Polymer Vol. 38 No. 13, pp. 3429–3432, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00 + 0.00

S0032-3861(97)00017-7

The structure of nylon 12,5 is characterized by two hydrogen bond directions as are other polyamides derived from glutaric acid

E. Navarro, J. A. Subirana and J. Puiggalí*
Departament d'Enginyeria Química, ETS d'Enginyers Industrials, Universitat Politècnica de Catalunya, Diagonal 647, Barcelona 08028, Spain
(Revised 18 December 1996)

The structure and morphology of lamellar crystals of nylon 12,5 have been investigated by transmission electron microscopy, electron diffraction and X-ray diffraction. The results obtained indicate that this nylon has a structure different from the conventional α, β and γ forms. Its features are similar to those previously reported for nylon 6,5, which has been shown to have its molecules packed in a network of hydrogen bonds with two spatial orientations (Navarro *et al.*, *Macromolecules*, **28**, 8742). Thus nylon 12,5 should be included in a new family of aliphatic polyamides. The structure derives from a particular conformation of the glutaric units and appears to be independent of the number of methylene groups present in the diamine residue. As a function of the method used in order to prepare the sample, a pseudohexagonal form can also be observed. It might be related to the γ form. © 1997 Elsevier Science Ltd.

(Keywords: polyamides; nylons; glutaric acid)

Introduction

It is well known that the structure of aliphatic polyamides falls into two general categories[1–3]. One, in which are represented all the commercially important nylons, includes the α and β forms. The second includes the γ form, which is the characteristic structure of many other polyamides. However, both categories are characterized by structures with a single hydrogen bond direction. In particular, a γ conformation is expected for nylons derived from even diamines and odd diacids, since an unfavourable hydrogen bond geometry derives from the extended zig-zag conformation of the molecular chains in the α and β structures.

Recently we have postulated a particular structure for nylon 6,5[4], in which each molecular chain is hydrogen bonded with its four neighbouring molecules, so that two directions of hydrogen bonds forming an angle of about 52° are present in the crystal. A rotation between the two amide groups of the glutaramide unit seems to be energetically favoured and causes an important change in the hydrogen bonding system. Similar characteristics have been derived from X-ray diffraction and from quantum mechanical calculations on model compounds[5–8].

Since the γ form is favoured when the number of methylene groups in the repeating unit increases[9], due to the improvement of the van der Waals interactions, we consider it of interest to report a preliminary study on the crystalline structure of nylon 12,5. Under some conditions we do find a conformation related to the γ form, but the most stable form appears to be similar to that described by us for nylon 6,5, with two directions of hydrogen bonding.

Experimental

A sample of nylon 12,5 with an intrinsic viscosity of 0.41 dl g^{-1}, measured in dichloroacetic acid at 25°C, was used in these experiments. The polymer was synthesized by thermal solid state polycondensation (220°C under a nitrogen atmosphere) of the nylon salt prepared from 1,12-diaminododecane and glutaric acid. A density of 1.09 g cm^{-3}, measured at 25°C by the flotation method in mixtures of ethanol and carbon tetrachloride, and a melting temperature of 215°C also characterize the sample.

Crystallization experiments were carried out from dilute solutions (0.1% w/v) in 1,4-butanediol at 120°C. For electron microscopy the crystals were deposited on carbon-coated grids and then shadowed with Pt–carbon at an angle of 15°. A Philips EM-301 electron microscope operating at either 80 kV or 100 kV for bright field and electron diffraction modes, respectively, was used. X-ray diagrams were recorded under vacuum at room temperature in a modified Statton camera (W. R. Warhus, Wilmington, DE) with Ni-filtered Cu K$_\alpha$ radiation. Patterns were internally calibrated with gold or calcite for electron or X-ray diffraction, respectively. For the sake of clarity, the pictures reproduced in this paper do not contain either gold or calcite.

Results and discussion

Strong reflections around 4.40 Å and 3.70 Å are characteristic of powder samples recovered from the synthesis medium or from the crystallization solutions (*Figure 1a*). Crystal mats did not show any appreciable orientation. Similar packing spacings are usually attributed to the α and β structures of nylons. However, there are some considerations that lead us to reject these structures in the case of nylon 12,5: (a) the unfavourable hydrogen bond geometry that would be established with an odd diacid (*Figure 2a*); (b) the deduced unit cell parameters (*Table 1*) which indicate, as explained below, a different organization of molecules than that found in conventional nylons; (c) the *mm* symmetry found in

---

* To whom correspondence should be addressed

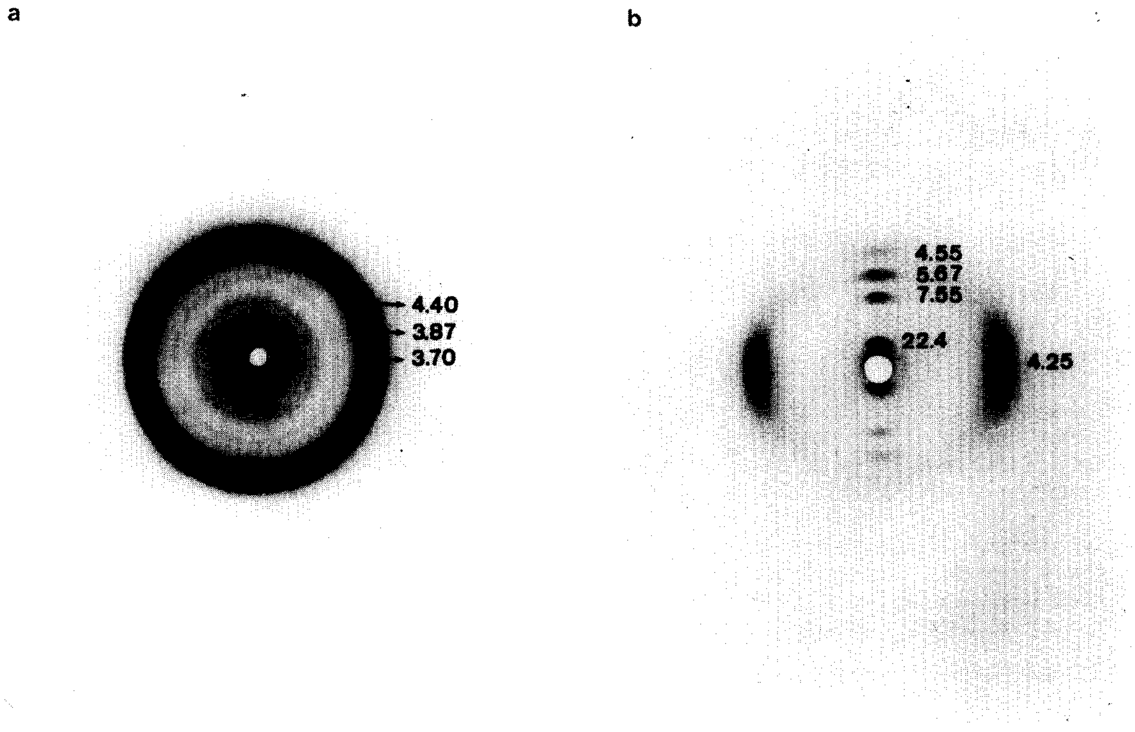

Figure 1 X-ray diffraction patterns of a powder sample recovered from the crystallization medium (a) and a fibre obtained from the melt (b). The meridional spacings observed in the fibre pattern are in agreement with the 002 (22.7 Å), 006 (7.56 Å), 008 (5.67 Å) and 0010 (4.54 Å) spacings of a pseudohexagonal lattice with $c = 45.4$ Å

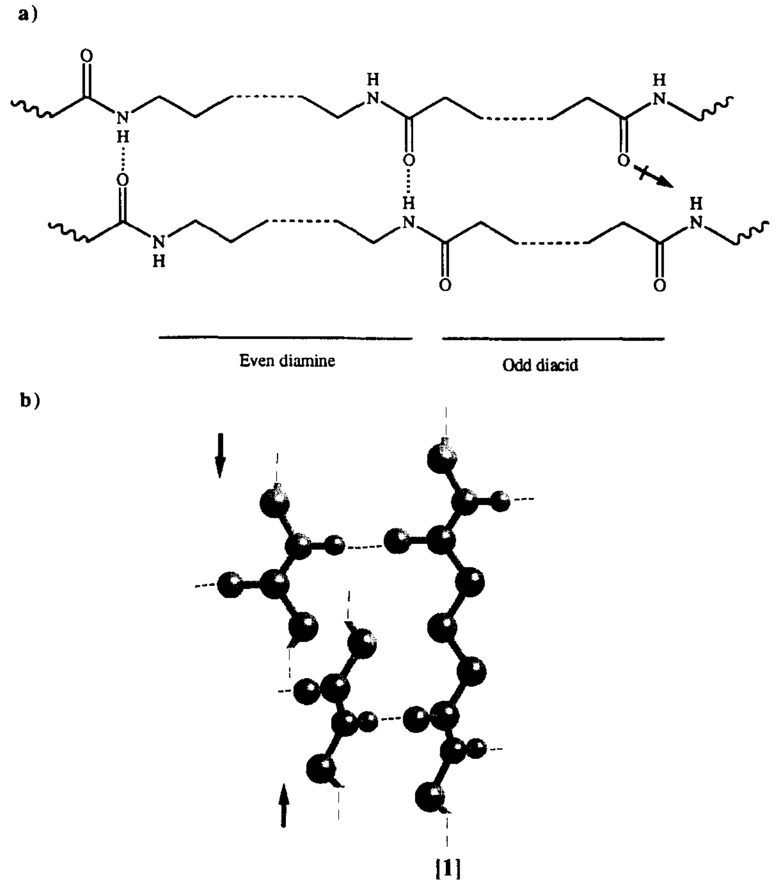

Figure 2 (a) In nylons obtained from even diamines the amide planes point in two directions at 180° when the chain has an extended conformation. Hydrogen bonds can be well established when the neighbouring molecules are shifted. This is not possible when the amide planes point in the same direction, as happens in odd diacid units. (b) A moderate distortion of the glutaric unit can produce a rotation of the peptide groups, which creates a good hydrogen bonding system, in two directions, when the neighbouring chains are conveniently shifted. Arrows indicate the corresponding shift directions with respect to the molecule labelled 1

Table 1 Observed and calculated diffraction spacings d_B (Å) for nylon 12,5

		Observed	
Index[a]	Calculated	X-ray diffraction[b,c]	Electron diffraction[b,c]
020	22.5	22.4 vs	
060	7.50	7.52 m	
080	5.62	5.63 m	
002	4.36	4.40 vs	4.36 vs
$1\bar{2}1$, $1\bar{3}1$, $1\bar{4}1$	3.83, 3.84, 3.83	3.87 m	3.85 m
101	3.72	3.70 s	
161	3.05	3.06 w	
181, 191	2.80, 2.69	2.71 w	
103, $1\bar{1}3$, $1\bar{2}3$, $1\bar{3}3$, $1\bar{4}3$	2.37, 2.39, 2.40, 2.40, 2.40	2.42 w	2.43 w
004	2.18		2.18 m
$2\bar{2}0$, $2\bar{3}0$, $2\bar{4}0$	2.10, 2.12, 2.13		2.13[d] w
$2\bar{2}2$, $2\bar{3}2$, $2\bar{4}2$	1.89, 1.90, 1.91		1.92[d] w

[a] On the basis of a monoclinic unit cell: $a = 4.28$ Å, b (chain axis) $= 46.8$ Å, $c = 8.72$ Å, $\alpha = \beta = 90°$, $\gamma = 106°$

[b] Abbreviations denote intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak

[c] The values shown correspond to a powder pattern (*Figure 1a*). The same values are obtained from crystal mats

[d] Observed only in accidentally tilted samples

the electron diffraction patterns (*Figure 4*) of lamellar crystals (*Figure 3*), which is in disagreement with the expected one for both the triclinic and the monoclinic (where the unique axis corresponds to the chain axis) structures of conventional nylons. In the same way, although a γ form is predicted[3] for nylons derived from odd diacids and/or odd diamines, the measured chain packing spacings are far away from the pseudohexagonal arrangement characteristic of the γ form. In fact, all the experimental data on nylon 12,5 can be well interpreted by assuming a structure with two hydrogen bond directions as suggested for nylon 6,5[4]. The main conformational feature of these polymers is the fact that every glutaryl unit produces a 50–55° rotation between the amide planes. Thus, hydrogen bonds should be established along two directions and their geometry will be optimum when the neighbouring chains are conveniently shifted (*Figure 2b*).

Lamellar crystals 3–5 μm long with a clear rhombic habit were obtained from isothermal crystallization in 1,4-butanediol (*Figure 3*). The crystal edges appear frequently serrated and give support to the idea that two hydrogen bond directions are present in the crystals. Although the irregular faces make it difficult to determine accurately the angle between them, a value close to 55° is found in agreement with the expected rotation of the two C–O directions in the glutaryl units. The lamellae are about 60 Å thick, as estimated from their shadow in the micrographs. In the powder pattern (*Figure 1a*) weak reflections at 15.1 Å, 12.0 Å, 9.9 Å and 8.6 Å are observed. They agree with the 4th (15 Å), 5th (12 Å), 6th (10 Å) and 7th (8.6 Å) orders of a basic spacing of 60 Å, attributed to the lamellar thickness. The fact that so many orders of diffraction are observed indicates that the lamellar width is fairly constant, as happens in other nylons[10]. Crystals of these nylons usually grow as stacks of lamellae in which neighbouring lamellae diffract coherently, at least in the main chain direction.

Slightly different electron diffraction patterns are

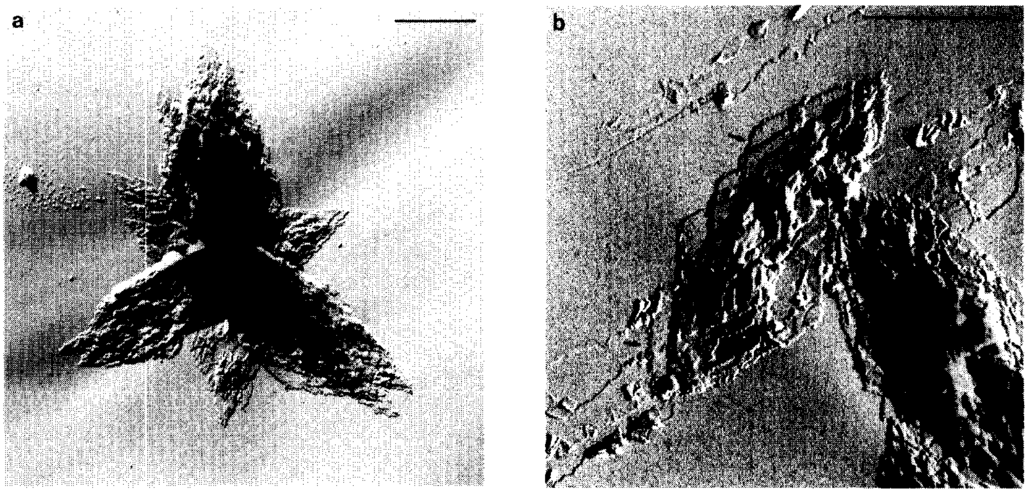

Figure 3 Lamellar crystals obtained from 1,4-butanediol solutions at 120°C. Note the rhombic habit of the crystals and their irregular edges (see arrows). (a) Crystalline aggregate composed of rhombic lamellae, some of which appear to be rolled and then flattened. (b) Individual lamellae which can be observed in the same preparation. Scale bar = 1 μm

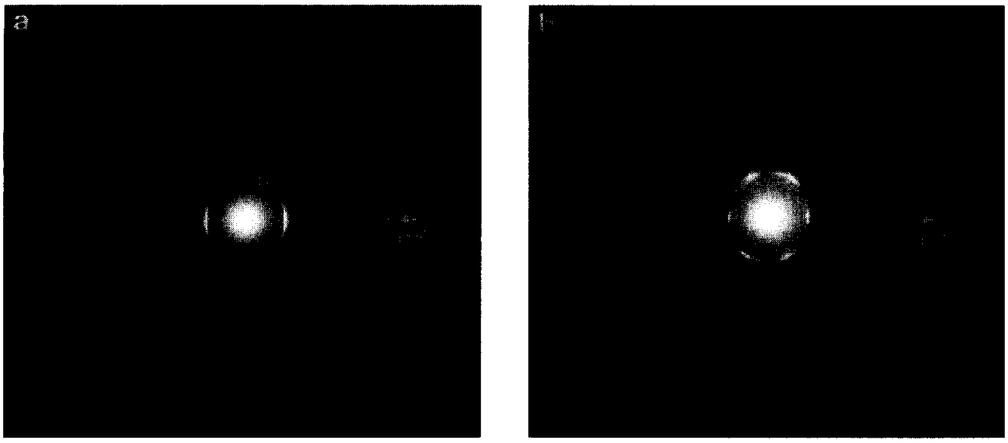

Figure 4 Electron diffraction patterns of the lamellar crystals of nylon 12,5. Note the sharpness of the 002 reflection and the different appearance of the *hkl* reflections (*b*, chain axis) in both samples (a and b), as discussed in the text

obtained from different crystals, as shown in *Figure 4*. An intense and sharp reflection is found in the c^* direction in all cases; it is interpreted as the 002 reflection, as shown in *Table 1*. On the other hand, the 101 reflection (which was present in nylon 6,5) is not found and instead we find reflections with a variable sharpness which we interpret as $1\bar{k}1$. They correspond to the poorly defined ring found in powder patterns (*Figure 1a*). We interpret the variability of these reflections as due to different degrees of tilting of the samples. These observations suggest that the molecular chains are inclined with respect to the lamellar surface in the *a* direction and correspond to the expected pattern for a crystal deposited over the 010 basal plane of a monoclinic structure. Unfortunately the monoclinic angle γ cannot be determined with precision, since X-ray fibre patterns corresponding to this structure are not available.

The electron diffraction and X-ray powder diffraction data are tentatively interpreted as a centred monoclinic unit cell, which fits the experimental diffraction spacings as given in *Table 1*. The calculated density of $1.17\,\mathrm{g\,cm^{-3}}$ is close to the experimental value if we take into account that the presence of amorphous material may reduce the density of the sample (by about 6%, in this case). The unit cell parameters are comparatively similar to those calculated for nylon 6,5. The value found for the *b* parameter also indicates a shortening of 0.2 Å per amide group with respect to the all-*trans* conformation, which is in agreement with a contracted conformation of the glutaric units. The monoclinic angle (106°) is different from that found in nylon 6,5 (114°), an observation which may be interpreted from slightly different conformational features in either polymer. In any case the organization of successive sheets of hydrogen-bonded molecules is quite different than that found in nylon 6,6, where a much larger shift along the chain axis direction is found.

In summary, although the *a* and *c* cell parameters are similar to those found in the α form of nylons, it is obvious that nylons *n*,5 have a quite different organization of hydrogen bonds. The spacing of the 020 reflection along the chain orientation is the most clear evidence in this respect, since in a triclinic unit cell (similar to that of nylon 6,6) the equivalent reflection should occur at a much smaller spacing.

The fibres obtained from the melt correspond to a different pseudohexagonal phase (*Figure 1b*) characterized by a single equatorial spacing at 4.25 Å and a shortening around 0.52 Å per amide group with respect to an extended conformation. This structure may be interpreted as a γ form, but a higher degree of disorder might be present in this case. In contrast to nylon 6,5, where this pseudohexagonal form could be transformed into the monoclinic one after annealing under stress, all the nylon 12,5 fibres break when they are annealed.

Acknowledgements

This research has been supported in part by DGICYT (Grant No. PB93-1067) and by the Comissionat per Universitats i Recerca de la Generalitat de Catalunya. E.N. acknowledges a predoctoral fellowship from the Departament d'Ensenyament de la Generalitat de Catalunya. We are thankful to J. L. Marcos for his help in experimental work.

References

1. Bunn, C. W. and Garner, E. V., *Proc. Roy. Soc. Lond.*, 1947, **A189**, 39.
2. Holmes, D. R., Bunn, C. W. and Smith, D. J., *J. Polym. Sci.*, 1955, **17**, 59.
3. Kinoshita, Y., *Makromol. Chem.*, 1959, **33**, 1.
4. Navarro, E., Franco, L., Subirana, J. A. and Puiggalí, J., *Macromolecules*, 1995, **28**, 8742.
5. Navarro, E., Alemán, C. and Puiggalí, J., *J. Am. Chem. Soc.*, 1995, **117**, 7307.
6. Alemán, C., Navarro, E. and Puiggalí, J., *J. Org. Chem.*, 1995, **60**, 6135.
7. Alemán, C., Navarro, E. and Puiggalí, J., *J. Phys. Chem.*, 1996, **100**, 16131.
8. Navarro, E., Alemán, C. and Puiggalí, J., *Macromolecules* (submitted).
9. Parker, J. P. and Lindenmeyer, P. H., *J. Appl. Polym. Sci.*, 1977, **21**, 821.
10. Subirana, J. A. and Aceituno, J. E., *Macromol. Symp.*, 1996, **102**, 317.