

Comparison of lamellar crystal structure and morphology of nylon 46 and nylon 5

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Abstract

A comparative study of the crystal structure of lamellar crystals of the isomeric nylons 46 and 5 was carried out. A lattice made of hydrogen-bonded sheets with chains in fully extended conformation and hydrogen bonds in the normal scheme was proposed for the two nylons according to the great similarities in morphology and diffraction data observed for their solution grown crystals. Energy calculations and modeling simulations showed that a model consisting of a statistical arrangement of progressive and alternating intersheet shearing is the most appropriate and consistent to describe the structure of both nylons. A preliminary investigation on the possibility of cocrystallizing nylon 46 and nylon 5 was undertaken. First experimental results were found to be compatible with the occurrence of cocrystallization. Molecular mechanics calculations indicated that insertion of one nylon in the crystal lattice of the other is energetically disfavored. However, cocrystals would be acceptable if they were made of homogeneous blocks of each nylon comprised of about 10 or more hydrogen-bonded sheets. © 2000 Published by Elsevier Science Ltd.

Keywords: Lamellar crystal structure; Nylon 46; Nylon 5

1. Introduction

Nylon 46 and nylon 5 are isomeric compounds; they have the same NHCO/CH_2 ratio and the amide groups equally spaced along the chain. The former is an even–even polyamide of $[n, n + 2]$ type with two centers of symmetry in the repeating unit whereas the latter is an odd n polyamide made of non-centrosymmetric chains. As illustrated in Fig. 1, all amide groups in an extended chain of nylon 5 are pointing in the same direction whereas in nylon 46 the amide groups are alternating in orientation. As a result, the chemical repeating unit in nylon 46 is twice as long as that of nylon 5, and the molecular symmetry of nylon 5 is m whereas that of nylon 46 is $2m$.

Nylon 46 (tetramethylene adipamide) was firstly synthesized by Carothers [1] and is nowadays marketed by DSM under the trade name Stanyl. The melting and thermal stability of this nylon outpace those of the more usual commercial nylons, such as nylon 6 or nylon 66. The crystal structure of nylon 46 consists of non-polar hydrogen-bonded sheets in fully extended conformation. Such structure was investigated by different authors. Thus, Gaymans et al. [2] and Kashima et al. [3] suggested a triclinic lattice in

space group $P1$ such as the α -form of nylon 66 [4]. On the other hand, Atkins et al. [5] proposed for nylon 46 crystals grown from solution, a monoclinic lattice with hydrogen-bonded sheets alternatively shearing up and down like in the α -form of nylon 6 [6]. A very detailed study of the structure of nylon 46 using electron microscopy, X-ray diffraction, energy calculations and modeling simulations has been recently reported by the authors [7]. We found that a lattice of hydrogen-bonded sheets sheared along the c -axis in a statistical mixture of alternating and progressive arrangements is the most appropriate model to describe nylon 46 lamellar crystals.

Nylon 5 (polypiperidinone) is a polyamide with a general pattern of properties close to nylon 46 that has not achieved commercial realization. Since hydrogen-bonded sheets made of nylon 5 are polar, the number of packing choices for this compound is higher than for nylon 46. Accordingly, the description of its crystal structure suffers from a greater degree of uncertainty. Two crystal models, one polar and the other non-polar, were initially recognized as possible for nylon 5 in a pioneering study carried out by Hasegawa et al [8]. Later a non-polar triclinic structure with hydrogen bonds set between antiparallel chains and sheets shearing progressively like in the β -form of nylon 6 has been reported on the basis of electron microscopy and X-ray

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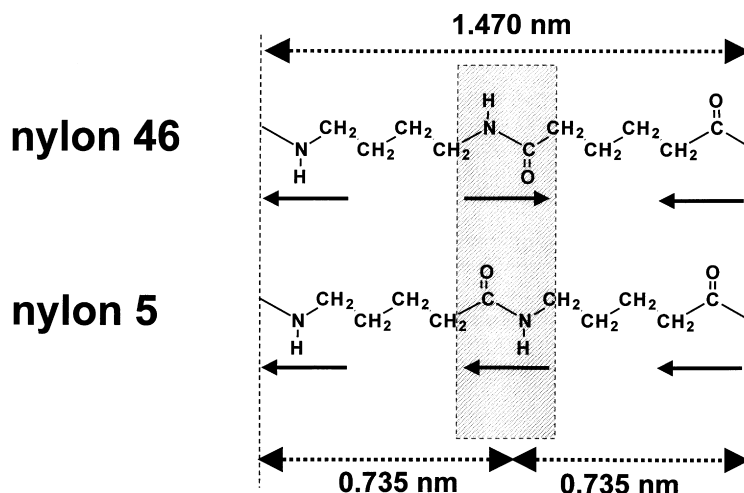


Fig. 1. Chemical structures of nylon 46 and nylon 5.

diffraction data of crystals grown from solution [9]. The lamellar crystals were described to be of accordion-type with the wavy surface containing 001 planes and chains oriented parallel to the crystal surface normal.

In this work, we present a comparative study on the crystal structure of nylon 46 and nylon 5. For this purpose, we have carried out an electron microscopic and X-ray diffraction study of lamellar crystals of the two nylons grown under the same experimental conditions. In addition, we have investigated the crystallization of a mixture of these two nylons to substantiate their structural similarities in a conclusive manner. A detailed energy analysis of the possible packing arrangements has been undertaken in order to discriminate between favorable and unfavorable structural models. Our results will reveal that the two isomeric nylons, as well as their mixture, have very similar crystal structures with only minor differences detected in the shear of the hydrogen-bonded sheets.

2. Structural background

The number of structures feasible for a crystal lattice of a nylon with the chains crystallized in the fully extended conformation is determined by the symmetry of the chain. Two types of hydrogen-bonded sheets are possible for both nylon 46 and nylon 5 depending on the scheme adopted by the hydrogen bonds. In the normal scheme (n), hydrogen bonds run normally to the chain axis whereas in the oblique scheme (o), they are arrayed at an angle of approximately 77° to the chain axis. Two models (I and II) are also feasible for the arrangement of the sheets along the *a*-axis depending on the sense of the shift. Moreover, two further choices (polar P) and non-polar (nP) have to be considered in the case of nylon 5 because the polarity of the hydrogen-bonded sheets of this nylon introduces an additional variable in the building of the structure. On the other hand, two models are conceivable for the stacking of the sheets if the shift along

the *c*-axis is taken into account and a constant shift, Δc , is assumed. According to the denominations given by Holmes et al. [6] for the two extended chain crystal forms of nylon 6, in the α -form the sheets are staggered up and down whereas in the β -form, they are progressively sheared. All these models are displayed in Fig. 2, which includes the nomenclature used in the present work. The result of combining these models is that 8 and 16 three-dimensional structures are feasible for nylon 46 and nylon 5 crystal lattices, respectively.

3. Experimental methods

The sample of nylon 46 used in this work was kindly supplied by Dr Eltink of DSM. The sample was fractionated by precipitation from a formic acid solution using ethanol as precipitant. The fraction selected for this study had an intrinsic viscosity in dichloroacetic acid of 0.9 dl g^{-1} , which corresponds to a molecular weight of 18,000 if the viscosity equation established for nylon 66 is applied [10]. The sample of nylon 5 was prepared by anionic ring polymerization of piperidinone as described in full detail elsewhere [11]. The intrinsic viscosity of this sample was 0.4 dl g^{-1} corresponding to a molecular weight of about 5000.

Samples to be studied by electron microscopy were processed in two ways. Films showing uniaxial orientation were prepared from a concentrated solution of the polymer in formic acid by stroking on a glass slide at room temperature. Highly birefringent zones selected under the polarizing optical microscope were coated with carbon and the composite film detached by floating on water surface. On the other hand, single crystals were obtained by crystallization from a dilute solution in glycerin at temperatures between 170 and 180°C . They were then collected by centrifugation and repeatedly washed with butanol. Carbon-coated copper grids were touched with drops of crystal suspension and

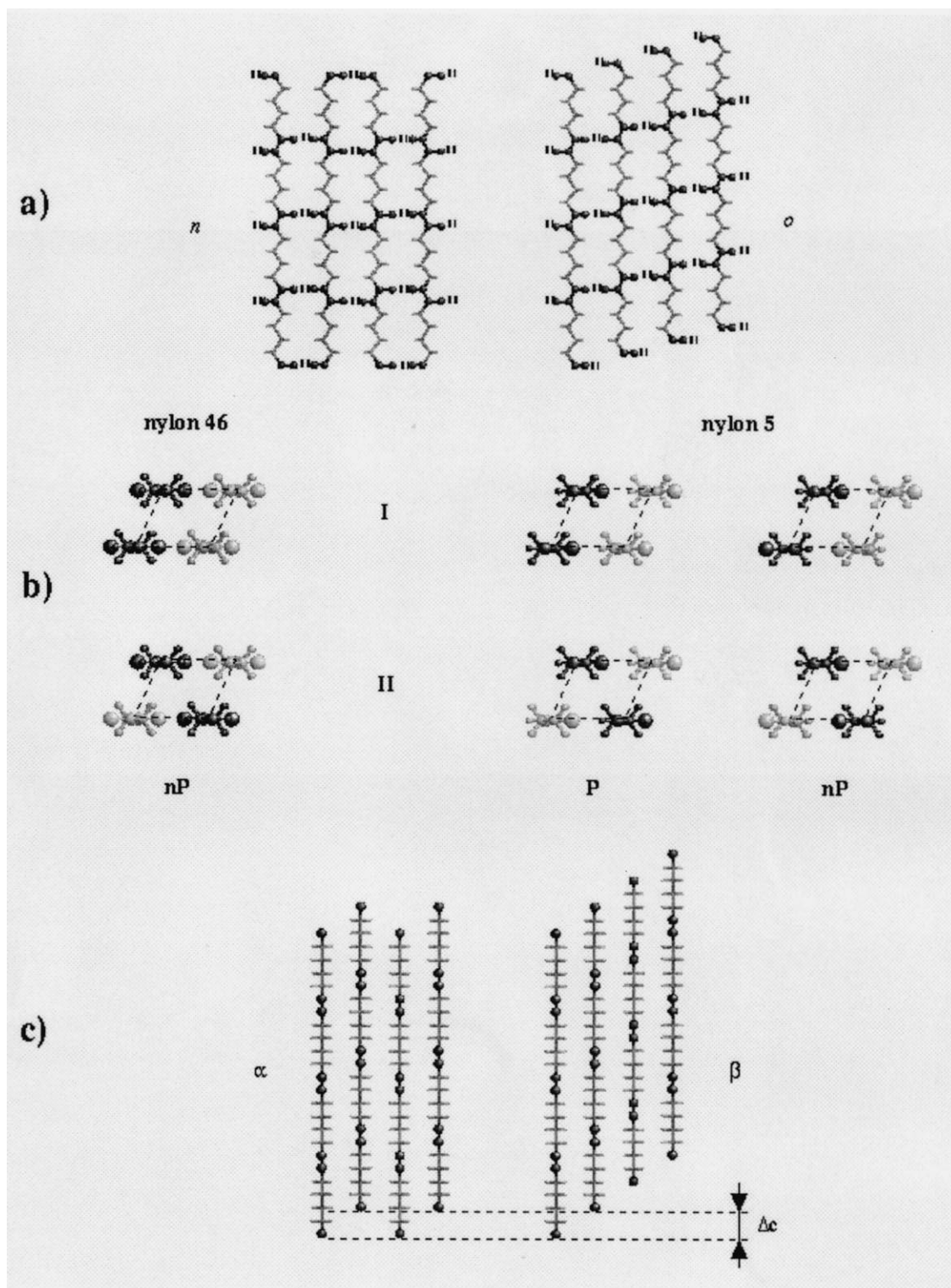


Fig. 2. Possible structures for nylon 46 and nylon 5 crystal lattices: (a) *normal* (n) and *oblique* (o) schemes for the hydrogen bonds within a sheet; (b) models for the arrangement of the sheets along the *a*-axis; and (c) models for the stacking of the sheets along the *c*-axis considering a constant shift Δc .

the solvent left to evaporate. For bright field observation, they were shadowed with Pt–C at an angle of 15° . For surface crystal examination, they were decorated with polyethylene vapors before shadowing according to Wittmann

and Lotz [12]. For electron diffraction, unshadowed samples calibrated with gold ($d_{111} = 0.235$ nm) were used.

For X-ray diffraction, DSC and NMR studies, sediments of crystals were prepared by slow filtration of their

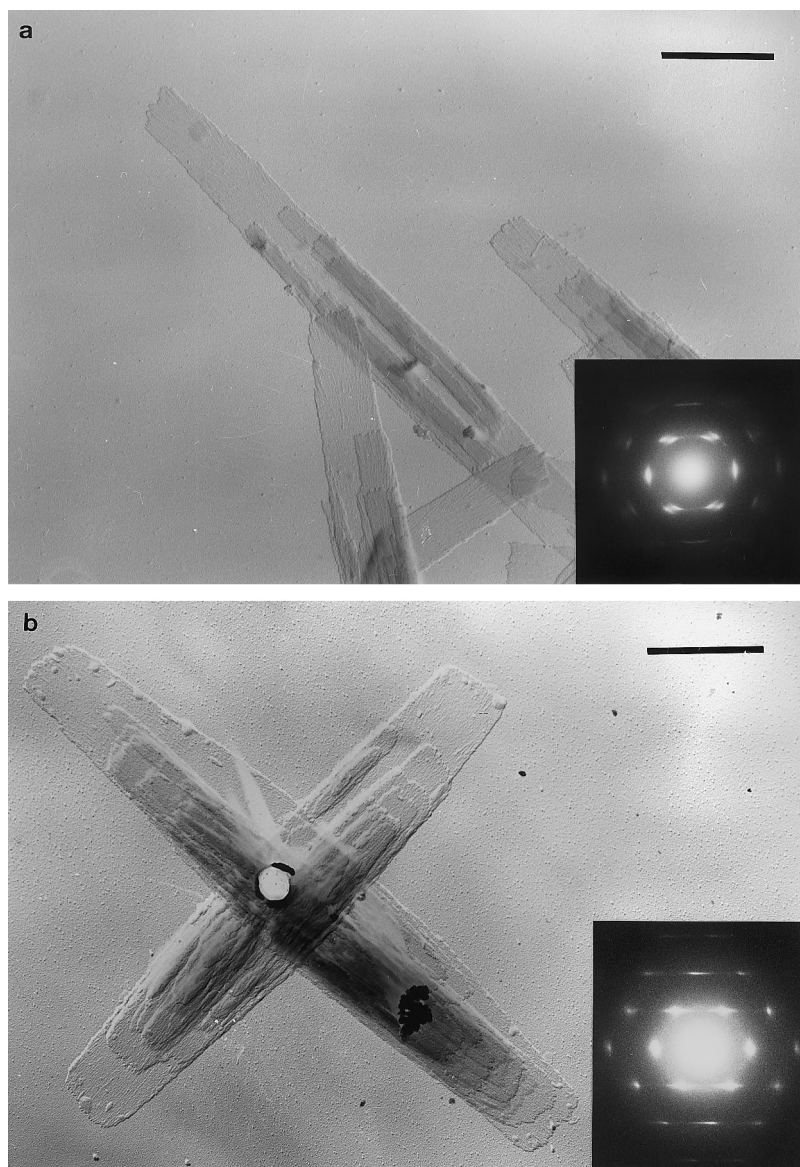


Fig. 3. Lamellar crystals of nylon 46 (a) and nylon 5 (b) grown from glycerin at 177°C. The scale bar represents 1 μm in both cases. Electron diffraction patterns are displayed as insets.

suspensions in butanol. X-ray diffraction patterns were recorded in a modified Statton camera (W.H. Warhus, Wilmington, DE, USA) with graphite-monochromatized copper radiation and they were calibrated with calcite. DSC measurements were made on a Perkin–Elmer DSC-4 instrument at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. ^{13}C NMR were registered on a Bruker AMX-300 instrument operating at 74.3 MHz with samples dissolved in a mixture of deuterated chloroform–trifluoroacetic acid.

4. Computational methods

The same computational strategy already adopted for the study of other nylons [7,13] was applied to nylon 46, nylon 5

and the mixture of them, i.e. energy evaluation of an infinite crystal. This method consists in the generation of the atomic coordinates of the nylon in its crystal lattice determined by diffraction analysis and the energy evaluation of the resulting structure. The program adopted was the PCSP [14] (prediction of crystal structure of polymers), which is able to explore the relative stability of the different arrangements that result for a given side-by-side packing when the azimuthal displacement of the molecules is varied. Accordingly, the method is able to find the lowest energy packing for each nylon.

The energy evaluation of a structure composed by nylon chains in the fully extended conformation was based on the contribution of both van der Waals and electrostatic interactions concerning non-bonded atoms close in the space. These interactions were computed by applying the 12–10

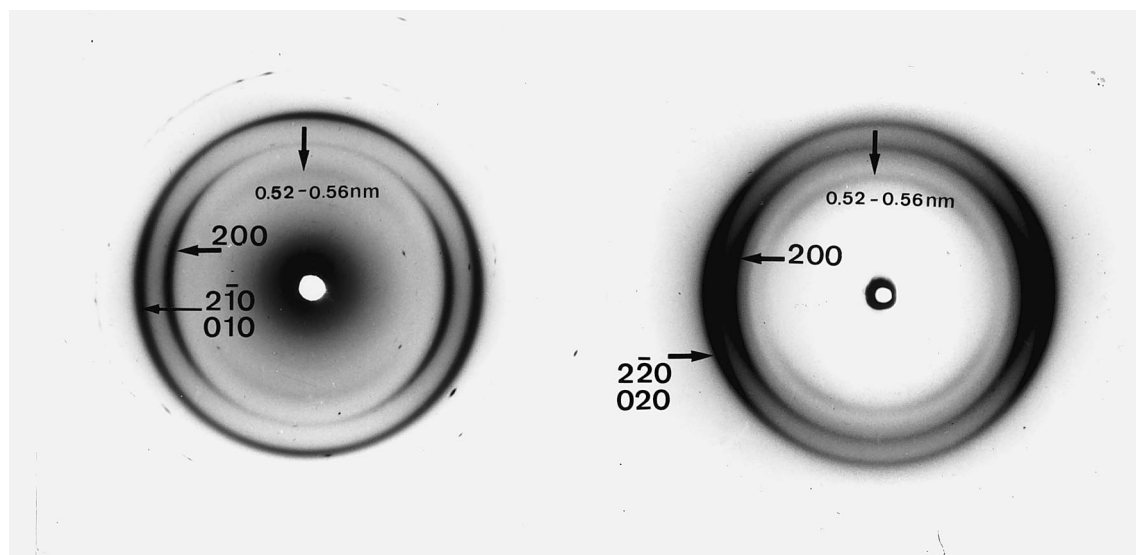


Fig. 4. X-ray diffraction patterns obtained for the sediment of lamellar crystals of nylon 5 (a) and nylon 46 (b).

and Coulombic expressions, respectively. Force-field parameters were taken from AMBER's set [15] with exception of the atomic charges, which were explicitly derived for nylon 46 and nylon 5 using a methodology previously developed by us [16]. The geometry of the nylon molecules was generated using equilibrium bond lengths and angles available in the AMBER libraries [16]. Periodic boundary conditions were applied in the a -, b - and c -axes. A cutoff limit of 0.8 nm was chosen, implying that all atoms of one unit interact with all atoms of another unit if at least one pair of atoms is within the limit. This means that, in practice, many interactions beyond the cutoff limit are taken into account as well. It is worth noting that PCSP calculations neglect both entropic and thermal effects. Nevertheless, these contributions to the relative stability between closely related structures as they are the crystal lattices composed of nylon 46 and nylon 5 chains can reasonably be assumed to be small.

X-ray and electron diffraction patterns were simulated for the most favorable structures using the Cerius² program [17]. Simulations were performed according to the type of sample used for the experiment and the spacing and intensity of the resulting reflections were compared with the experimentally observed values.

All the calculations were performed on Indigo O₂ Silicon Graphics workstation at our laboratory and on IBM-SP2 at the C⁴.

5. Results and discussion

5.1. Nylon 46 and nylon 5 lamellar crystals

Separate electron microscopic studies of nylon 46 and nylon 5 single crystals grown from solution were recently reported [7,9]. The lamellar crystals of both nylons were obtained in glycerin under similar crystallization conditions

including concentration, time and temperature. On re-examining these works, we noticed that nylon 46 crystals are quite similar in morphology to nylon 5 crystals. These two nylons form lamellar morphologies with approximately rectangular shape and about 0.5 μm wide and 7–8 nm thick. For an appropriate comparison between the two nylons, representative pictures of nylon 46 and nylon 5 crystals and their characteristic electron diffraction patterns are reproduced in Fig. 3.

The electron diffraction patterns produced by these crystals correspond in both cases to a twinned structure with the composition plane running parallel to the long dimension of the crystal. The Bragg spacings measured in these patterns are practically indistinguishable for the two nylons and correspond to the projection down the chain axis of almost identical $hk0$ crystal lattices. The parameters determined for on the basis of such measurements were [$a^* = 2.29 \text{ nm}^{-1}$, $b^* = 2.63 \text{ nm}^{-1}$, $\gamma^* = 65^\circ$] and [$a^* = 2.32 \text{ nm}^{-1}$, $b^* = 2.63 \text{ nm}^{-1}$, $\gamma^* = 63^\circ$] for nylon 46 and nylon 5, respectively. The only significant difference between the diagrams of the two nylons is the wider breadth displayed by the signals of nylon 5, which indicates that a lower ordering is attained in the crystal packing of this nylon.

The X-ray diffraction pattern obtained for the sediment of lamellar crystals of nylon 5 (Fig. 4a) is practically indistinguishable from that of nylon 46 (Fig. 4b). Both patterns show two strong equatorial reflections associated to the side-by-side packing of the chains. They also contain a rather diffuse arced signal centered around the meridian with a spacing 0.52–0.56 nm and displaying medium-to-weak intensity. This signal is related to the periodicity of the structure along the chain axis and is indexed as 102 or 101 for nylon 46 and nylon 5, respectively. Occasionally, an extremely weak reflection was detected on the meridian with a spacing of 0.73 nm, which in principle could be

Table 1
X-ray and electron observed and calculated spacings for nylon 46 and nylon 5

d_{obs} (nm)						d_{cald} (nm) ^a	hkl^a
Single crystal ^b		Mat ^c		Film ^d			
46	5	46	5	46	5	46	5
		7.5 s	6.8 s			Lamellae	Lamellae
		3.8 m	3.4 m			Lamellae	Lamellae
		0.73 vwv				Lamellae	Lamellae
0.436 vs	0.430 vs	0.436 s	0.434 s	0.440 vs	0.430 vs	0.436	2 0 0
0.380 vs	0.380 vs	0.378 vs	0.380 vs	0.370 vs	0.372 vs	0.376	2 -1 0
0.380 vs	0.380 vs					0.376	0 1 0
0.241 m	0.245 m	0.238 m	0.243 m	0.239 w	0.232 w	0.241	2 1 0
0.241 m	0.248 m					0.238	4 -1 0
0.219 w	0.225 vw	0.222 w	0.221 w			0.219	4 0 0
0.212 w	0.220 w	0.214 w	0.214 w			0.212	2 -2 0
0.192 m	0.200 m					0.192	0 2 0
0.190 w	0.196 vw					0.190	4 -2 0
0.163 w	0.164 vw					0.163	6 -1 0
		0.52–0.56 w	0.52–0.56 w			0.56	1 0 2 (-1 1 2)
				0.233	0.225 m	0.233	1 1 6 (-1 2 6)
				0.218	0.217 m	0.218	0 2 6 (0 1 6)
				0.193	0.195 w	0.193	2 0 6 (-2 3 6)
				0.122	0.120 m	0.122	0 2 12 (0 1 12)
							0 4 6 (0 2 6)

^a Calculated spacings and indexing for a *P1* triclinic structure with a unit cell having the following parameters: Nylon 46, $a = 0.965$ nm, $b = 0.505$ nm, $c = 1.470$ nm, $\alpha = 55.5^\circ$, $\beta = 90^\circ$, $\gamma = 110.8^\circ$ (two chains in antiparallel arrangement, $\Delta c = 2.33$ c/12). Nylon 5, $a = 0.965$ nm, $b = 1.010$ nm, $c = 0.735$ nm, $\alpha = 55.5^\circ$, $\beta = 90^\circ$, $\gamma = 110.8^\circ$ (four chains in antiparallel arrangement and inverted polarity, $\Delta c = 2.33$ c/12). Indexes in brackets are for a unit cell with $\alpha = 42.9^\circ$, $\gamma = 107^\circ$ and $b = 0.613$ or 1.226 nm for nylon 46 and nylon 5, respectively, which results from a $\Delta c = 3.66$ c/12. In all cases, the crystal volume is 0.133 nm³ residue⁻¹ which results in a calculated density of 1.28 g ml⁻¹ for the two nylons.

^b Lamellar crystals grown in glycerin at 177°C .

^c X-ray diffraction data obtained from sediments of crystals.

^d Obtained by stroking from a formic acid solution. Intensities visually estimated and denoted by vs: very strong, s: strong, m: medium, w: weak, vw: very weak, vwv: very very weak.

associated to the distance and half distance of the repeating unit of nylon 5 and nylon 46, respectively. However, it can be also made to correspond to the scattering emanating from the stack of ~ 7 – 8 nm-thick lamellae [7]. Table 1 lists the observed and calculated X-ray and electron diffraction spacings for the two nylons.

5.2. Cocrystallization of nylon 5 and nylon 46

In view of the astonishing similarities existing between nylon 46 and nylon 5 single crystals, we decided to investigate the simultaneous crystallization of the two nylons. For this, a mixture containing equal amounts of nylon 46 and nylon 5 was dissolved in glycerin at 200 – 220°C to have a 0.1% (w/w) solution. This solution was immediately cooled down to 177°C where crystallization took place in a few hours. The evolved crystals were collected by centrifugation and analyzed by NMR and differential scanning calorimetry prior to being studied by electron microscopy.

The ¹³C spectrum of the crystals obtained in the crystallization of the nylon mixture is shown in Fig. 5 together with those recorded from the crystals produced in the crystallization of nylons 46 and 5 separately. The chemical shifts of the signals appearing in each spectrum are compared in

Table 2. The spectrum of the mixture contains seven methylene signals, three of them arising from nylon 46 and the remaining four coming from nylon 5. According to expectations, two carbonyl peaks are observed. A comparative estimation of the areas of the respective peaks revealed that approximately equal amounts of the two nylons are contained in the precipitate formed upon crystallization. In Fig. 6, the DSC traces of the crystals of nylon 46 and nylon 5 crystallized separately are compared with those recorded from a mixture of such crystals and from the crystals obtained in the crystallization of the two nylons together. Data for melting peaks measured for each case are listed in Table 2. Sharp endothermic peaks at 287 and 280°C attributable to the melting of the crystals are, respectively, observed for nylon 46 and nylon 5. As logically expected, two peaks at exactly the same temperatures are found in the thermogram registered from a sample prepared by physical mixing of the crystals of the two nylons. On the contrary, the trace produced by the sample crystallized from the mixed solution was found to consist of a single peak at 289°C . This result is consistent with that should be expected if nylon 46 and nylon 5 were incorporated in the same crystal lattice.

The crystals obtained in the crystallization of the mixed solution are shown in Fig. 7. They are similar in shape and

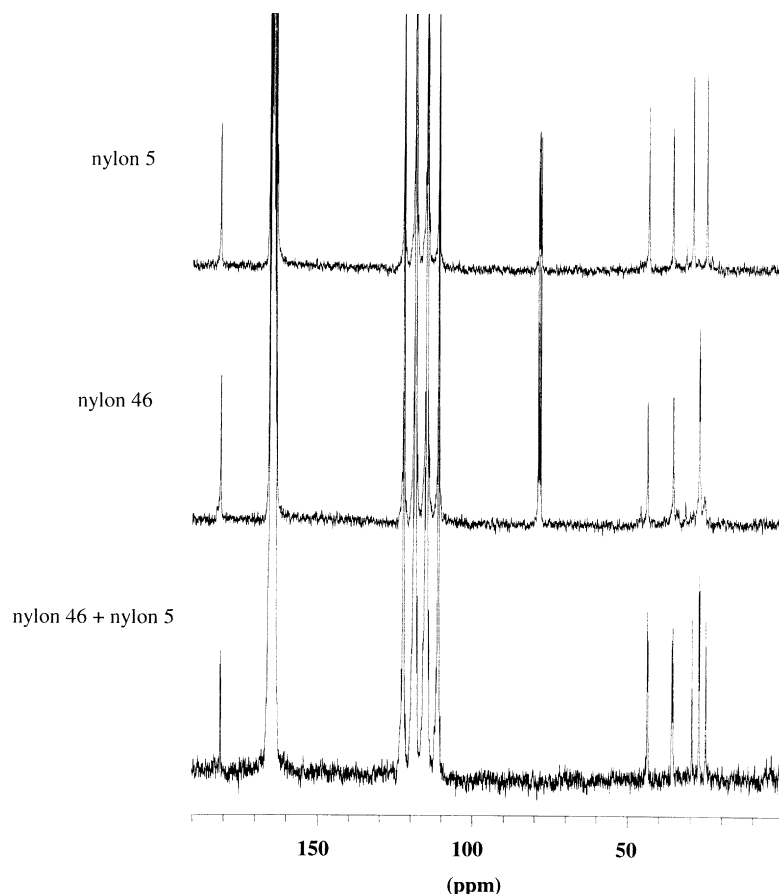


Fig. 5. ^{13}C NMR spectra of nylon solutions (from top to bottom): nylon 5 crystals, nylon 46 crystals, and mixed crystals grown from a solution containing equal amounts of nylon 46 and nylon 5.

size to those obtained in the crystallization of the separated nylons although the serrated nature of the tips is even more noticeable. Decoration with polyethylene afforded disordered patterns with no signs revealing the occurrence of regular chain folding; this is also the result obtained in the polyethylene decoration of individual lamellar crystals of both nylon 46 and nylon 5 when crystallized under the same conditions that are used here for the crystallization of the mixture. The electron diffraction pattern recorded

from these mixed crystals is similar in symmetry and spacing to those obtained from pure crystals but reflections display a considerable breadth indicating a crystal disorder of characteristics similar to that observed for nylon 5 crystals. The X-ray diffraction pattern recorded from the sediment of mixed crystals contains the expected reflections, specifically that spacing 0.52–0.56 nm, which has its homologs in the pictures recorded from nylon 46 and nylon 5 sediments. On the other hand, no reflection in the proximity

Table 2

Chemical shifts in the ^{13}C NMR spectra and melting temperatures of grown solution crystals of nylons 5 and 46 and their mixtures (crystals grown in glycerin at 177°C)

Sample	δ (ppm)					T (°C)
Nylon 46 crystals ^a	179.35	42.06	33.95	25.59	25.36	287
Nylon 5 crystals ^a	179.71	42.09	34.40	27.90	23.52	280
Nylon 46 + nylon 5 crystal mixture ^b						280, 287
(Nylon 46 + nylon 5) mixed crystals ^c	179.71; 179.35	42.05; 42.01	34.40; 33.83	27.94; 25.51	23.53; 25.29	289

^a Crystals obtained from pure nylons.

^b Sample consisting of a (1:1) physical mixture of nylon 46 and nylon 5 crystals.

^c Crystals grown from a solution containing a (1:1) mixture of nylon 46 and nylon 5.

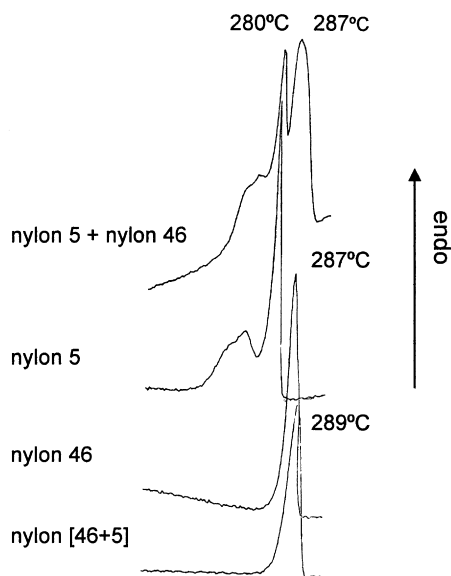


Fig. 6. Heating DSC traces of sediments of nylon crystals (from top to bottom): physical mixture of individual nylon 46 and nylon 5 crystals, individual nylon 46 crystals, individual nylon 5 crystals, crystals grown from a mixed solution containing equal amounts of the two nylons.

of 0.75 nm ascribable to the period of the chain of a structure with both $\alpha = \beta = 90^\circ$ (002 or 001 for nylon 46 and nylon 5, respectively) could be detected in such a diagram.

5.3. Electron diffraction of oriented films

Ultrathin uniaxially oriented films suitable for electron diffraction were prepared by stroking from concentrated formic acid solutions of nylon 46, nylon 5 and of a mixture of equal amounts of the two polymers. As can be seen in Fig.

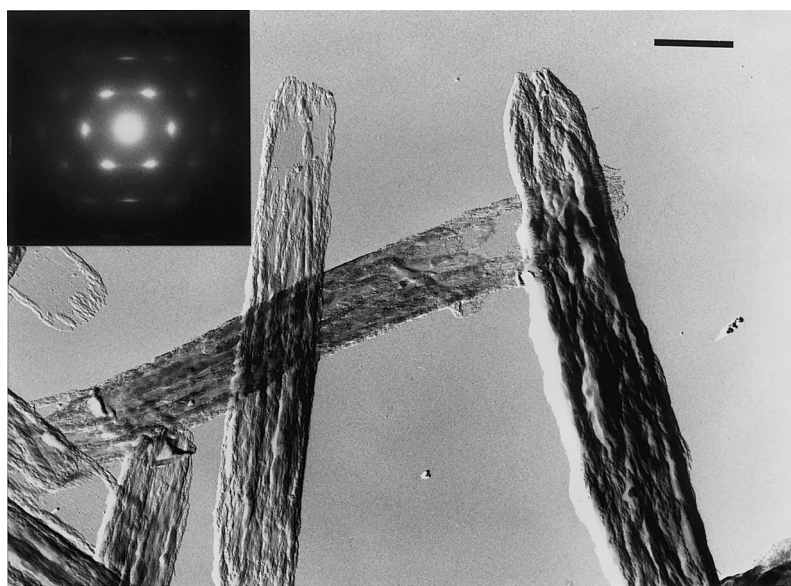


Fig. 7. Lamellar crystals grown at 177°C from a glycerin solution containing equal amounts of nylon 46 and nylon 5. The electron diffraction pattern obtained from one of them is shown in the inset.

8, very similar fiber diffraction patterns were produced by this method. Thus, the two fingerprint reflections at 0.44 and 0.37 nm on the equator of the three diagrams display similar intensities and orientation degrees. Also the 0.24 nm layer-line, indexed as $hk6$ for nylon 46 and $hk3$ for nylon 5 appears with similar characteristics.

The fact that the layer line at 0.24 nm appears in the diagram of the mixture as an array of discrete spots is taken as demonstrative that hydrogen-bonded sheets of the two nylons are mixed up keeping a certain longitudinal register. Worthy of notice is also the reflection appearing on the meridian with a spacing of 0.122 nm indicative of the presence of a fully extended conformation. These results are consistent with a statistical lattice having the same reciprocal ab^* plane as the individual nylons but with a c parameter of 0.75 nm.

5.4. Crystal structure of nylon 46 and nylon 5

The diffraction results obtained for nylon 46 and nylon 5 indicate that for the two compounds, the hydrogen-bonded sheets are separated 0.38 nm and the interchain distance within the sheets is 0.48 nm (Fig. 9). However, the hydrogen bond scheme in the sheets, the model of stacking that is adopted by these sheets as well as the magnitude of the displacement between adjacent sheets in the c -direction (Δc) can not be determined from the information provided by electron and X-ray diffractions. All these possibilities have been examined by energy calculations.

The profiles representing the energy of system against Δc for all the feasible models of nylon 46 and nylon 5 are displayed in Fig. 10. The extent of the displacement is expressed as $c/12$ or $c/6$ units for nylon 46 and nylon 5, respectively. For a more straightforward comparison,

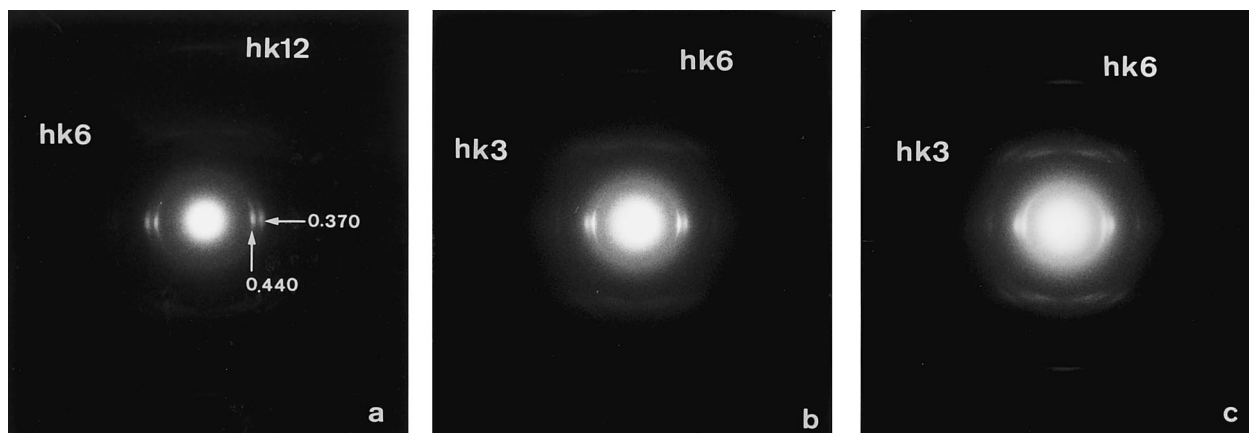


Fig. 8. Electron diffraction of oriented films of nylon 46 (a), nylon 5 (b) and a (1:1) mixture of the two nylons. The chain axis is vertical and the apparent camera length is the same for the three diagrams.

energy differences are referred to one residue in the case of nylon 5 and to a half of residue in the case of nylon 46.

All the traces corresponding to nylon 46 (Fig. 10a) are perfectly symmetrical with respect to the half point of the plot. This means that, from a structural point of view, the residue of nylon 46 can be taken as the half of the chemical residue and therefore similarity with nylon 5 made more evident. Furthermore, two pseudosymmetrical points at $3 c/12$ and $9 c/12$ are found for models with a normal arrangement of hydrogen bonds indicating that two crystal struc-

tures with the same model but with shears Δc and $(c/2) - \Delta c$ have very similar packing energies. As can be seen, a low-energy region between $1.5 c/12$ and $4.5 c/12$ is found, out of which the energy suddenly increases. Models falling out of this region can be discarded. The most stable minima within this region correspond to the displacements of 2.33 and 3.66 main chain atoms. Such energy minima are for model I with hydrogen bonds in the normal scheme and sheets progressively staggered in a β -arrangement.

Fig. 10b shows the energy plot obtained for nylon 5. In

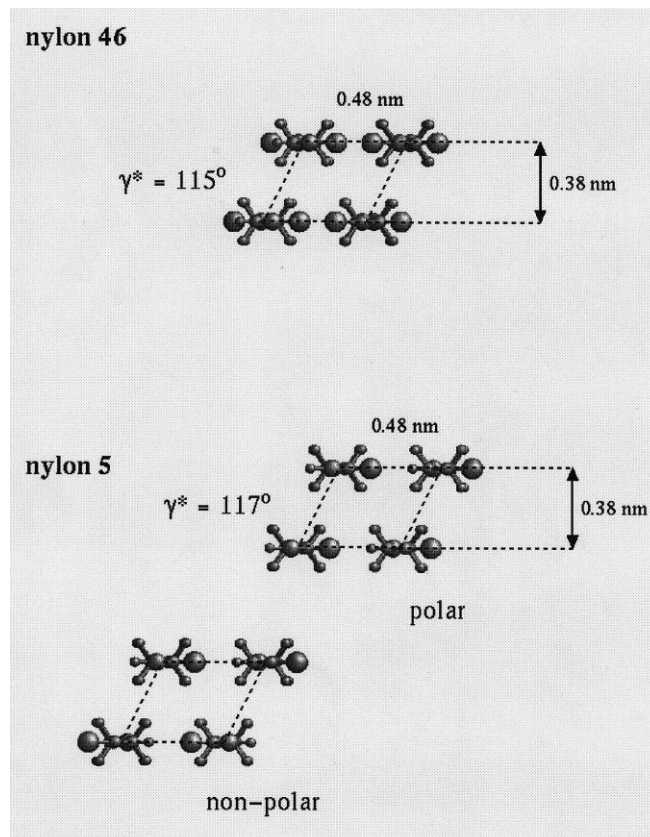


Fig. 9. Schematic representation of the information for the crystal structures of nylon 46 and nylon 5 obtained from X-ray and electron diffraction.

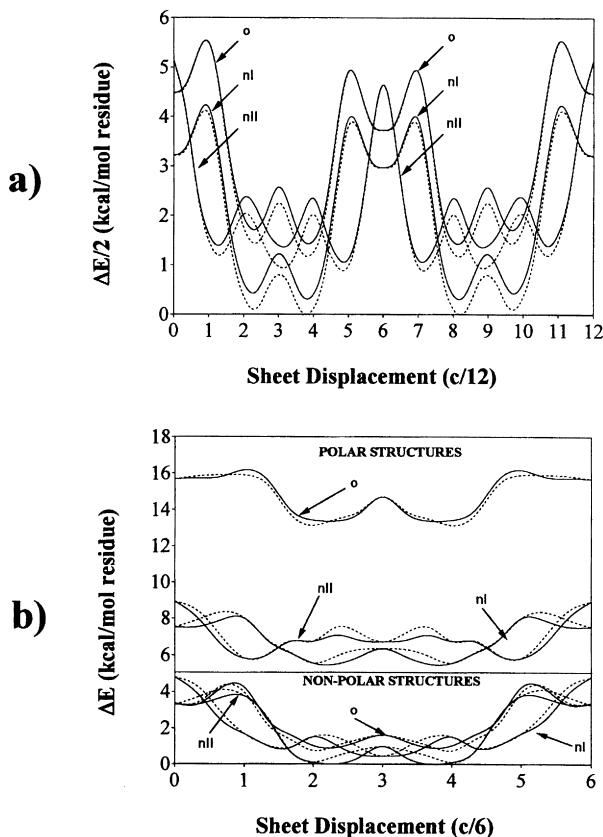


Fig. 10. Energy profiles vs c -displacement for nylon 46 (a) and nylon 5 (b) crystal models. Solid and dotted lines stand for α - and β -models, respectively.

this case, all the polar models are disfavored by more than $5 \text{ kcal mol}^{-1} \text{ residue}^{-1}$ with respect to their analogous non-polar models whichever is the displacement along the c -axis. Such an energy difference is great enough to discard the existence of polar structures in nylon 5 crystals. A detailed inspection to the non-polar structures reveals that the overall shape of the traces is quite similar to those obtained for nylon 46 with energy minima appearing for the same sheet displacements. In this case, however, absolute minima for nylon 5 are found for the α II model in the normal scheme and for the β I model in the oblique scheme, the latter only for a displacement of $3.66 \text{ c}/12$. The energy of models I and II become closer for a displacement of $3 \text{ c}/12$; at this point the α - and β -arrangements turn out to be identical.

As shown in Table 1, indexing of all the diffraction data for nylon 46 and nylon 5 can be satisfactorily made on the basis of a common crystal lattice. An excellent correspondence between observed and calculated data is achieved for a shift displacement between successive sheets of either 2.33 or 3.66 main chain atoms. However no differences can be appreciated, which allow us to discriminate between α - and β -arrangements. The energy traces displayed in Fig. 10 show that for both nylons the difference in energy between the two more stable models is very low, less than

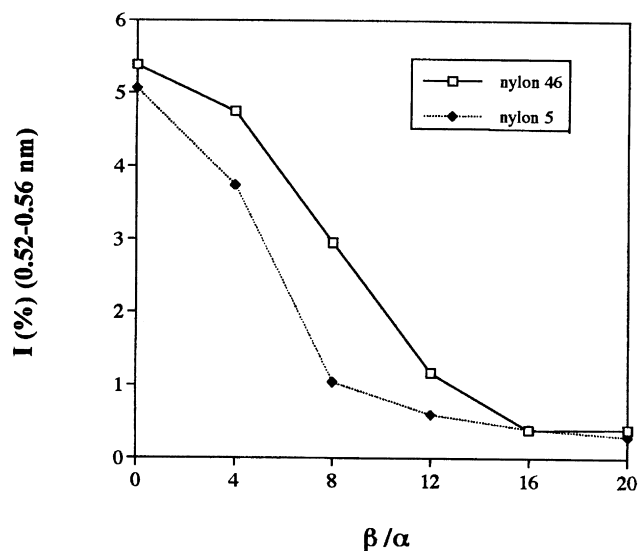


Fig. 11. Intensity fluctuation of the $0.52\text{--}0.56 \text{ nm}$ diffraction scattering of nylon 46 and nylon 5 crystals as a function of the ratio in α - and β -forms.

$0.5 \text{ kcal mol}^{-1} \text{ residue}^{-1}$. Accordingly, the structure of both nylon 46 and nylon 5 should be assumed to consist of a mixture α - and β -arrangements. A structure of particular interest is that with a constant sheet displacement of $3 \text{ c}/12$, which could be taken as intermediate between the two favored models. This structure would be α and β at the same time and fully compatible with experimental diffraction results. We will not insist further on this structure since it presents a local energy maximum in the energy plot. On the other hand, a disordered structure with a sheet shearing distance oscillating at random between 2.33 and $3.66 \text{ c}/12$ would be in disagreement with the discrete scattering observed in the fiber electron diffraction patterns shown in Fig. 8.

The more stable models for the two nylons were built with the Cerius² software and their X-ray diffraction patterns were simulated for sediments of lamellar crystals with the same dimensions as those experimentally observed. Models with displacements of 2.33 and $3.66 \text{ c}/12$ produce diffraction scattering profiles that are identical in the case of nylon 5 and almost indistinguishable in the case of nylon 46. The calculated intensities for reflections with spacings below 0.24 nm do not show significant differences when different models are compared. The $0.52\text{--}0.56 \text{ nm}$ diffuse signal observed in the X-ray diagram is poorly simulated by structures in the β -form except when the sheets displacement is a half of the distance between amide groups, i.e. for $3 \text{ c}/12$. The absence of the 0.73 nm reflection in the X-ray diagrams of nylon 46 and nylon 5, as it is experimentally found, appears to be compatible with any arrangement except for an α -form with sheets displaced one main chain bond, i.e. $\text{c}/12$. In this case, such reflection should be present with an intensity higher than that displayed by the $0.52\text{--}0.56 \text{ nm}$ signal, which is contrary to all observations.

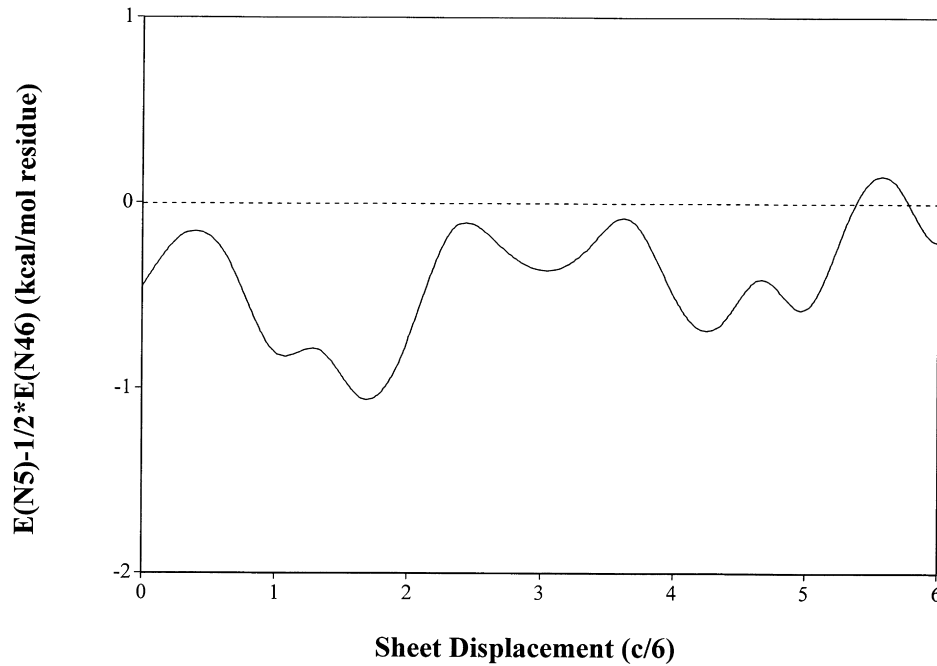


Fig. 12. Energy difference profile vs c -displacement between the most stable model of nylon 46 and that of nylon 5.

Both energy calculations and modeling simulations point to a statistical structure composed of α - and β -arrangements with a displacement between sheets of 2.33 or 3.66 main chain bonds as the most favored model for nylon 46 and nylon 5. In order to evaluate the content in α - and β -forms in the two nylons, we have compared the simulated X-ray diffraction patterns with the experimental one for these two favored models. Fig. 11 represents the calculated intensity of the 0.52–0.56 nm signal against the β/α ratio for both nylon 46 and nylon 5. This signal appears to be the only one

sensitive to variations of the structure along the c -axis with a calculated intensity oscillating between about 5 and 0%. It should be remarked that this signal has been indexed as 102 and 101 for nylon 46 and nylon 5, respectively, and that the 00 l reflection (002 or 001 according to the nylon) falls out this spacing interval. The maximum value corresponds to a β/α ratio equal to 0, which is a pure α -structure. The minimum value corresponds to a pure β -form. The intensity experimentally measured for the 0.52–0.56 nm-signal is about 4%. This indicates that crystals could be composed

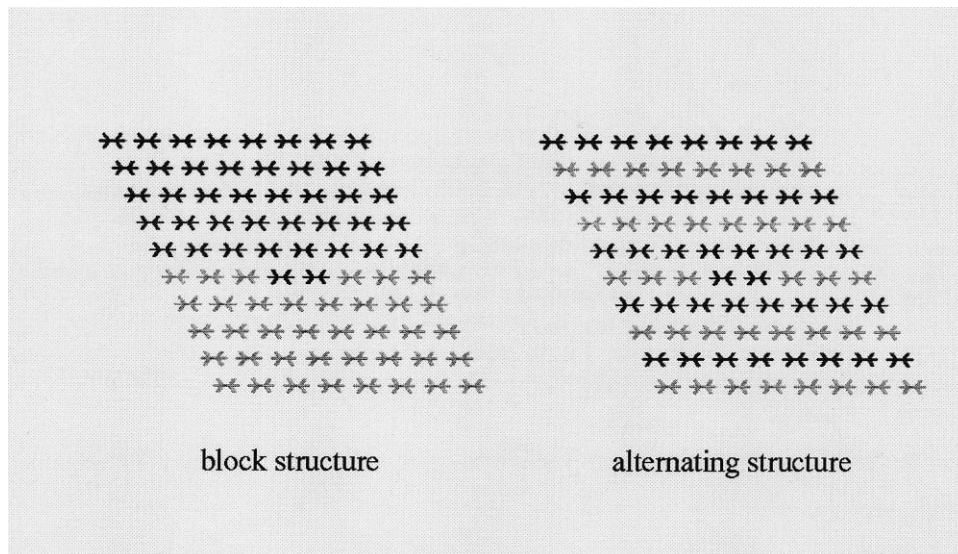


Fig. 13. Schematic representation of block and alternating structures for the cocrystals of nylon 46 and nylon 5 as viewed along down the c -axis.

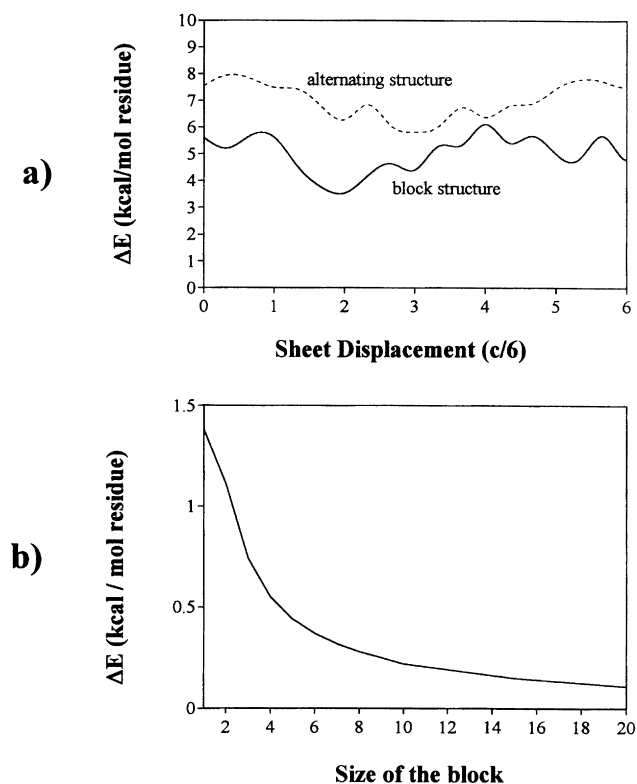


Fig. 14. (a) Energy profiles vs *c*-displacement for the two structures considered for the cocrystals of nylon 46 and nylon 5. (b) Energy profiles vs the size of the block.

of a mixture of both forms with a α/β ratio between 3 and 6. Although the β -form appears to be predominant in both nylons, the content in α -form is slightly higher in nylon 5.

The description of crystals of nylon 46 and nylon 5 as a mixture of α - and β -arrangements is consistent with experimental data reported in this work. Thus, the absence of the 00 l reflection (001 for nylon 5 or 002 for nylon 46) in the X-ray diffraction patterns leads to discard the occurrence of pure α or β structures compatible with energy packing results. Furthermore, the striated appearance displayed by the crystal surface is considered to be a consequence of the accordion-type nature of the lamella with a frequency of plying proportional to the content in α -form.

5.5. Energy analysis of mixed crystals of nylon 46 and nylon 5

In principle, cocrystallization of nylon 5 and nylon 46 would be feasible if the energies of their respective crystal lattices were similar for a common crystal model. Fig. 12 shows the energy difference between nylon 5 and nylon 46 crystals against the sheet displacement. Differences in energy are less than 1 kcal mol⁻¹ residue⁻¹ for the whole range of displacements. It is interesting to notice that the smaller differences appear for those displacements at which individual nylon crystals display energy minima. These results indicate that the system fulfills the basic energy

requirements needed for the cocrystallization of nylon 46 and nylon 5.

An energy analysis was performed on simulated cocrystals in order to predict the compatibility of the two nylons to share a common crystal lattice. For this purpose, some assumptions were considered. We used the most favored crystal models for each nylon and hydrogen-bonded sheets are composed of a single nylon. Although a large number of combinations is possible, we examined only those structures containing equal number of sheets of the two nylons. Two cases, which are illustrated in Fig. 13, were considered: (i) a structure made of blocks of nylon 46 sheets and blocks of nylon 5 sheets; and (ii) a structure made of alternating sheets of nylon 46 and nylon 5. In both cases, the energy of two adjacent pairs of chains, one of nylon 46 and the other of nylon 5, was computed and the result compared with the values obtained for each separated nylon.

Fig. 14a shows the energy profiles obtained for the two cocrystal models. The energy values are referred to nylon 46, although no significant differences resulted when they were referred to nylon 5. For the two models, we find an energy surplus between 4 and 8 kcal mol⁻¹ residue⁻¹. Statistical models containing equal amounts of the two nylons would have energies intermediate between those computed for the two extreme models. These results reveal that the alternating model is clearly disfavored and that the block model would be only acceptable if the frequency of defects is reasonably low.

In order to determine what can be the acceptable size for the blocks in a cocrystal of nylon 46 and nylon 5, a model consisting of one block of nylon 46 inserted in a crystal of nylon 5 was analyzed. The energy of the two central chains of every sheet of nylon 46 was evaluated for a block increasing in size from 1 to 20 sheets. Fig. 14b represents the average energy for all the central chain pairs of the nylon 46 block against the size of the block expressed as the number of sheets comprised in the block. We see that energy rapidly decreases with the size of the block made of 10 or more sheets. This means that the existence of blocks with such a size or larger would be energetically acceptable. Similar conclusions were reached when the analysis was carried out on a model made of a block of nylon 5 inserted in a crystal of nylon 46.

6. Conclusions

The conclusions drawn from this study may be summarized as follows:

- (i) Nylon 46 and nylon 5 lamellar crystals have essentially the same structure, which is made of hydrogen-bonded sheets with the chains in fully extended conformation and hydrogen bonds arranged in the normal scheme.
- (ii) The most favored model for the stacking of the sheets

consists of a statistical mixture of α - and β -forms. The displacement between successive sheets is such that the amide groups become separated by ± 2.3 main chain atoms along the c -axis of the structure.

(iii) Experimental results are compatible with the occurrence of cocrystallization of nylon 46 and nylon 5. However, energy calculations indicate that the insertion of a nylon in the crystal lattice of the other is disfavored. Cocrystals, if they exist, will be preferentially made of homogeneous blocks of each nylon provided that the blocks are comprised of about 10 hydrogen-bonded sheets at least.

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