Morphology and crystalline structure of nylon-2/6

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We have studied by X-ray diffraction and electron microscopy the crystalline structure of the copolyamide nylon-2/6 or poly(glycyl-ε-aminocaproic acid). We have found a hexagonal form of the type known for polyglycine II with helical chains linked intermolecularly at an interchain distance of 4.79 Å. We have obtained single crystals of this form from a formic acid solution. We have previously described this form in other nylons, so that it appears to be a new general structure for nylons, found in copolyamides which contain glycine or related monomers. We have also observed another modification made of hydrogen-bonded sheets which appear as ribbonlike lamellar crystals. The intersheet spacing measured for the latter form is 3.65 Å, intermediate between those found in polyglycine I and in the α form of nylon-6.

(Keywords: nylon-2/6; regular copolyamide; nylon crystallization; nylon single crystals; nylon structure)

INTRODUCTION

In general, hydrogen bonds are the major factor in deciding the specific molecular conformation adopted by a polyamide chain in the solid state. A layered structure based on a bidimensional arrangement of the hydrogen bonds is the only crystalline model observed in standard nylons[1]. In contrast, polyglycine, a polypeptide which can be regarded as nylon-2, is able to adopt a different structure (PGII) made of threefold helices[2]. In this structure each chain becomes hydrogen bonded to its six neighbours so that a three-dimensional scheme of hydrogen bridges is generated. The PGII model is of particular interest as a similar arrangement is found in collagen fibres[3].

We have recently reported that the PGII structure is also adopted by nylons-2/3[4], 2/3/3 and 1/3 (submitted for publication). In this paper we describe a structural study carried out on nylon-2/6, a regularly alternating copolyamide made of glycine and ε-aminocaproic acid. This nylon has the same average concentration of amide groups as nylon-4, but it is much more hydrophilic and thermally stable. A particular feature of this polymer is its biodegradability[5].

EXPERIMENTAL

Synthesis of nylon-2/6

Nylon-2/6 was prepared by polycondensation of the glycyl-ε-aminocaproic pentachlorophenyl ester bromohydrate. Polymerization was carried out at room temperature over a period of five days with dimethylsulphoxide as solvent and triethylamine as initiator. The polymer was separated from the reaction mixture by adding ethyl ether. The crude material was then washed successively with water, ethanol and ethyl ether. The chemical constitution of the polymer was ascertained by elemental analysis, infra-red spectroscopy and chromatography. A relative content of glycine to ε-aminocaproic acid equal to unity was observed in a chromatogram of a sample of nylon-2/6 hydrolysed with 6N HCl at 110°C. An intrinsic viscosity of $0.32\,\mathrm{dl\,g^{-1}}$ was determined for this polymer in dichloroacetic acid at 25°C. On the other hand a number average molecular weight of 7000 was estimated by the 2,4-dinitrofluorobenzene method[6]. Density measurements were performed by the flotation method. Mixtures of water and aqueous 25% potassium iodide solutions were used. A value of $1.32\,\mathrm{g\,ml^{-1}}$ was found at 25°C.

Structural methods

Strong hydrogen-bond-breaking solvents are required in order to dissolve nylon-2/6. Crystallization is then achieved by adding a precipitating agent (water or n-butanol) to a dilute solution of the polymer in either formic acid or dichloroacetic acid. Crystals are separated by centrifugation and then washed twice with n-butanol.

Samples for X-ray diffraction were prepared by drying the sediment of crystals under vacuum. Powder diagrams were recorded at room temperature in a modified Statton camera (W. R. Warhus, Wilmington, Delaware, USA) with Cu Kα radiation from a graphite monochromator.

Crystals for electron microscopy were shadowed with platinum–carbon at an angle of 15°. Evaporated gold was used for internal calibration of the electron diffraction patterns. We used a Philips EM-301 electron microscope operating at 80 kV in bright-field mode and at 100 kV in the selected-area mode. The flux of electrons was kept at a minimum in all cases. Specimens were tilted at definite angles in a eucentric goniometer stage.

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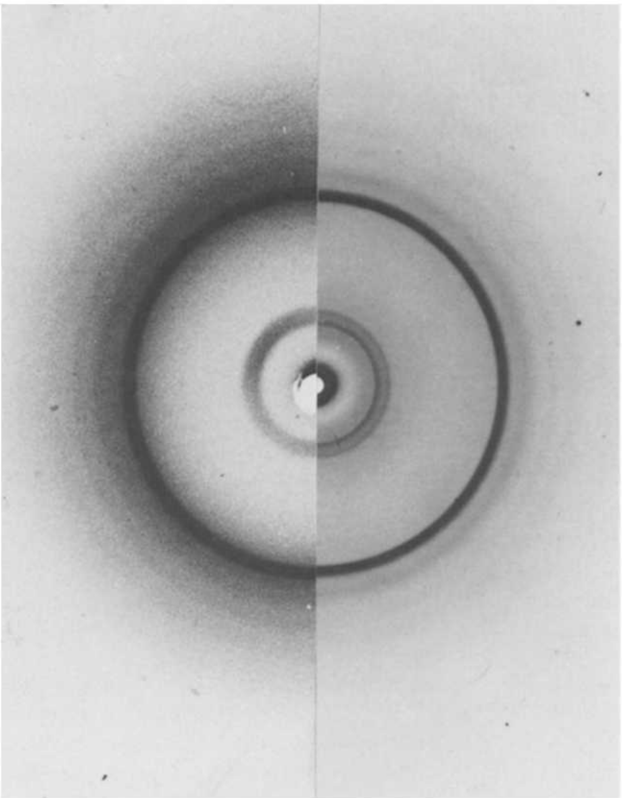

Figure 1 X-ray powder diffraction pattern of nylon-2/6 in the hexagonal form. Two patterns are shown in order to illustrate the small structural variations discussed in the text. The strongest ring corresponds to the 1 0 0 spacing

RESULTS

X-ray diffraction

As has been observed with polyglycine and nylon-2/3, no orientation is obtained when a concentrated solution of nylon-2/6 is stretched by the standard laboratory procedures. The powder X-ray diagrams shown in *Figure 1* were recorded from samples that had been crystallized from formic acid by adding an equivalent volume of water at 96°C. The spacings calculated from such patterns are given in *Table 1*. A very strong ring with Bragg spacing at about 4.15 Å is always present, while all other reflections are rather weak. These are features normally observed in powder diagrams of polymers with the PGII structure[2,4]. We interpret our results as due to a threefold helix with three residues per two turns which can easily be constructed with the nylon-2/6 chain. A residue height of about 11.7 Å results and both NH and CO groups are pointing into three directions at 120° angles. Such a helix fits well in a hexagonal lattice with $a = 4.79$ Å, where each chain is linked by hydrogen bonds to its six neighbours (*Figure 2*). Other structures differing in the up–down arrangement of neighbouring chains may also be imagined. As no data are provided to justify a larger cell, we have chosen the simplest, containing one chain. The calculated density for this structure turns out to be 1.32, in full agreement with the observed density.

With respect to the X-ray patterns shown in *Figure 1*, we should note that, after several recrystallizations in hot formic acid, the diffuse ring at about 11.5 Å is replaced by two sharp reflections at 12.14 and 10.17 Å, which are sometimes accompanied by a very weak ring at 8.73 Å. These values might correspond to the fifth, sixth and seventh orders of a basic 60.9 Å spacing, but no reflection at low angles could be found in this region. Another puzzling feature of some of our patterns is the presence of diffuse rings at 3.65 and 3.87 Å, whereas in other cases only the ring at 3.73 Å is observed. All these features are found in the two patterns presented in *Figure 1*.

With the results presently available it does not appear possible to determine with accuracy the dimensions of the polymer chains in the *c* direction, as well as the relation in the orientation of neighbouring molecules. We are trying to obtain oriented samples with this objective.

Significant changes are detected in the X-ray powder diagram of nylon-2/6 when the sample has been

Table 1 Observed spacings *d* (Å) for the hexagonal form of nylon-2/6

X-ray (powder pattern)[a]	Electron diffraction (single-crystal tilt angle, approx.) 0°	15°	30°	40°
12.14 m				
(11.5 d)				
10.17 w				
8.73 vw				
4.15 vs	4.15	4.10		
(3.87 w)			3.88	
3.73 m				
(3.65 w)				
3.36 m				3.40
3.09 w				
2.81 w				
2.40 m	2.39			
2.32 w				

[a] Intensities are visually estimated: vs, very strong; m, medium; w, weak; vw, very weak; d, diffuse. The spacings in parentheses are only observed in some cases, as discussed in detail in the text. All measurements are the average of several values. A maximum error of 1% is estimated

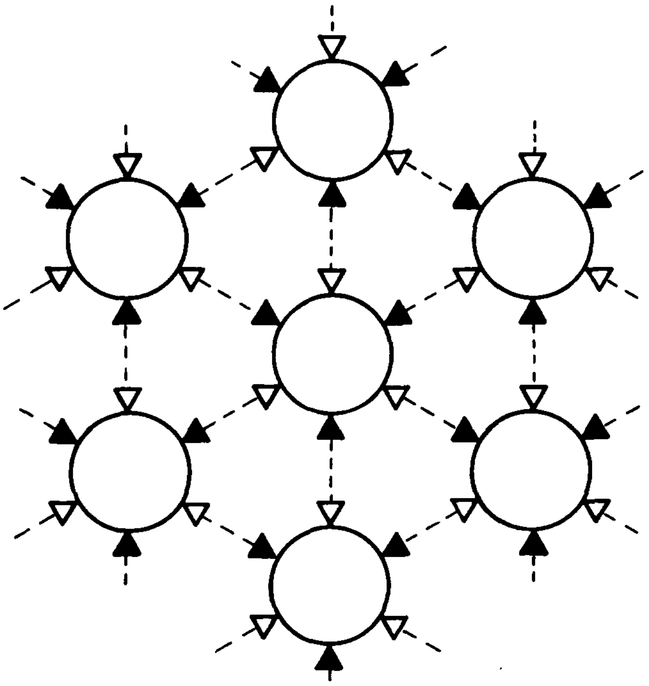

Figure 2 Scheme of the hexagonal lattice of nylon-2/6. The projected chain axes are indicated as circles and the hydrogen bond directions by broken lines. Full and empty triangles stand for CO and NH respectively

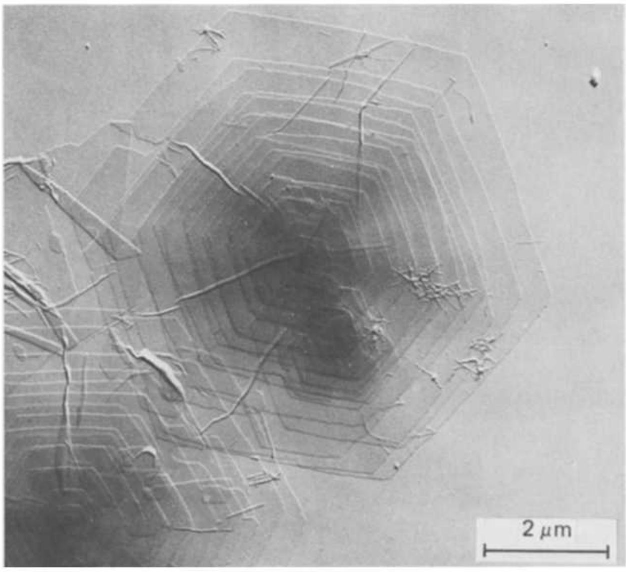

Figure 3 Lamellar crystals of nylon-2/6 in the hexagonal form Crystallized from formic acid–water

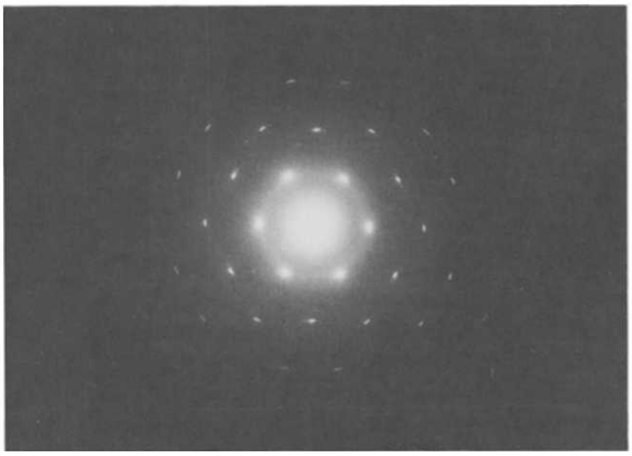

Figure 4 Single-crystal electron diffraction pattern of a hexagonal crystal such as that shown in *Figure 3*; $a = 4.79$ Å

crystallized from dichloroacetic acid instead of formic acid. A new reflection with a 4.38 Å spacing appears and the intensity of the ring at 3.63 Å is notably increased. As we will see below, a second crystalline form is generated under these conditions.

Hexagonal crystals

Well defined hexagonal lamellae of nylon-2/6 are formed when the polymer is precipitated from formic acid by adding one-and-a-half volumes of n-butanol at 96°C. They are about 50 Å thick and their sides are several micrometres long, as shown in *Figure 3*. The electron diffraction pattern of these crystals is shown in *Figure 4*. It is interpreted as arising from the projection along the *c* axis of the hexagonal lattice described above. The polymer chains are nearly normal to the basal plane of the lamellae and they must therefore be folded back and forth. When the crystal is tilted at different angles around its 1 1 0 axis, some of the electron diffraction spots are displaced, as indicated in *Table 1*. This change is due to both the thin nature of the crystals and the appearance of *h* 0 *l* reflections in the pattern.

Thick toroidal morphologies known as doughnuts are in turn produced when precipitation of nylon-2/6 is induced by adding water instead of n-butanol. The same result is also observed when the crystallization temperature is lowered. Such entities diffract the electrons as single crystals, so that the diagrams obtained are indistinguishable from that shown in *Figure 4*. Some polypeptides are known to give this kind of structure[7,8] and we have also observed them in precipitates of nylons-2/3, 2/3/3 and 1/3 (to be published). To our knowledge no satisfactory interpretation for the formation of these morphologies has been given so far. In some of our preparations of nylon-2/6 we have encountered structures intermediate between a doughnut-shaped morphology and a single crystal (*Figure 5*). These intermediate structures suggest an explanation for the origin of 'doughnuts', since abundant screw dislocations are seen to emerge on the periphery of hexagonal lamellae. Although no simple reason is found to justify such a preference, the doughnut shape appears to be a consequence of an exaggerated development of such overgrowths on the borders of the hexagons.

Extended chain form

Long 40–50 Å thick ribbonlike lamellae are occasionally found in the precipitates of nylon-2/6 obtained from formic acid (*Figure 6*). They tend to form networks usually associated with the hexagonal crystals which are clearly predominant in this type of preparation. Such ribbons are unfortunately too narrow to give adequate single-crystal electron diffraction patterns. Their electron diffraction powder diagram contains only

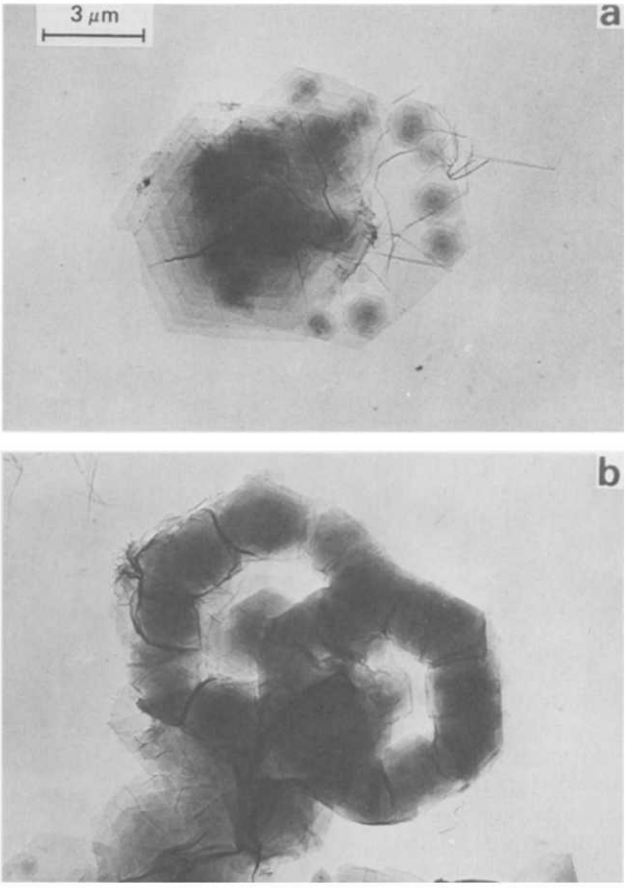

Figure 5 Two successive stages in the formation of doughnut-like morphologies in nylon-2/6. (a) Peripheral overgrowths start to appear on a large lamella. (b) Further overgrowing results in a doughnut shape

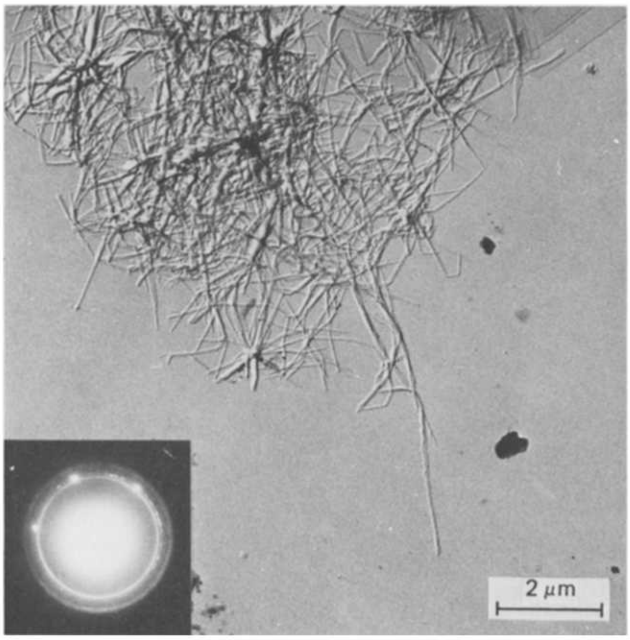

Figure 6 Ribbonlike lamellae of the monoclinic form of nylon-2/6 and their electron diffraction pattern (inset)

two rings with spacings of 4.38 and 3.65 Å. These values coincide with those obtained by X-ray diffraction from a sample of nylon-2/6 precipitated from dichloroacetic acid, a solvent which apparently enhances the growth of this second crystalline form.

A great resemblance in both morphology and diffraction spacings exists between these ribbonlike crystals and those described for the rippled sheet structure of polyglycine (PGI)[9,10] as well as for the α form of nylon-6[11]. This analogy leads us to conclude that they have a sheet structure made of extended chains. The intersheet spacing is thus 3.65 Å, a figure intermediate between those corresponding to PGI (3.45 Å) and nylon-6 (3.8 Å). It is indeed a reasonable average value. The 4.38 Å spacing corresponds to the interplanar distance and is indexed as 1 0 0, since this value is practically identical with that found in both PGI and nylon-6. By analogy, a monoclinic lattice with $a = 4.76$ Å, $c = 3.96$ Å, $\beta = 113°$ is suggested. Although we have no data concerning the chain axis, an essentially extended chain conformation must be assumed. Any shortening of the molecules (as happens in the γ form) would result in a hexagonal or quasihexagonal packing of the chains.

DISCUSSION

The observations reported in the present work demonstrate that the major crystalline structure for nylon-2/6 is hexagonal, with $a = 4.79$ Å. Unfortunately, we have not been able to obtain any clear information on the chain axis to define precisely the molecular conformation of this structure. We favour the 10*3/2 helix with an approximate height of 11.7 Å for the glycyl-ε-aminocaproyl residue. This value corresponds to those found in PGII (3.1 Å) and in nylon-6 (8.6 Å). In this manner, the pentamethylene sequence is kept in a nearly favourable zigzag conformation.

A γ structure commonly found in even nylons[11] could be thought to account for the hexagonal form of nylon-2/6. In fact a close relation exists between the PGII and the γ structure, but in the latter the polymer chains have a twofold screw axis. Consequently the hydrogen bonds are all pointing into the same direction and the lattice turns out to be pseudohexagonal. As a result, the lamellae of nylons in the γ form invariably develop an elongated habit[12-14]. The hexagonal shape displayed by nylon-2/6 crystals, as well as their sixfold electron diffraction patterns, are strong evidence against the existence of a γ phase.

A hexagonal lattice similar to that described here for nylon-2/6 has already been described by us in nylon-2/3[4]. In nylons-2/3/3 and 1/3, the same structure is also found (submitted for publication). Sufficient information has been obtained from all these studies in order to conclude that we are dealing with a family of polyamides with a common crystal structure similar to that described for polyglycine II[2]. The outstanding feature of such a structure is the existence of an infinite network of hydrogen bonds that firmly binds all the molecules.

The minor second crystalline form which we have detected for nylon-2/6 appears to be made of hydrogen-bonded sheets. A similar dimorphism is displayed by nylon-2/3[4] and polyglycine[2]. In both cases a crystalline form with its chains in an extended or nearly extended conformation coexists with the hexagonal form. This extended chain structure is the only one found in the usual commercial nylons.

A striking conclusion of these studies is that the insertion of glycine into a polyamide chain allows a structural diversity. This unusual structural behaviour may have interesting practical consequences for this family of polyamides.

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