

# Structural studies of nylon 13,13

A. PRIETO, I. IRIBARREN, S. MUÑOZ-GUERRA

*Departamento de Ingeniería Química, Universidad Politécnica de Cataluña, ETS de Ingenieros Industriales, Diagonal 647, 08028 Barcelona, Spain*

A structural study of nylon 13,13 has been carried out by means of X-rays and electron microscopy. Both X-ray and electron diffraction data, obtained from oriented films as well as from lamellar crystals prepared in solution, evidenced that nylon 13,13 adopts a  $\gamma$  structure in a monoclinic lattice of parameters  $a_0 = 0.488$  nm,  $b_0 = 0.473$  nm,  $c_0 = 3.40$  nm,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 121^\circ$ . As expected from the constitution of the nylon, no trace of structure with chains in fully extended conformation ( $\alpha$ -form) was observed throughout this study.

## 1. Introduction

Nylon 13,13 is the polyamide of AABB type with the lowest density of amide groups along the chain that has been synthesized so far. According to the widely known classification of nylons made by Kinoshita [1], it belongs to class **D** which comprises polyamides from aliphatic diamines and diacids, both of them with an odd number of methylene units. This author postulated that all members of class **D** should adopt predominantly the quasi-hexagonal  $\gamma$ -form with a crystal structure having the crystallographical space group *Pm*. The crystal structure of nylons 7,9 [1], 5,7 [2], and 7,7 [3] has been studied and the model found for every case is in agreement with Kinoshita's prediction. However the  $\alpha$ -form, also expected to occur as a minor form, was never observed. Up to the present, no structural data at all are available for nylon 13,13.

In this paper we want to report the X-ray diffraction and electron microscopy results we have obtained in the analysis of nylon 13,13. It is the purpose of this work to disclose what type of crystal model is taken up by this nylon, and to see if the occurrence of the particularly long polymethylene segment may alter the structural behaviour usually observed for odd-odd nylons. The interest of this study is supported as well by the possibility of nylon 13,13 to be pyroelectrically and piezoelectrically active, as in the case of nylon 5,7 [4]. Some years ago the Southern Research Institute carried out exploratory research to estimate the potential utility of nylon 13,13 for industrial applications [5-7]. It was shown there that its physical properties were very similar to those of nylon 11, the most significant difference being its lower sensitivity to water [8]. This would make nylon 13,13 the material of preference for those electrical uses requiring a great stability of properties under varying humidity conditions.

## 2. Experimental procedure

The sample of nylon 13,13 used throughout these studies was kindly supplied by Dr E. Pryde of the US

Department of Agriculture, Peoria, Illinois. It was prepared from brassilic acid (1,13-tridecanoic acid) and 1,13-diaminetridecane by melt polymerization. The intrinsic viscosity of this sample, measured in dichloroacetic acid, was  $0.44$  dl g<sup>-1</sup>, which corresponds to a molecular weight of about 10 000 if the viscosimetric equation established for nylon 12 is used for computation [9].

Uniaxially oriented films for electron microscopy were prepared by stroking from the melt on a glass slide. Doubly oriented films were epitaxially grown on benzoic acid by following the technique of Wittman and Lotz [10]. Isothermal crystallizations were conducted in 1,5-pentanediol; 0.1% solutions were prepared by heating at 220 °C under a nitrogen atmosphere and then left to crystallize at 140 °C for a period of 3 h. Crystals were recovered by centrifugation and repeatedly washed with 1-butanol. Preparations for electron microscopy were processed in the usual way and shadowed with Pt-C at an angle of 14°. Electron diffraction diagrams were recorded in the selected-area mode at 100 kV and were internally calibrated with gold ( $d_{111} = 0.235$  nm).

X-ray diffraction was taken from films oriented by stretching under heating at about 80 °C and from mats of crystals grown in solution. Mats were prepared by gentle filtering of n-butanol suspensions under a slight vacuum. A modified Statton camera (Warhus, Wilmington, Delaware, USA) with CuK $\alpha$  radiation from a graphite monochromator was used for these experiments.

## 3. Results and discussion

The thermal properties of nylon 13,13 were investigated by differential scanning calorimetry (DSC). In order to determine the effect of thermal history on the crystallization behaviour, the following experiments were carried out. One of the samples was firstly melted at 200 °C and then subjected to the following treatments: (a) quenched to room temperature at 320 °C min<sup>-1</sup>, (b) held at 145 °C for 3 h and quenched,

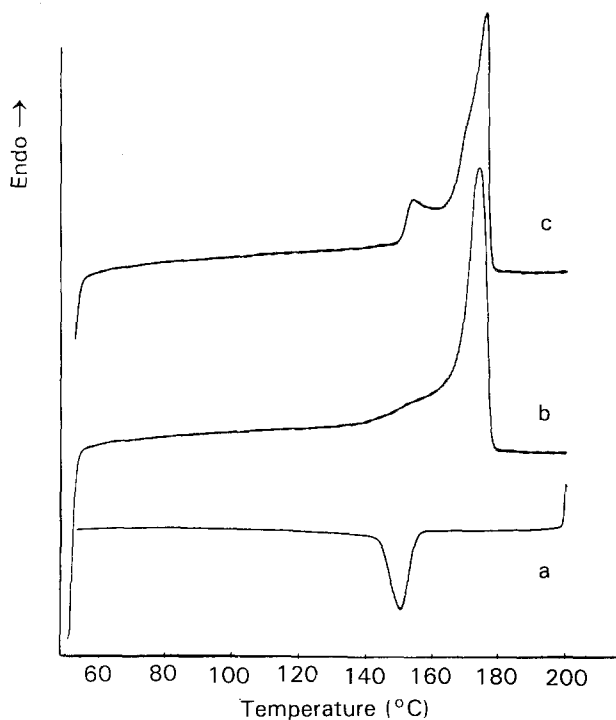


Figure 1 DSC thermograms of nylon 13,13: (a) cooled down from 200°C to room temperature at 5°C min<sup>-1</sup>, (b) heated at 10°C min<sup>-1</sup> after treatment (a), (c) quenched sample heated at 10°C min<sup>-1</sup> after being held at 145°C for 3 h.

(c) held at 160°C for 14 h and quenched, (d) cooled down to room temperature at 5°C min<sup>-1</sup>. The melting behaviour of each sample was then observed at a heating rate of 10°C min<sup>-1</sup>. All these treatments were performed in the DSC sample chamber under a nitrogen atmosphere.

A single endotherm was found in all cases, with a second minor peak appearing only in the sample treated as in (b) above (Fig. 1). The highest heat of fusion observed was 17.1 cal g<sup>-1</sup> (71.6 J g<sup>-1</sup>) with a melting point of 173.5°C. Such rather simple behaviour contrasts with that usually observed for other odd nylons containing a shorter number of methylenes (e.g. nylon 5,7 [2]) which tend to give two melting peaks. Double melting is generally interpreted as corresponding to two well-defined crystallite sizes which develop due to the thickness requirements imposed by the formation of hydrogen bonds.

Investigation of the crystal structure of nylon 13,13 was carried out by X-ray diffraction and electron microscopy. Fig. 2 shows the X-ray diffraction pattern of a film uniaxially oriented. The spacings of the reflections observed along the meridian are consistent with a fibre axis repeat of 3.4 nm, and no systematic absence is detected. The strong broad reflection on the equator actually comprises two reflections corresponding to 0.40 and 0.42 nm, as could be clearly revealed when the diagram was taken with the plane of the film tilted 30° to the vertical (inset to Fig. 2). The whole diagram may be indexed on the basis of a monoclinic lattice of parameters  $a_0 = 0.488$  nm,  $b_0 = 0.473$  nm and  $c_0 = 3.40$  nm,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 121^\circ$ . The calculated crystalline density for this structure is 1.05 g ml<sup>-1</sup>, in fair agreement with the value of 1.03 g ml<sup>-1</sup> measured by flotation in toluene-carbon

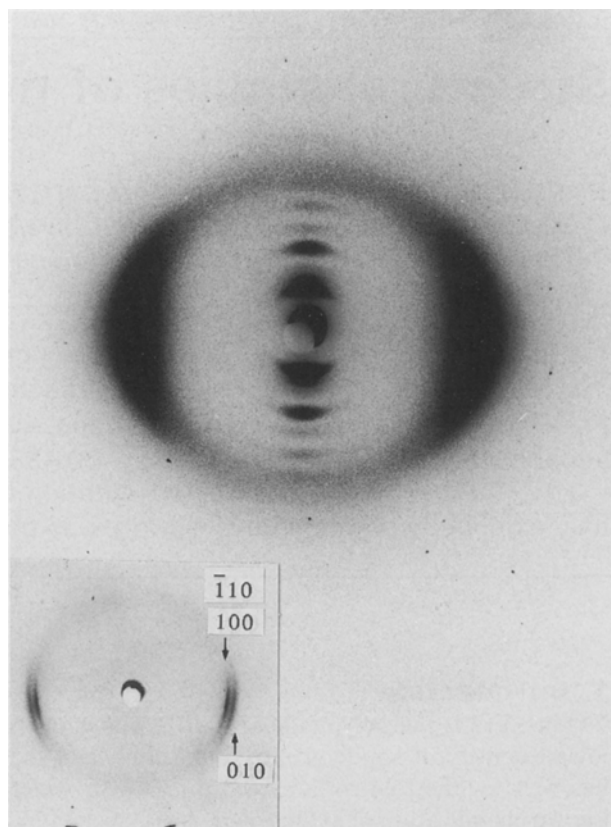


Figure 2 X-ray diagrams from a film of nylon 13,13 oriented by stretching at 80°C. The direction of drawing is vertical and the film plane was placed normal to the beam. Inset: diagram recorded with the film tilted 30°.

tetrachloride. There is only one chain passing through the unit cell and it is in  $\gamma$ -conformation. The fully extended all-*trans* structure should have a fibre axis chain repeat of 3.47 nm.

In order to support the conclusions derived from the X-ray analysis as well as to explore the ability of this nylon to adopt crystal structures other than the  $\gamma$ -form, an electron microscopy study on both films and lamellar crystals was undertaken. The electron diffraction (ED) diagram from an ultrathin film of nylon 13,13 prepared by stroking is shown in Fig. 3a. Due to the higher resolution achieved with this technique, most of the main reflections expected to arise from the basal plane of the unit cell can be discerned along the equator. On the other hand, the 0028 reflection appearing on the meridian at 0.121 nm allows an accurate measurement of the identity period of the chain, which confirms the value of 3.40 nm previously computed from X-ray diffraction.

Epitaxial crystallization has proven to be a reliable method to obtain doubly oriented films of nylons in the  $\alpha$ -structure [11, 12]. It is well known that films prepared in such a manner become oriented with the hydrogen bond-containing planes lying parallel to the substrate surface. Therefore an ED pattern displaying reflections other than those typically appearing in fibre or powder diagrams is usually registered. The diagram shown in Fig. 3b was taken from a film of nylon 13,13 epitaxially grown on benzoic acid. As expected from the orientation of the lattice with respect to the electron beam, the  $\bar{2}10$  reflection is

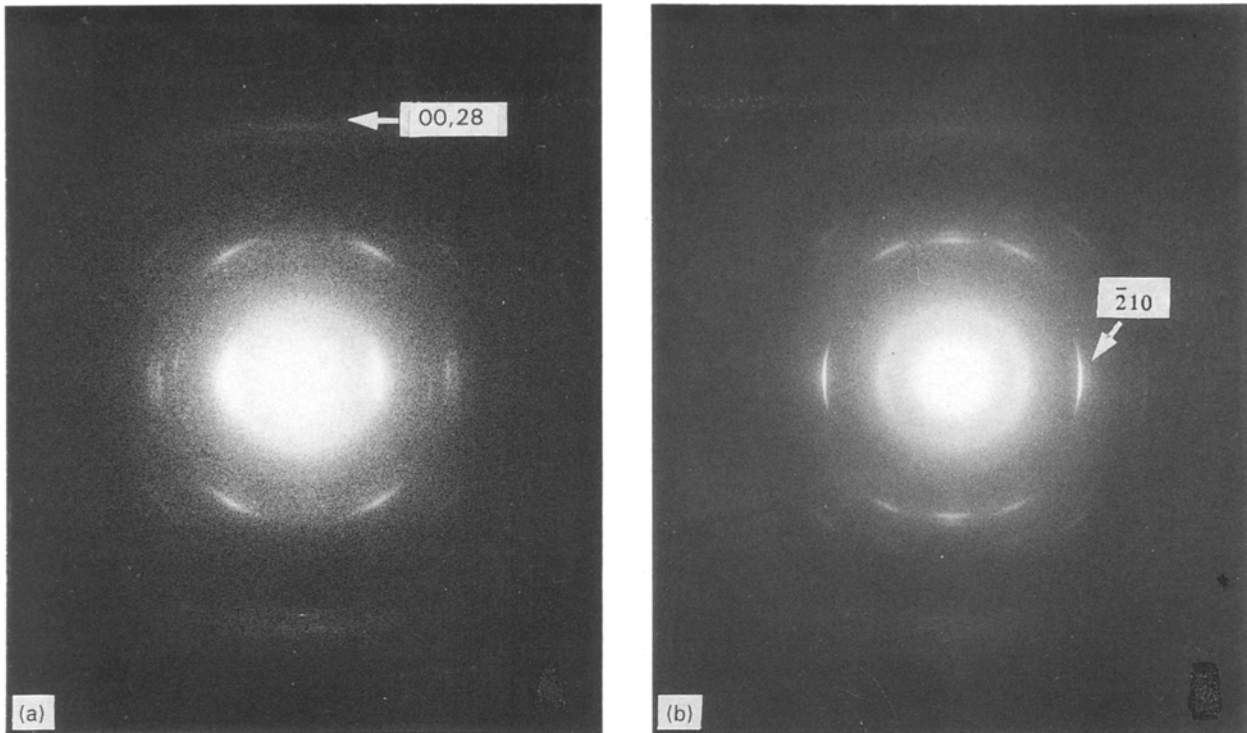


Figure 3 Electron diffraction diagrams of nylon 13,13: (a) film prepared by stroking, (b) film grown on benzoic acid. In both cases the chain direction is vertical.

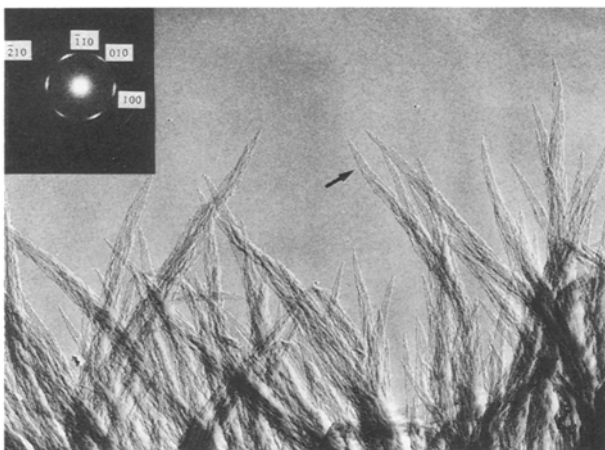


Figure 4 Lamellar crystals of nylon 13,13 formed in 1,5-pentandiol at 140°C. The bar denotes 1  $\mu\text{m}$ . Inset: electron diffraction diagram taken from the arrowed crystal and inserted in corresponding orientation.

brought into sight with particular intensity. Hence it is deduced that 010 planes are oriented normal to the beam, and they should contain the hydrogen bonds. The other reflections included in the diagram may be also accounted for on the basis of the unit cell defined above.

Crystallization of nylon 13,13 from dilute solution rendered lath crystals like those displayed in Fig. 4. The elongated morphology displayed by these crystals is consistent with the occurrence of a crystal  $\gamma$ -structure, as confirmed by their electron diffraction analysis. The single-crystal ED diagram in the inset of Fig. 4 consists of the 110, 010 and  $\bar{1}10$  pairs of reflections and its orientation with respect to the crystal reveals that 010 planes (hydrogen bond planes) run parallel to the long direction of the crystal. As the nylon 13,13 chain is adirectional, no restriction

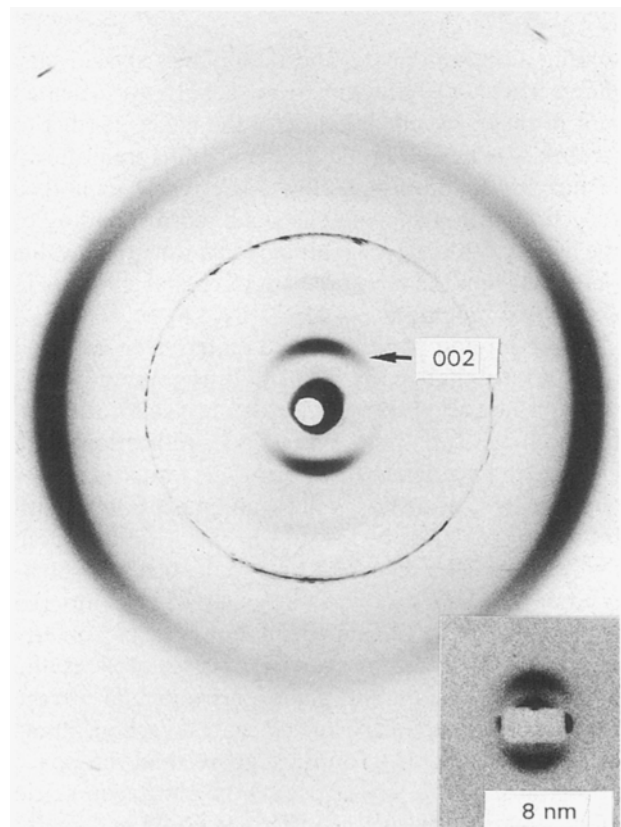


Figure 5 X-ray diagram taken from an oriented sediment of nylon 13,13 crystals placed with the surface parallel to the beam. The thin grainy ring arises from  $\text{MoS}_2$  used for internal calibration. Inset: reflection observed at low angle with a spacing of 8.0 nm corresponding to the lamellar thickness.

may be anticipated for the planes containing chain folding. Nevertheless, by analogy with the model followed in single crystals of odd nylons [13], the serrated edge of the crystals shown in Fig. 4 suggests that

TABLE I Observed and calculated spacings of nylon 13, 13

Observed spacing (nm)				Calculated spacings (nm) <sup>a</sup>	Indexing <sup>a</sup>		
Uniaxially oriented film		Doubly oriented film ED	Lamellar crystals				
X-rays	ED		X-rays	ED			
3.3-3.4(vw)			3.3-3.4(vw)		3.40	001	
1.7(vs)			1.7(vs)		1.70	002	
1.15(w)			1.15(w)		1.13	003	
0.85(s)			0.85(s)		0.850	004	
0.67(w)			0.680(w)		0.680	005	
0.575(w)			0.560(w)		0.566	006	
0.490(w)			0.480(w)		0.486	007	
0.385(vw)					0.377	009	
0.315(vw)					0.309	0011	
0.288(vw)					0.283	0012	
		0.242(w)			0.243	0014	
		0.222(m)			0.227	0015	
	0.210(w)				0.212	0016	
		0.159(vw)			0.162	0021	
	0.121(m)	0.122(vw)			0.121	0028	
0.420(vs)	0.420(vs)		0.420(vs)	0.420(vs)	0.419	0418	100 $\bar{1}$ 10
0.400(vs)	0.403(vs)		0.402(vs)	0.405(s)	0.406		010
				0.245(w)	0.244		210
2.40(w)	2.40(w)		0.239(w)		0.244	0.237	$\bar{2}$ 10 110
		0.240(s)			0.240		$\bar{2}$ 10
		0.158(w)			0.157		$\bar{3}$ 10

<sup>a</sup>Calculated and indexed on the basis of a monoclinic unit cell of parameters  $a_0 = 0.488$  nm,  $b_0 = 0.473$  nm,  $c_0 = 3.40$  nm,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 121^\circ$ .

folding along both 100 and 010 planes should take place. The X-ray diagram from a partially oriented mat of these crystals taken with the beam parallel to its surface (Fig. 5) is similar to the fibre diagram shown in Fig. 1a; in addition, its low-angle region exhibits a reflection with a spacing of 8.0 nm, corresponding to the lamellar thickness, in fair agreement with the value obtained from the measurement of crystal shadows in electron micrographs.

A fair amount of diffraction data has been gathered to conclude that nylon 13,13 adopts predominantly the  $\gamma$ -structure (Table I). Neither crystallization at high temperature nor epitaxial crystallization were effective in producing the  $\alpha$ -form. The lattice is monoclinic with parameters values comparing well with those reported for the  $\gamma$ -form of both odd and even nylons [14]. The repeating unit of the chain is shortened by 0.035 nm for the amide group when compared with the fully extended conformation. The lack of any systematic absence in the diagrams, as well as the occurrence of a mirror plane perpendicular to the chain axis through each of the central carbon atoms between the amide groups, suggest that the space group must be  $Pm$ . The lattice is non-centrosymmetric and therefore a piezoelectric activity could be anticipated for this nylon.

### Acknowledgements

We are greatly indebted to Dr Pryde for providing us with a sample of nylon 13,13. Financial support for

this work was given by the Dirección General de Investigación Científica y Técnica, Grant Nos PA-86-0218-CO3-02 and PB-90-0597.

### References

1. Y. KINOSHITA, *Makromol. Chem.* **33** (1959) 1.
2. J.-C. LIN, M. H. LITT and G. FROYER, *J. Polym. Sci. Polym. Chem. Edn.* **19** (1981) 165.
3. Y. KINOSHITA, *Makromol. Chem.* **33** (1959) 21.
4. M. LITT, C.-H. HSU and P. BASU, *J. Appl. Phys.* **48** (1977) 2208.
5. T. K. MIWA and I. A. WOLFF, *J. Amer. Oil Chem. Soc.* **40** (1963) 742.
6. R. W. MILLER, F. R. EARLE, I. A. WOLFF and A. JONES, *ibid.* **42** (1965) 817.
7. F. R. EARLE, J. E. PETERS, I. A. WOLFF and G. O. WHITE, *ibid.* **43** (1966) 330.
8. R. B. PERKINS, J. J. RODEN III, A. C. TANQUARY and I. A. WOLFF, *Modern Plast.* (1969) 136.
9. Z. TUZAR, P. KRATOCHVIL and M. BOCHDANECKY, *Adv. Polym. Sci.* **30** (1979) 117.
10. J. C. WITTMANN and B. LOTZ, *J. Polym. Sci. Polym. Phys. Edn* **23** (1985) 205.
11. J. PUIGGALÍ, S. M. MUÑOZ-GUERRA and B. LOTZ, *Macromolecules* **19** (1986) 1119.
12. J. PUIGGALÍ and S. M. MUÑOZ-GUERRA, *J. Polym. Sci. Polym. Phys. Edn* **27** (1989) 1563.
13. S. MUÑOZ-GUERRA, A. PRIETO and J. M. MONTSERRAT, *J. Mater. Sci.* **27** (1992) 89.
14. H. TADOKORO, "Structure of Crystalline Polymers" (Wiley, New York, 1979) pp. 369-371.

Received 2 March  
and accepted 10 December 1992