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Structural studies of poly[(2*S*,3*S*)-2,3-dimethoxybutylene alkanamide]s

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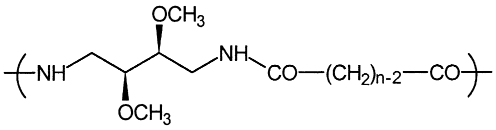
Abstract

The structural characterization of a series of stereoregular polyamides 4,*n* ($n = 8$, 10, 12), which were obtained from polycondensation of (2*S*,3*S*)-2,3-dimethoxy-1,4-butanediamine with aliphatic dicarboxylic acids, has been carried out. X-ray diffraction of powder and fiber samples were analyzed together with electron diffraction patterns of single crystals obtained by isothermal crystallization in solution. Experimental results based on lattice parameters data were used to build a preliminary crystal model using the Cerius program. The main characteristic of the proposed model is the presence of intermolecular hydrogen bonds along the crystal *a* direction, similarly arranged to conventional nylons.

Keywords: Polymer structure; X-ray diffraction; Single crystal electron microscopy

1. Introduction

The crystal structure of polyamides derived from L-tartaric acid and 1,*n* alkanediamines, which are denoted P*n*DMLT, were studied in preceeding works. More specifically, polymers with $n = 4$, 6, 8 and 12 showed the great influence of the L-tartaric chiral fragment on the chain conformation, subsequent hydrogen bonding geometry and chain packing into the crystal cell [1]. Moreover, the polyamide P12DMLT showed two crystalline forms [2], their differences being mainly related with the orientation of the chain into the crystal and not with the chain packing. Both racemic systems constituted by copolymers with L and D units in the repeat unit, for $n = 6$ and physical mixtures made from P6DMLT and P6DMDT displayed the same structural behavior [3]. In such cases the isomorphic substitution of L-units by D-units only induced changes in the symmetry of the crystal cell, whereas the chain packing also remained unaltered. Structural characterization of poly(dodecamethylen-di-*O*-methylen-L-tartaramide) also displayed the persistence of *gauche* effect on the chain conformation [4]. This work is related with the crystal structure of poly(2,3-dimethoxybutylene alkanamide)s, abbreviated PDMBA*n* (where *n* indicates the number of carbon atoms in the diacid) with $n = 8$, 10 and 12:



The polyamides PDMBA*n* are isomers of the corresponding poly(*n*-methylen-di-*O*-methyl-L-tartaramide)s P*n*DMLT.

Both family of polyamides, poly(*n*-methylen-di-*O*-methyl-L-tartaramide)s and poly(2,3-dimethoxybuthylene alkanamide)s are chemically modified polyamides to obtain good mechanical and thermal properties with a potential as materials for biomedical applications [5]. These two polyamides series differ one from another only in the position occupied by the chiral unit with respect to the amide group. Whereas the physicochemical characteristics of two families are similar, as well as the thermal and mechanical properties [6], significant changes in structure and related properties can be expected from such modification in the chemical structure.

2. Experimental

The polyamides PDMBA*n* used in this work were prepared by polycondensation of 2*R*-3*R*-2,3-dimethoxy-1,4-butanediamine with the ester pentaclorophenylic of the

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Table 1
Characteristics of polyamides PDMBA*n*

PDMBA*n*	M_w[a]	M_n[a]	T_m (°C)[b]	T_g (°C)[b]	$[\alpha]_D^{23}$[c]
PDMBA8	62,700	28,600	172	52	−11.5
PDMBA10	26,900	19,500	154	35	−10.4
PDMBA12	44,800	29,200	153	33	−9.13

Data taken from Ref. 6.

[a] Measured by GPC on trifluoroacetylated samples and calibrated against polystyrene standards.

[b] Determined by DSC.

[c] Measured in formic acid.

diacid in chloroform solution as described in detail elsewhere [6]. The most relevant data of these polytartaramides are given in Tables 1 and 2.

Polymer films were prepared by casting from formic acid solution and fibers were obtained by stretching the polymer from the melt and subsequent annealing at a temperature near to the melting point. Optical microscopy was performed with a Nikon Labophot polarizing microscope fitted with a Nikon FX-35DX camera. Melting and annealing experiments were carried out on a Perkin–Elmer DSC-4 instrument using 3–5 mg of polymer samples. Thermograms were recorded at heating rate of 10 °C/min and they were calibrated with indium.

Densities were measured at 25 °C on pieces of polymer films by the flotation method in a KBr 25% (w/w) solution.

X-ray diffraction patterns were registered in an evacuated flat-film Wharus camera with Ni-filtered Cu Kα radiation of wavelength 1.54 Å. Calibration was internally made with molybdenum sulfide ($d_{002} = 6.147$ Å).

Single crystals were grown by isothermal crystallization from diluted solutions (0.1%) of polymer in glycerine or by solution-precipitation in formic acid *n*-butanol system. Single crystals were recovered by centrifugation and repeatedly washed with *n*-butanol.

Crystals to be observed in the bright field were shadowed with Pt carbon at an angle of approximately 15°, whereas unshadowed samples were used for electron diffraction examination. Electron diffraction diagrams were recorded in the selected area mode under a minimum flux of radiation and were internally calibrated with gold ($d_{111} = 2.35$ Å). A Philips EM-301 electron microscope operating at 80 and 100 kV for bright field and electron diffraction modes, respectively, was used in this work.

Table 2
Thermal properties of polyamides PDMBA*n*

PDMBA*n*	T_1 (°C)	T_2 (°C)	T_3 (°C)	ΔH (J/g)
PDMBA8	170	125	176	41.6
PDMBA10	155	95	–	41.2
PDMBA12	153	–	–	28.7

T_1: Melting temperature obtained from the first heating; T_2: non isothermal crystallization temperature; T_3: melting temperature after annealing below T_1 for a few minutes; ΔH: melting heat.

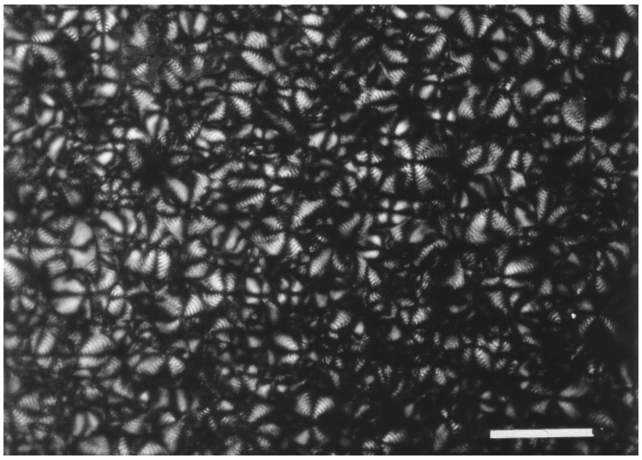

Fig. 1. Spherulites of PDMBA12 obtained by casting from formic acid. Scale bar: 100 μm.

Crystal model building was made for PDMBA8 using the Cerius program [7]. For this purpose the unit cell parameters and the symmetry determined by X-ray and electron diffraction, were considered.

Adjustments were made to satisfy contour conditions, as the coincidence in the space at both ends of the repeating unit.

3. Results and discussion

3.1. Thermal analysis, optical microscopy and X-ray powder diffraction

Films of PDMBA8, PDMBA10 and PDMBA12, which were obtained by slow evaporation of formic acid solutions,

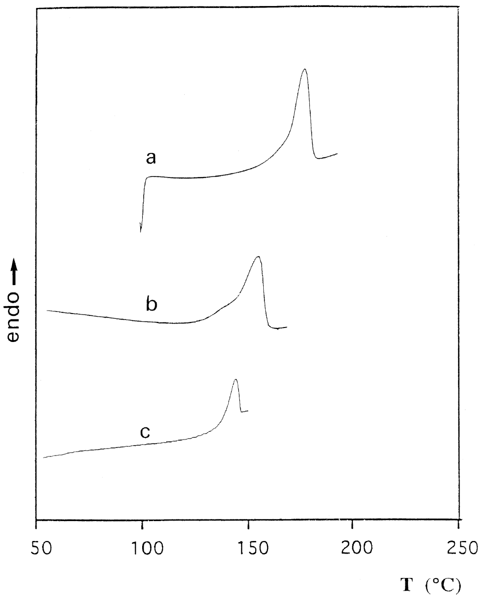

Fig. 2. Heating DSC traces of PDMBA*n* samples. (a) PDMB8, (b) PDMB10, (c) PDMB12.

Table 3
Characteristic spacings (Å) appearing in X-ray powder diagrams of PDMBA*n*

PDMBA8	PDMBA10	PDMBA12
10.2 (w)	11.6 (w)	12.8 (w)
7.65 (s)	7.32 (s)	6.77 (s)
5.08 (s)	5.03 (s)	5.01 (s)
4.53 (vw)	4.57 (vw)	4.60 (vw)
4.31 (vs)	4.32 (vs)	4.28 (vs)
4.00 (vw)	4.15 (vw)	4.03 (vw)
3.53 (m)	3.57 (m)	3.63 (m)

Intensities visually estimated and denoted as: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

show a well spherulitic texture and display a notable birefringence (Fig. 1).

Thermal behavior of PDMBA*n* is similar to that of the isomers P*n*DMLT. Although PDMB8 exhibits a double peak during the first heating, the annealing at 150 °C for a few minutes simplifies the endotherm to a single peak (Fig. 2). The melting temperature decreases with *n*, the melting heat being of the same order in all cases, i.e. about 40 J/g (Table 2).

Powder X-ray diagrams registered from polymer ‘as prepared’ indicate that a notable crystallinity is present in all cases (Fig. 3). Characteristic spacings of these patterns are summarized in Table 3.

Common reflections about 4.6, 5.0 and 4.3 Å suggest a similar packing of the polymer chains for $n = 8$, 10 and 12, whereas the spacing of the first reflection increase with *n*, and can be related with the repeat of the chain along the *c*-axis.

Table 4
Observed and calculated spacings (Å) for PDMBA8

Layer line	X-ray		Single crystal	Calculated[a]	*h*	*k*
	Powder	Fiber				
$l = 0$	5.01 (vs)	5.04 (vs)	5.08	5.08	0	1
	4.31 (vs)	4.29 (vs)	4.34	4.31	1	0
$l = 1$	11.3 (w)	11.2 (w)	–	11.2	0	−1
	7.32 (vs)	7.34 (vs)	–	7.37	0	0
	4.57 (vs)	4.60 (vs)	–	4.57	−1	0
	3.59 (s)	3.58 (s)	–	3.63	1	−2
	–	–	3.55	3.61	1	−1
$l = 2$	–	8.42 (w)	–	8.39	0	−1
	–	4.15 (s)	–	4.15	1	−2
$l = 3$	–	6.23 (vw)	–	6.19	0	−2
	–	3.75 (vw)	–	3.71	0	−3
$l = 4$	4.31 (vs)	4.25 (vs)	–	4.20	0	−3
	–	3.35 (vw)	–	3.33	−1	−2
	–	2.80 (vw)	–	2.81	0	−4
$l = 5$	–	3.75 (w)	–	3.71	0	−3
	2.78	2.76 (vw)	–	2.74	−1	−2
$l = 6$	3.14 (vw)	3.12 (vw)	–	3.09	0	−4
$l = 7$	–	2.62 (vw)	–	2.60	0	−4
	2.33 (vw)	2.34 (vw)	–	2.33	0	−5

[a] On the basis of a unit cell with parameters: $a = 4.75$ Å, $b = 13.1$ Å, $c = 18.7$ Å, $\alpha = 150.7$, $\beta = 90.0$, $\gamma = 101.3$.

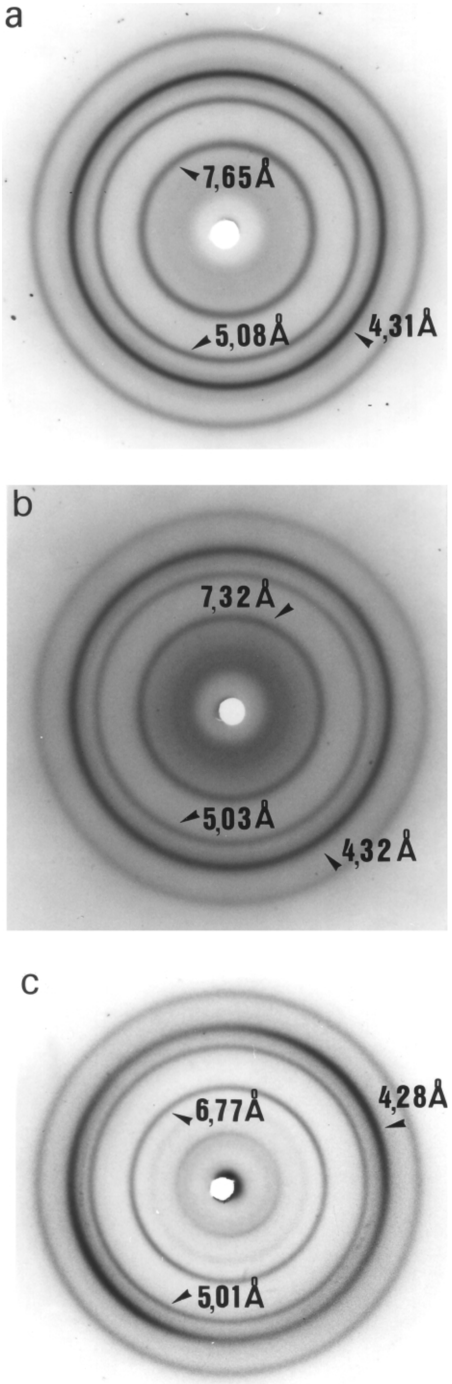

Fig. 3. Powder X-ray diagrams of PDMBA*n* (a) PDMBA8, (b) PDMBA10, (c) PDMBA12.

3.2. Fiber X-ray diffraction and electron microscopy

Fiber X-ray diffraction of polyamides PDMBA8, PDMBA10 and PDMBA12 were registered for samples of the polymers obtained by stretching from the melt and subsequent annealing at temperature near the melting point (Fig. 4).

It is remarkable the high degree of orientation and crystallinity obtained in all cases and the resemblance

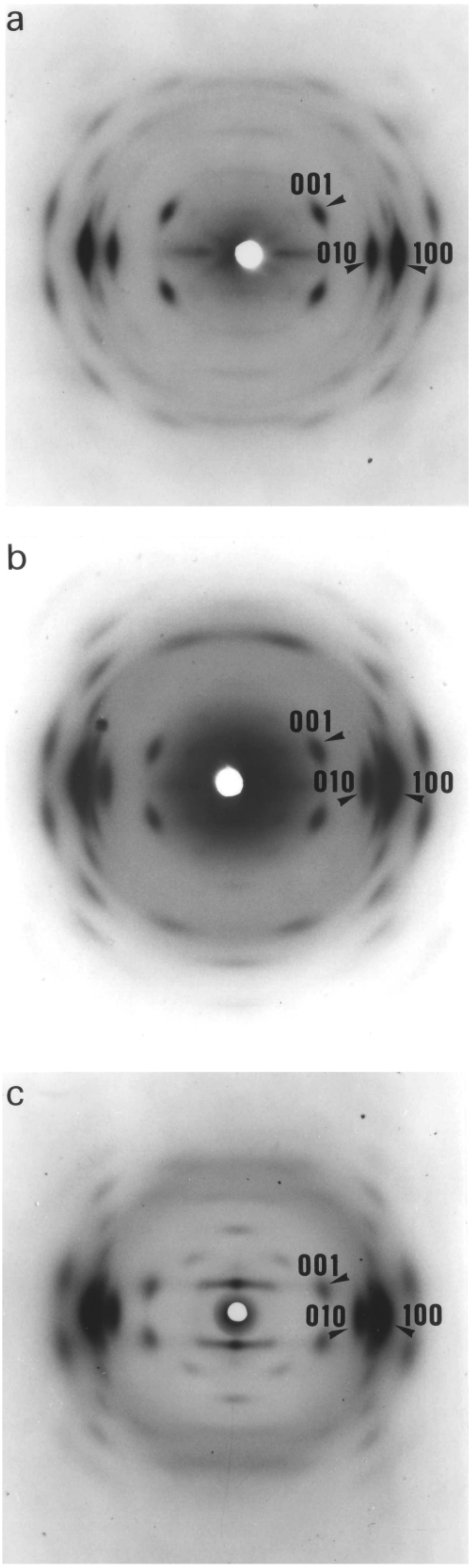

Fig. 4. Fiber X-ray diagrams of PDMBA*n*. (a) PDMBA8, (b) PDMBA10, (c) PDMBA12.

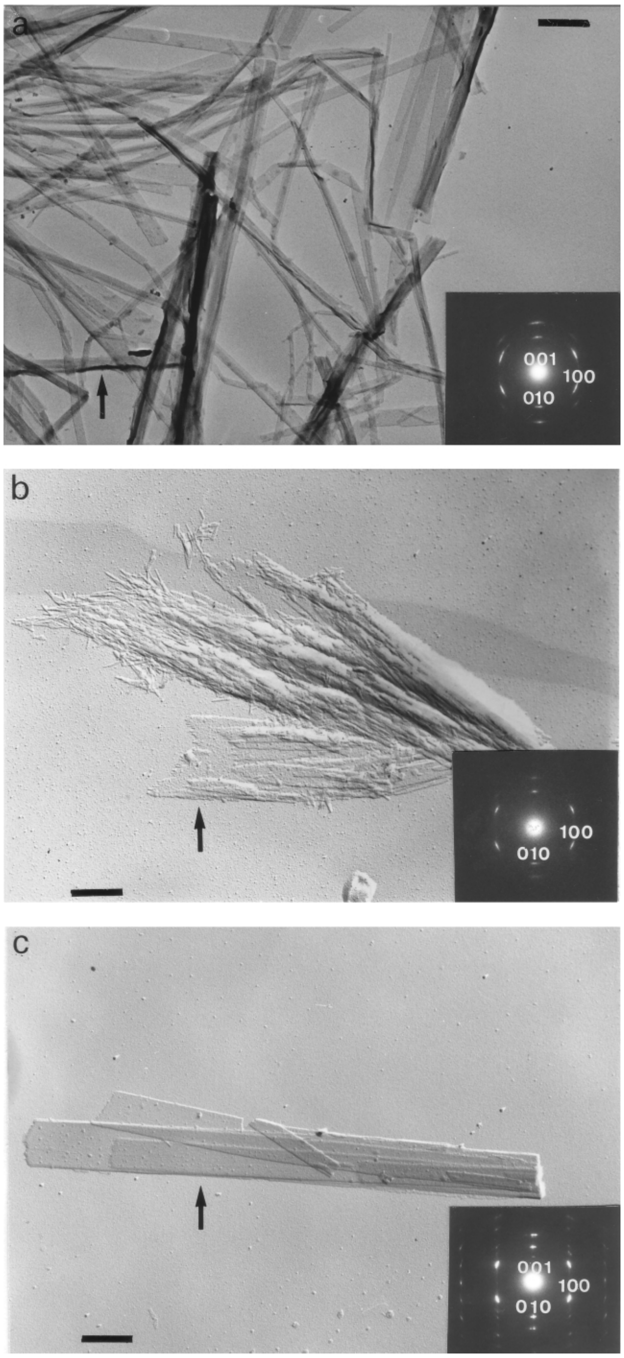

Fig. 5. Lamellar crystals of PDMBA*n* grown in glycerine (crystallization conditions displayed in Table 6). (a) PDMBA8, (b) PDMBA10, (c) PDMBA12. Arrows indicate the orientation of the crystal relative to the diffraction pattern. Scale bar: 1 μm.

of the three patterns. This similarity is obvious in the equator of the diagrams and the correlative distribution of the reflections along the different layer lines of the fiber diagrams. The interplanar spacings and Miller indexes *hkl* are summarized in Table 4 for PDMB8, assuming a triclinic unit cell. Comparison among the lattice parameters of the three polyamides indicates that the *c*-axis, *b*-axis and α angle increase slightly with n,

Table 5
Crystallographic characteristics of polyamides PDMBA*n*

PDMBA*n*	a^a	b^a	c^a	α	β	γ	$d_{calcd}{}^b$	$d_{obsd}{}^b$	Space group
PDMBA8	4.75	11.3	16.4	150.7	90.0	101.3	1.18	1.07	$P1$
PDMBA10	4.75	13.1	18.7	154.6	90.0	100.6	1.08	1.08	$P1$
PDMBA12	4.67	15.4	21.0	159.2	90.0	98.7	1.18	1.07	$P1$

[a] Lattice parameters *a*, *b*, *c* in Å.

[b] Densities in g/mL.

this feature being related with the arrangement of the chains into the unit cell.

Experimental densities are in excellent accordance with the values calculated by assuming a triclinic unit cell with one repeat constitutional unit. Table 5 shows the crystallographic characteristics of the polyamides PDMBA*n*.

Single crystals of the three polyamides were obtained by isothermal crystallization using glycerin as solvent.

They have a uniform rectangular morphology, the width ranging from 0.5 to 2 μm, although the lamella perfection increases in PDMB10 and PDMB12 (Fig. 5).

In the case of PDMB12, the lamellae are rolled themselves. The anisometry of these crystals is characteristic of a growth along a preferential direction, which corresponds to the hydrogen bond formation [8]. The thickness estimated from electron micrographs of Pt-carbon shadowed specimens is of about 60 Å, this value being usually observed for polyamide lamellae with chains arranged in a layered structure [9]. Morphological characteristics and crystallization conditions of PDMBA*n* are indicated in Table 6.

Electron diffraction patterns obtained from the crystals consist of a rectangular array of 4.70×10.12 Å^2 (inset Fig. 5) and may be straightforwardly interpreted as arising from the projection down the *c*-axis of the crystal lattices defined above.

It is important to emphasize the presence of *hkl* reflections with $l \neq 0$, clearly visible in the PDMB12 (001 reflection indicated in Fig. 5) which are indicative of partial inclination of lamellae along the [100] direction. The orientation of the electron diffraction diagrams with respect to the lamellae indicates that the [100] is the crystal growth preferential direction. This direction has the basic spacing of 4.7–4.8 Å, which corresponds to the chains separated by hydrogen bonds.

Table 6
Crystallization conditions and morphological characteristics of polyamides PDMBA*n*

PDMBA*n*	T_s (°C)^a	T_c (°C)^b	Solvent	Width (μm)	Thickness (Å)
PDMBA8	200	110	Glycerine	0.5	60–70
PDMBA10	195	90	Glycerine	1.0–1.5	60–70
PDMBA12	190	109	Glycerine	0.7	60–70

[a] Polymer solution temperature.

[b] Isothermal crystallization temperature.

3.3. Preliminary results of molecular modeling with Cerius

The chemical constitution of polyamides PDMBA*n* is very different to that of the polytartaramides P*n*DMLT, particularity the unit containing the two chiral centers.

In P*n*DMLT the unit CHOMe–CHOMe (Me = methyl group) is surrounded by the carbonyl groups of two amide bonds, whereas in PDMBA*n* this unit is placed between two methylene groups, allowing a greater conformational flexibility. These differences are responsible for the changes in the thermal and structural properties.

The shortening of the chain repeat length with respect to that of the fully extended conformation (between 1.1 and 1.5 Å) suggests a partial folding in the asymmetric unit of PDMBA*n*. Moreover, the conformation of these polymers cannot be considered as a γ-form of nylons [10] for which a smaller shortening has been observed, i.e. 0.35 Å by amide group or 0.7 Å by repeat constitutional unit in nylons of AABB type. As a consequence, a new conformational model intermediate between that of the conventional nylons and that found for polytartaramides P*n*DMLT should be considered. On the other hand, the correlation between the *n* and the chain repeat length shows that a common conformation must be assumed for all members of the series.

Cerius has been reported to be a useful tool in the structural study of polymers if sufficient diffraction data are

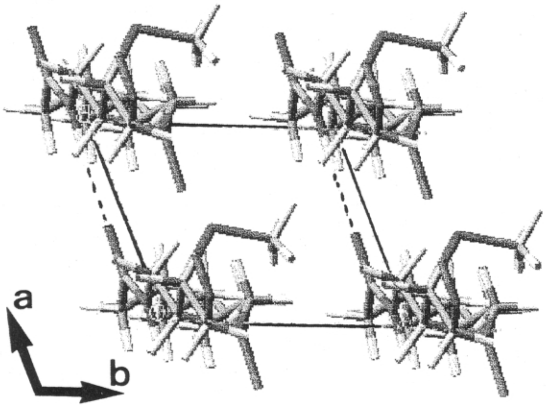

Fig. 6. Preliminary scheme of the projection along the *c*-axis of the crystal structure in PDMB8. Hydrogen bonds are parallels to *a*-axis.

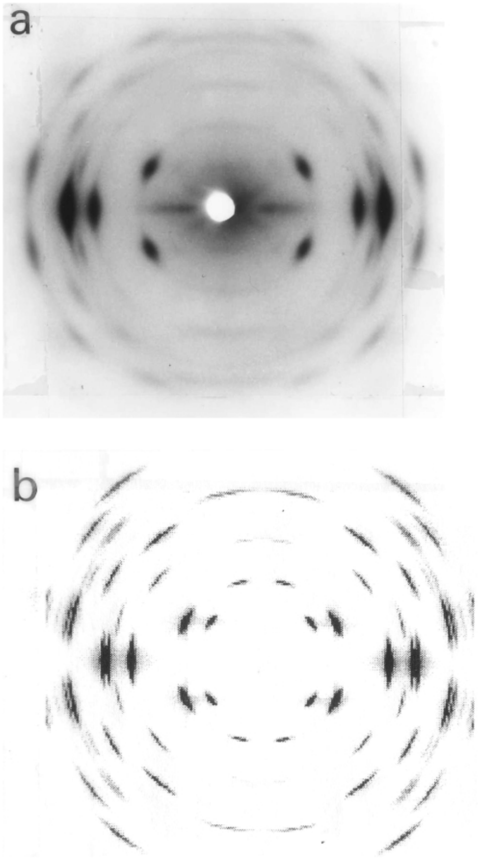

Fig. 7. Experimental (a) and simulated (b) fiber X-ray diagrams obtained from crystallographic data of PDMB8.

available and the conformation of the asymmetric unit is known [11–14].

Based only on the crystallographic data, a preliminary model was built by assuming the hydrogen bond formation in the *a*-direction. Torsion angles of ±120° were selected for the bonds defined in the CHOMe–CHOMe unit.

The asymmetric unit was accommodated into the unit cell, the position and orientation of the chain being subsequently adjusted to obtain a good concordance between the experimental and simulated diffraction patterns.

The model for PDMLB8 is represented in Fig. 6 and the experimental and simulated fiber X-ray diagrams are compared in Fig. 7. An acceptable concordance was achieved in both position and intensities of reflections. Although this model should be refined in the near future on the basis of a complete conformational analysis of the polymer chain, a few interesting structural characteristics can be pointed for these polyamides from the Fig. 7. The presence of a packing and layered structure, as well as an intermolecular hydrogen bonds arrangement similar to the conventional nylons and related polytartaramides P*n*DMLT are the most important features. Moreover, the different placement of the chiral centers into the repeat unit is the beginning of a more complete study of the conformational possibilities of these polytartaramides PDMBA*n*.

4. Conclusions

A structural study of the polyamides derived from L-tartaric acid with the chiral fragment located at the diamine fragment has been carried out. A great crystallinity was exhibited in all cases and powder and fiber X-ray diagrams allowed establish the crystallographic characteristics of their structures. The electron diffraction of single crystals obtained from isothermal crystallization supplied complementary information about the hydrogen bonding direction and corroborated the unit cell proposed from X-ray diffraction data. A preliminary investigation of molecular models suggests an intermedium conformation between that of the γ-form of the nylons and that corresponding to the isomer polyamides P*n*DMLT. However, a more complete analysis is necessary to obtain concluding results in the latter field.

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