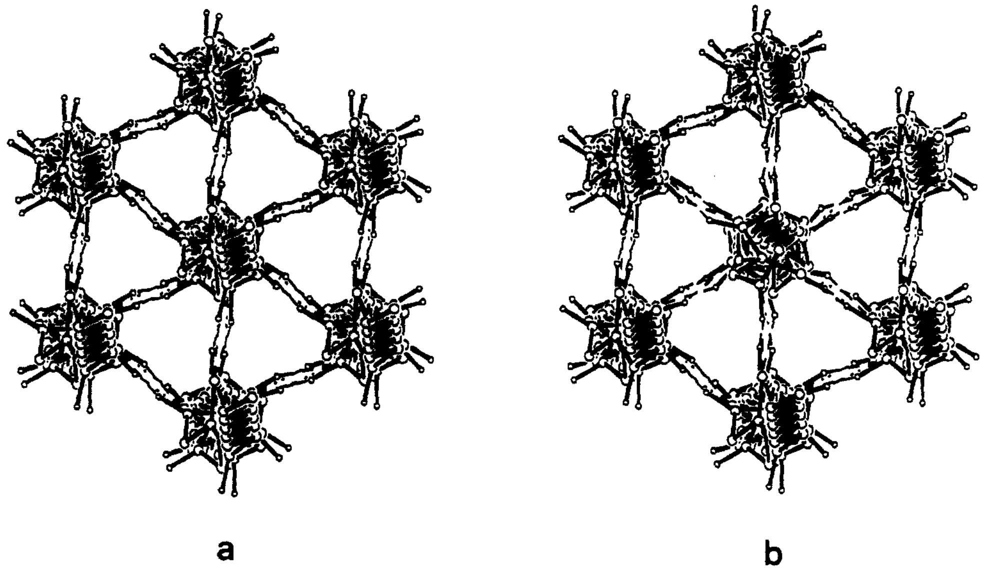


Figure 8. Molecular drawing of form II of nylon 2/12 made with the ORTEP program.[28] Seven chains viewed down the *c*-axis are shown, and only hydrogen atoms involved in hydrogen bonds are represented. (a) Parallel structure: All chains are pointing up. (b) Antiparallel structure: The orientation of the central chain is down with respect to its six up-pointing neighbors. In both cases, all hydrogen bonds (represented by dashed lines) can be satisfactorily formed.

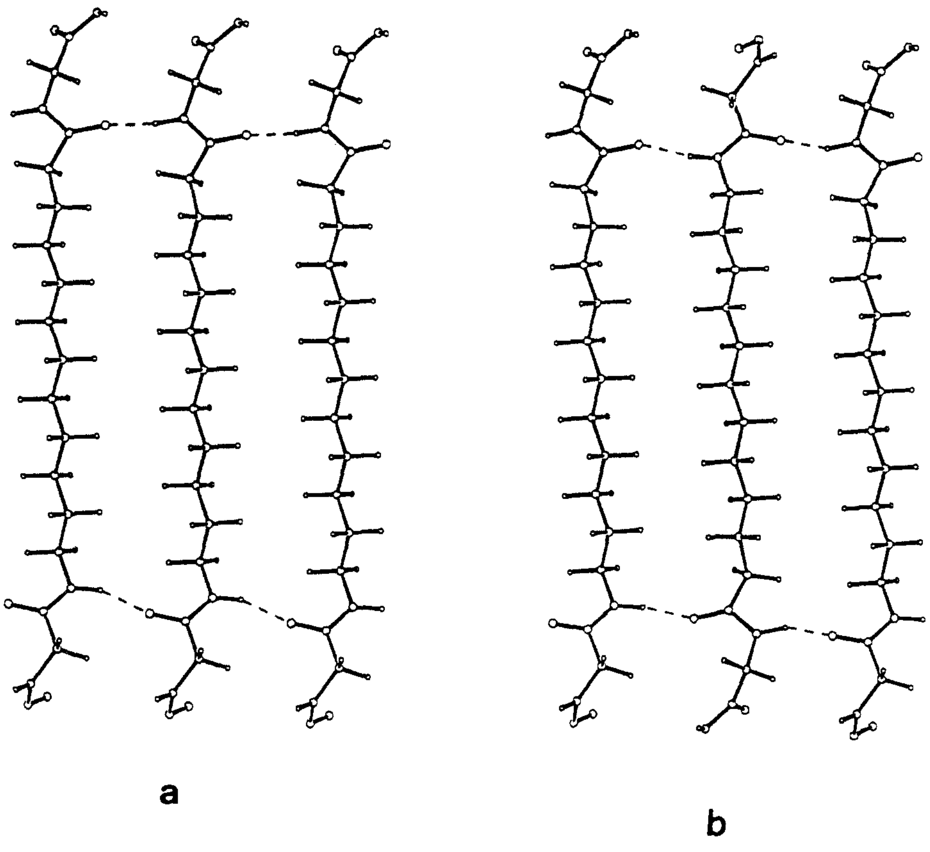


Figure 9. Side view of the structure of form II of nylon 2/12 showing three coplanar neighboring chains. The relative orientation of the chains is up–up–up in (a) and up–down–up in (b). Only the chain segment included in the lamellar core has been represented.

contained in the lamella and how adjacent re-entry may take place. In order to have a uniform distribution of hydrogen bonds in the lamella over the three 120° directions, which would be desirable in order to approximate the hexagonal symmetry, the molecular stem must include a number of amide groups that is a multiple of three. It is found however that those molecular arrangements able to satisfy such a condition result in lamellar heights that deviate significantly from the observed value.

A model consisting of a lamellar core constituted by the sequence —(—glycyl—12-aminododecanoyl—glycyl—)— with the contiguous polymethylene segments being used to make the re-entrant loops seems compatible with most of the geometrical features exhibited by the crystals (Figure 10a). In this model two glycine units involving four hydrogen bonds per chain are included in the core. As a consequence, the density of hydrogen bonds along one of the three bonded directions becomes doubled. The atomic distribution resulting from this molecular arrangement is consistent with the profile of intensities observed for the meridional reflections appearing in the X-ray diagrams produced by crystal mats. In a first approximation, it may be considered that the main scattering planes

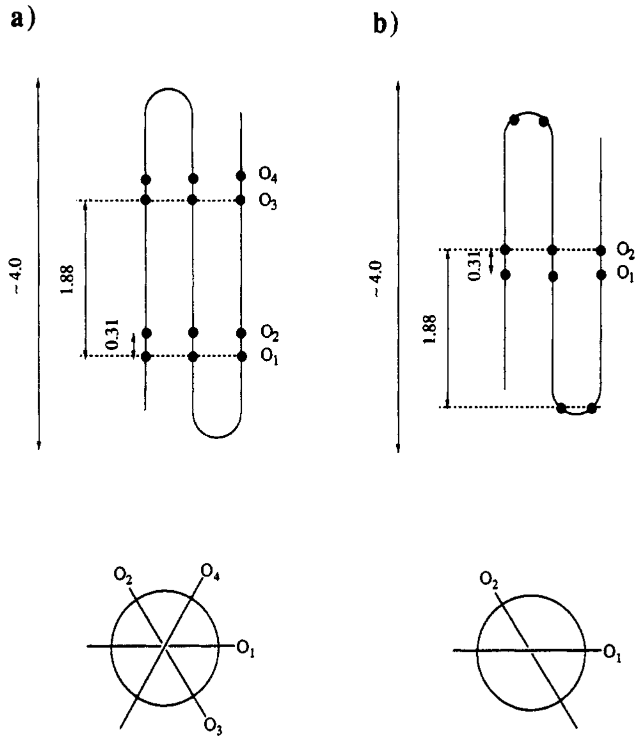


Figure 10. Schemes of the two models for the molecular organization within the lamellae of nylon 2/12 in the 6-fold helical conformation explained in the text. Drawings at the bottom show how hydrogen bonds contained in the core become aligned along the 100, 010, and 110 directions of the crystal in each respective model.

responsible for the meridional reflections should be those containing the carbonyl oxygen atoms. The one-dimensional Fourier transform for this model is given by the product of a two-unit repeat and the cosine distribution of two points separated by 0.31 nm corresponding to the glycine residue height. Whereas the former factor vanishes at odd orders of 3.76 nm, the second one does it at 0.62 nm. This simple calculation leads us to anticipate that only reflections corresponding to even orders of the lamellar height, except those in the proximity of 0.62 nm, should appear, which is in full agreement with our observations.

A second arrangement based on chain foldings involving the amide groups at the re-entrant loops may be alternatively conceived (Figure 10b). This type of arrangement has been recently proposed by Atkins et al.[30] for lamellae of nylon 4,6, where one amide group is located on the top of every fold. The model cannot be straightforwardly applied to nylon 2/12 due to the restriction toward chain bending imposed by both the presence of the short glycine residue and the directionality of the chain. In this case two amide units will be required to form the loop instead. Consequently, only one glycine unit per molecular segment will comprise the lamellar core. This model appears to be disfavored with respect to the former because only two directions of hydrogen bonds will occur within the lamella.

In order to explain the hexagonal symmetry displayed by the reciprocal lattice, a twinned texture involving three twinning domains rotated at 120° to each other could be invoked for the lamellae of nylon 2/12. However, no sign of symmetry other than hexagonal has been detected for the diffraction diagrams recorded from small areas (~0.5 μm) selected on what could be any of the three different sectors of such crystals. This indicates that the occurrence of twinning may be only acceptable if the size of the domains is significantly smaller than the area used for diffraction. Microsectorization is perfectly compatible with the morphological features displayed by the rounded lamellae with serrated edges obtained from glycerine at high temperatures (Figure 5a). Such a structure can be envisaged as a disordered lattice consisting of 6-fold helices with hydrogen bonds randomly addressed along three directions at 120° to each other. On the contrary, this does not seem to be the case for the well-outlined hexagonal lamellae grown in formic acid–butanol (Figure 5b), where an ordered molecular arrangement should be expected according to the smooth growth edges exhibited by these crystals. The hexagonal symmetry of the electron diffraction patterns obtained in this case may be explained if one takes into account the occurrence of plentiful overgrowths in these crystals. In fact, three overgrown lamellae in crystallographical alignment will be enough to comprise the whole repeating unit of the 6-fold helix needed to render a perfect hexagonal reciprocal lattice.

The other crystal modification of nylon 2/12, form I, only appears under certain crystallization conditions and, in any case, as a minor phase accompanying the predominant form II. As with nylons 2/3 and 2/11, epitaxial crystallization turns out to be the only method capable of rendering oriented films in form I suitable for structural examination. No samples containing this form could be obtained in sufficient amount for X-ray or DSC studies.

As revealed by electron diffraction, form I is made of hydrogen-bonded sheets with fully extended chains arranged in antiparallel mode. Sheets are spaced by a distance of 0.370 nm, which is a value within the range usually observed for the α-form of nylons but significantly different from the 0.345 nm interlayer spacing found for the β-structure of polyglycine (Polyglycine I). In analogy with most of the nylons crystallized in the α-form,[31] sheets are shifted along the *a* axis, which is the axis containing the hydrogen bonds, by a distance of about *a*/6. The distribution of the reflections along layer lines concerning both spacings and intensities strongly suggests the occurrence of a staggered structure, although no data are available to ascertain the magnitude of the displacement along the *c* axis. A model consisting of a similar arrangement was proposed for form I of nylon 2/3.[3] In that case an orthorhombic lattice was favored because displacements of successive sheets along axes *a* and *c* were rational numbers. In the present case, the absence of orthogonality observed in electron diffraction patterns points to a triclinic lattice closer to the α-structure of nylon 66.

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