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Polymer 40 (1999) 6887–6892

polymer

Polymer Communication

Structure of odd–even nylons derived from 2-methylpentamethylenediamine. Effect of the side methyl group

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Received 15 January 1999; received in revised form 26 March 1999; accepted 7 April 1999

Abstract

Structure and morphology of lamellar crystals of two polyamides derived from 2-methylpentamethylenediamine (MPMD) and dibasic acids with 4 or 8 methylenes have been studied by transmission electron microscopy, electron diffraction and X-ray diffraction. The crystallographic unit cell of MPMD-6 is triclinic with $a = 4.85$, $b = 5.90$, c (chain axis) $= 30.4$ Å, $\alpha = 115.40$, $\beta = 99.9$ and $\gamma = 61.1°$, the chain axis direction is not coincident with the c^* reciprocal axis. These dimensions suggest a hydrogen-bonded sheet structure with a single hydrogen bond direction and a twist of 180° in the odd diamine unit. MPMD-10 shows two crystalline structures. The most abundant being a monoclinic unit cell with $a = 4.79$, $b = 5.67$, c (chain axis) $= 36.3$ Å and $\gamma = 61.8°$. The less abundant structure was only observed in oriented fibers and was similar to the MPMD-6 crystalline structure. Single crystals of both MPMD-6 and MPMD-10 polyamides grow preferentially along their single hydrogen bond direction.

Keywords: Polyamides; Nylons; 2-Methylpentamethylenediamine

1. Introduction

2-Methylpentamethylenediamine (MPMD) is an isomeric compound of hexamethylenediamine (HMD) and it is sold by DuPont under the trade name Dytek® A. This compound was used as a polymer intermediate to investigate how the incorporation of MPMD affects the crystalline structure of nylon 6,6, and how the homopolymer can crystallize [1]. Preliminary powder X-ray diffraction studies were carried on with the MPMD-6 homopolymer and demonstrated two different structures depending on the temperature of crystallization. The room temperature structure was characterized by strong reflections at spacings of 13.2, 5.22, 4.52 and 4.24 Å, which were indexed using a putative monoclinic unit cell with parameters $a = 4.83$, $b = 5.94$, c (chain axis) $= 13.4$ Å and $\gamma = 61.33°$. This cell was only used to estimate the crystal density since a triclinic cell was also possible, but not unambiguously determined, due to the paucity of reflections in the powder pattern. The structure of some even–odd polyamides (nylons 6,5 [2], 12,5 [3] and 6,9 [4]) as well as some odd–even polyamides (nylons 9,2 [5], 5,6 [6] and 5, 10 [7]) have been recently investigated. In all the cases, reflections close to the characteristic spacings of the layered α structure [8] of commercial polyamides (i.e. nylons 6,6 [9], 6,10 [9] and 6 [10]) can be found. These results were surprising, since a γ form was predicted [11] due to the non-optimal hydrogen bond geometry that is established, when nylons with odd diamine or diacid units adopt the extended conformation of the α form. Thus, a modification of this structure based on a deviation towards 150° (or −150°) for the two φ_i (CH_2CH_2–NHCO) or ψ_i (CH_2CH_2–CONH) torsional angles of the odd unit was postulated. As a consequence, the two amide groups of the odd unit rotate in opposite directions from the plane constituted by the methylene carbons, giving rise to a structure with two hydrogen bond directions. Their chain axis projected unit cell is in all cases, a centered rectangular one where the dimensions of the two diagonals (2×4.79 Å) are in agreement with the characteristic distance between hydrogen bonded chains.

The scope of the present work is to collect more structural data on MPMD-6, and to study the polymer MPMD-10 where a long polymethylene segment exists (Scheme 1). Thus, the influence of the methyl side group on the crystal structure will be studied, taking into account the structural data recently obtained for the related nylons 5,6 [6] and 5,10 [7].

2. Experimental section

MPMD-6 and MPMD-10 samples of high molecular

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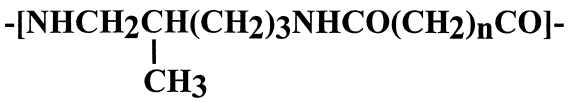
0032-3861/99/$ - see front matter
PII: S0032-3861(99)00285-2



n = 4 MPMD-6

n = 8 MPMD-10

Scheme 1.

weights were kindly provided by DuPont. The density of the fiber samples was measured at 25°C by the flotation method in mixtures of ethanol and carbon tetrachloride.

Crystallization experiments were carried out isothermally from dilute solutions (0.05–0.1% (w/v)) in 2-methyl-2,4-pentanediol (MPD). Polymers were dissolved at 220°C and solutions were transferred to constant-temperature baths in the 30–135°C interval for 1–2 h. For electron microscopy study, the crystals were deposited on carbon coated grids which were then shadowed with Pt–carbon at an angle of 15°. A Philips EM-301 electron microscope, operating at either 80 or 100 kV for bright field and electron diffraction modes, respectively, was used throughout this work. Electron diffraction patterns were recorded by the selected area method on Kodak Tri-X films. The patterns were internally calibrated with gold ($d_{111} = 2.35$ Å). A polymer decoration was achieved evaporating polyethylene onto the surface of single crystals, as described by Wittmann and Lotz [12].

X-ray diagrams were recorded under vacuum at room temperature, and calcite ($d_B = 3.035$ Å) was used for calibration. A modified Statton camera (W.R. Warhus, Wilmington, DE) with Ni-filtered copper radiation of wavelength 1.542 Å was used for these experiments. Patterns were recorded from either polymer powders, fibers or mats of single crystals, which were prepared by slow filtration of a crystal suspension through a glass filter.

3. Results and discussion

Both MPMD-6 and MPMD-10 nylons crystallized from dilute solutions as lath-like crystals (Figs. 1(a) and 2(a)), which frequently display outstanding longitudinal striations have an average thickness of ca. 60 Å. In general, the electron diffraction patterns (Fig. 1(b)) have split diffraction spots that indicate a twinned structure. However, it is possible to get in some cases of single crystal patterns (Figs. 1(c) and 2(b)) that correspond to oblique unit cells. The reflections at 5.16 ($01\bar{2}$) and 5.00 Å (010) for MPMD-6 and MPMD-10, respectively, appear perpendicularly oriented to the longitudinal direction of the crystals and are not split in the twinned patterns. Decoration experiments showed (Figs. 1(d) and 2(c)) that polyethylene bars were deposited perpendicularly to the growth direction of the crystal, and so it may be concluded that molecular folding takes place in this direction [12].

Similar X-ray diffraction spacings were measured for MPMD-6 samples obtained at different preparation

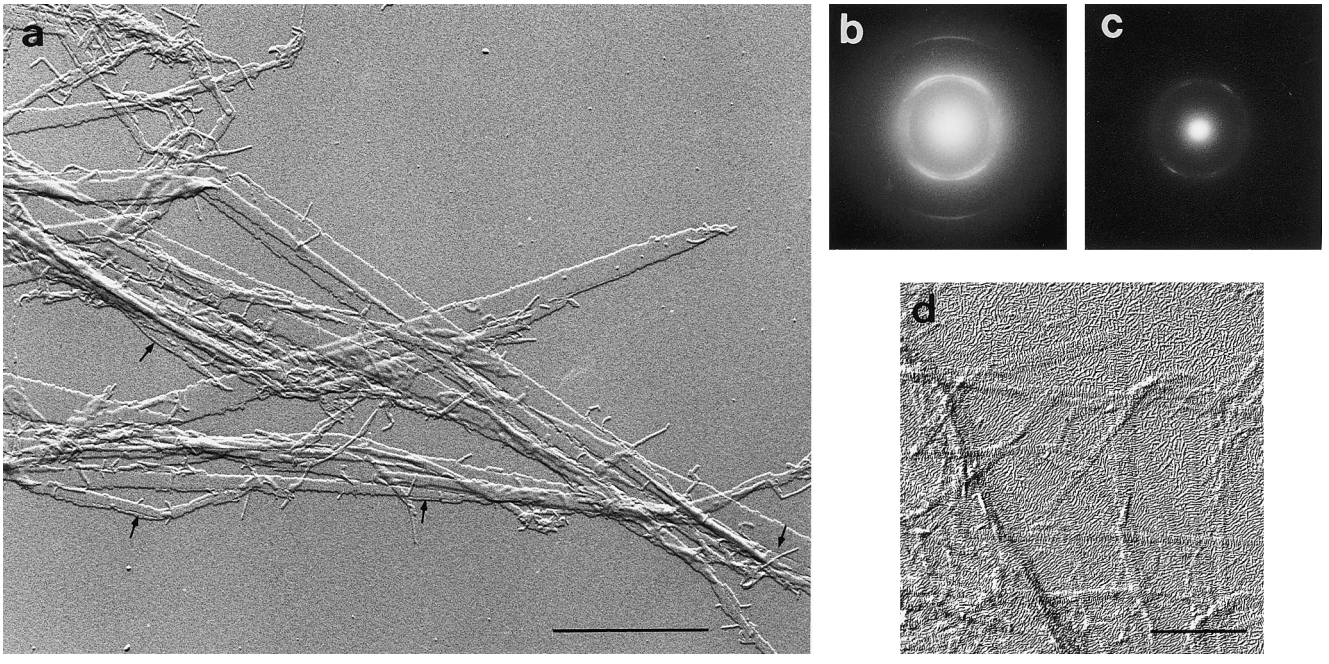


Fig. 1. (a) Lamellar crystals of MPMD-6 obtained from a dilute solution (0.1% (w/v)) in 2-methyl-2,4-pentanediol at 78°C. Arrows indicate longitudinal striations. (b) twinned electron diffraction pattern usually observed in the MPMD-6 crystals. The external reflection at 2.40 Å is oriented in the longitudinal direction of the lamellar crystals. (c) Single crystal electron diffraction pattern of MPMD-6. (d) Electron micrograph of MPMD-6 crystals decorated with polyethylene that reveals a folding habit parallel to the long axis of the crystals, and consequently along the hydrogen-bonded sheets. Molecular chains have to be folded in the lamella due to the polymer molecular weight and the reduced lamellar thickness (ca. 60 Å). Scale bars 1 μm.

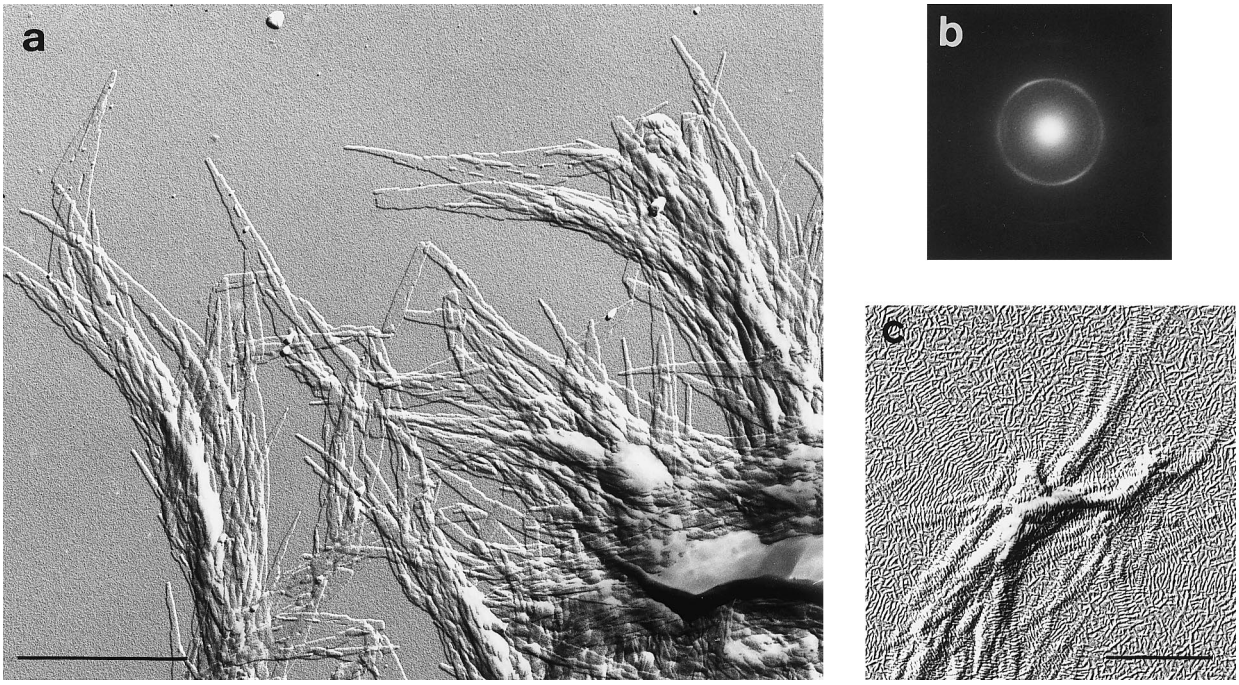


Fig. 2. (a) Lamellar crystals of MPMD-10 obtained from a dilute solution (0.1% (w/v)) in 2-methyl-2,4-pentanediol at 32°C. (b) Single crystal electron diffraction pattern of MPMD-10. The 2.40 Å reflection is oriented in the crystal growth direction, indicating that hydrogen bonds run parallel to this direction. (c) Polyethylene decoration of MPMD-10 single crystals. The decorating rods are frequently oriented perpendicular to the long edges. Scale bars 1 μm.

conditions. The electron diffraction pattern and the non-meridional 00*l* reflections observed in the fiber pattern (Fig. 3), indicate a triclinic structure. A unit cell of parameters: $a = 4.85$; $b = 5.90$; $c = 30.4$ Å; $\alpha = 115.40$; $\beta = 99.9$; and $\gamma = 61.1°$ could be deduced from these diffraction data (Table 1). Note that the 5.16 Å reflection appear in the second layer line (Fig. 3) and so it is indexed as $(01\bar{2})$. This interpretation seems also compatible with the electron diffraction pattern, since the $(01\bar{2})$ planes become oriented practically perpendicular to the lamellar surface due to the tilting of the molecular chains (α and $\beta \neq 90°$). Furthermore, a calculated density of 1.09 g/cc is in close agreement with the experimental measure of 1.05 g/cm^3. The chain axis projected unit cell ($a_p = 4.77$; $b_p = 5.32$ Å; and $\gamma_p = 63°$) points to a structure with a single hydrogen bond direction, which differs from that postulated for the related nylon 5,6 [6]. In this sense, a model with two hydrogen bond directions appears improbable due to the steric hindrances of the side methyl groups. Note also, that they have to be randomly distributed among four possible positions, since MPMD contains an asymmetric carbon and is believed to be a mixture of the two isomers. Moreover, it is expected that the two ends of the diamine enter the polymer chain at random. A 180° twist must exist within the odd diamine moiety in order to establish hydrogen bonds in a single direction and with an optimal geometry, when the diacid unit takes an extended conformation. This kind of twist can be obtained when both φ_i torsional angles of the diamine unit are close to 70°. However, in this case the *c* parameter must be shorter than the experimental value, and

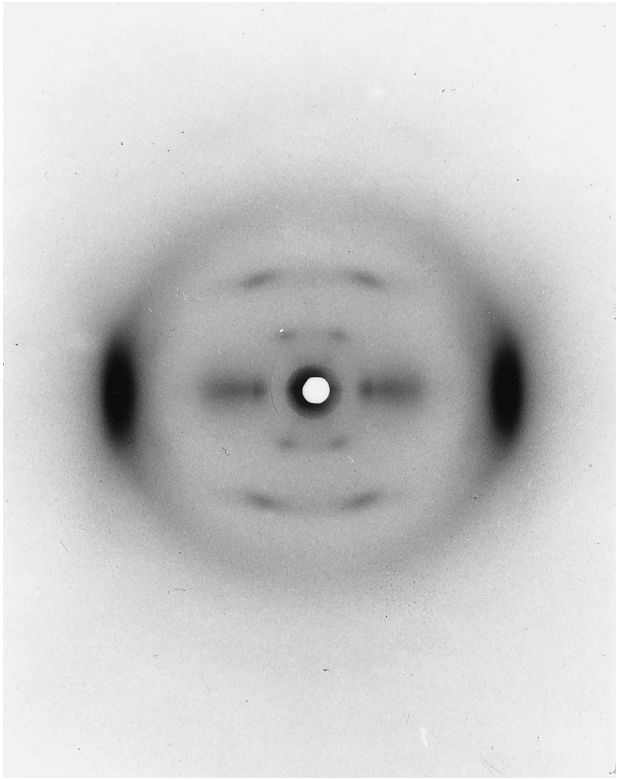


Fig. 3. Fiber diffraction pattern of MPMD-6 where non-meridional 00*l* reflections are characteristic. A cc^* angle of 25.3° can be measured as well as a fiber repeat period of 30.4 Å. This value is shorter than both the expected one for an all-*trans* conformation (31.8 Å), and that found in the α-like phase of the related nylon 5,6 [6].

Table 1
Measured and calculated diffraction spacings for different MPMD-6 samples

Index[a]	Calculated	Single crystal[b,c]	Fiber[b,d]
001	27.4		27.3 vw off-M
002	13.72		13.76 m off-M
003	9.15		9.14 vw off-M
004	6.86		6.90 s off-M
01$\bar{2}$	5.16	5.16 w	5.18 w off-M
11$\bar{2}$	4.52	4.52 m }	4.54–4.26 vs E
100	4.24	4.24 vs }	
103	3.92		3.92 w off-M
10$\bar{4}$	3.68		3.63 w off-M
11$\bar{8}$	3.22		3.26 w off-M
01$\bar{9}$	3.22		3.17 w M
21$\bar{2}$, 21$\bar{1}$, 21$\bar{0}$	2.42, 2.41, 2.40	2.40 m	2.41 m E
11$\bar{1}\bar{1}$	2.53		2.53 w off-M
11$\bar{1}\bar{2}$	2.35		2.36 w M

[a] On the basis of a triclinic cell: $a = 4.85$, $b = 5.90$, $c = 30.4$ Å, $\alpha = 115.40$, $\beta = 99.9$ and $\gamma = 61.1°$.
[b] Abbreviations denote intensities or orientation: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; M meridional; E, equatorial; and off-M, off meridional.
[c] Electron diffraction data.
[d] X-ray diffraction data.

so it may be supposed that the dihedral angles adjacent to the $CH(CH_3)$ group may be also deviated from 180°, in order to contribute to the twist of the diamine unit. In this sense, a conformational study of a MPMD model compound has recently been done by using ab initio quantum mechanical calculations [13]. The results of this study show that the φ_i angles are stabilized in a skew conformation, whereas the $NHCH_2–CH(CH_3)CH_2$ torsion angle tends toward a *gauche* conformation. A molecular symmetry close to 2/*c* is expected to exist as the methyl groups are randomly distributed, and so both a binary axis perpendicular to the chain direction through the middle of the diamine unit and, a center of symmetry in the middle of the diacid moiety, are possible. As a consequence, the chain repeat period is constituted by two chemical repeat units in which diamine moieties have an opposite twist sense. Note that this symmetry is not a crystallographic one, since the unit cell is triclinic, and thus weak 00*l* reflections (*l* = odd) are observed. The cell dimensions indicate a sheet structure where hydrogen-bonded chains are shifted along the chain direction by ca. *c*/38, according to the β triclinic angle, and consecutive sheets are shifted along both the hydrogen bond direction (ca. half hydrogen bond distance) and along the chain axis direction (ca. *c*/10.4). The orientation of the electron diffraction pattern with respect to the morphology, shows that the single crystals preferentially grow along the hydrogen bonding direction, and that the twinning plane corresponds to the hydrogen-bonded sheets. The longitudinal dislocations, which appear in the crystals, are thus regarded as morphological evidence for a structural disorder in the arrangement of these sheets. It is worth also to note the low intensity of the (010) reflection (a weak signal at 4.79 Å can only be detected and differentiated from the intense signal at 4.52 Å in powder patterns). This observation indicates a deviation from an all-*trans* conformation that smears out the electron density in the *b* direction.

Two different crystalline structures have been found for MPMD-10. The first one is obtained either by solution crystallized samples or by fibers directly obtained from the melt (Fig. 4(a)). In this case, a meridional orientation is observed for the 00*l* reflections and so a monoclinic unit cell of parameters: $a = 4.79$; $b = 5.67$; $c = 36.3$ Å; and $\gamma = 61.8°$ can be deduced (Table 2). A calculated density of 1.04 g/cm^3 is in good agreement with the experimental value of 1.03 g/cm^3. The structure is again characterized by a single hydrogen bond direction (along *a*), that runs parallel to the crystal growth direction and a space group that does not obey the molecular symmetry. Thus, the 00*l* reflections with *l* = odd are clearly visible in the diffraction

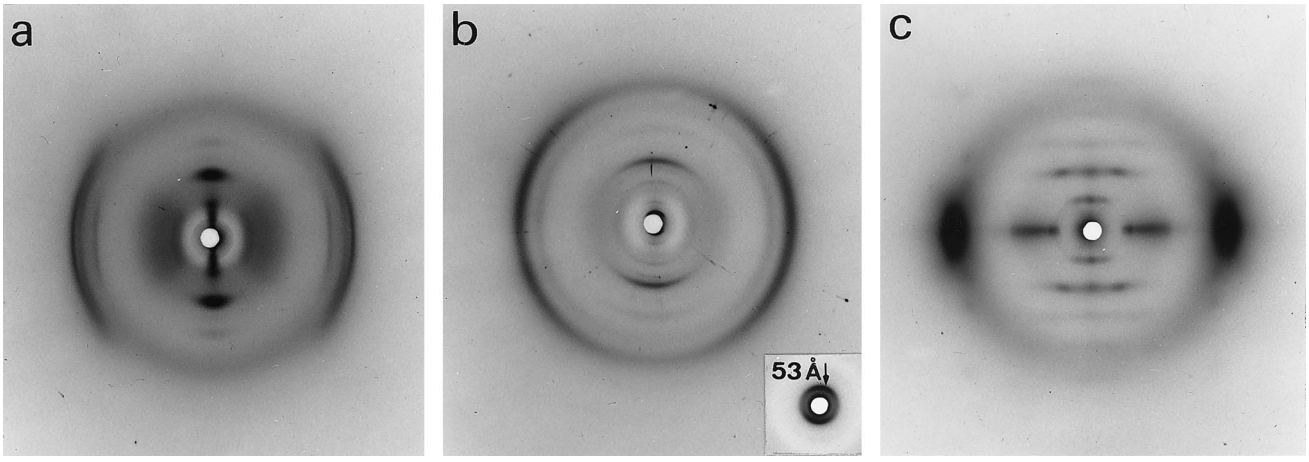


Fig. 4. (a) X-ray diffraction pattern of MPMD-10 fibers directly obtained from the melt. (b) Mat of sedimented crystals of MPMD-10. The inset corresponds to the low-angle pattern where the first lamellar order can be measured. (c) New non-meridional 00*l* reflections appear in the X-ray diffraction pattern when MPMD fibers were annealed under stress at 120°C.

Table 2
Measured and calculated diffraction spacings for different MPMD-10 samples

Index[a]	Calculated	Single crystal[b,c]	Fiber[b,d]	Crystal mat[b,d]
1st lameller order	53			53 s M
2nd lamellar order	26.5			26.7 w M
002	18.1		17.9 s M	
3rd lamellar order	17.7			17.5 w M
4th lamellar order	13.25			13.4 m M
003	12.10		12.10 w M	
5th lameller order	10.60			10.5 w M
004	9.08		9.08 vs M	9.00 s M
005	7.26		7.26 w M	7.25 w M
006	6.05		6.05 m M	6.04 m M
010	5.00	5.00 w	5.00 vw E	
011	4.95		4.94 m off-M	4.94 m E
013	4.62		4.62 vw off-M	
008	4.54		4.52 vw off-M	
110	4.41	4.40 s	4.44 s E	
100	4.22	4.22 s	4.22 vs E	4.30 vs E
015	4.11		4.13 w off-M	
104	3.83		3.82 m off-M	
017	3.60		3.60 vw off-M	
019	3.14		3.08 vw off-M	
00, 12	3.02		3.00 vw off-M	
01, 13	2.44		2.36 w off-M	
210	2.39	2.40 w	2.40 m E	
01, 15	2.18		2.16 w off-M	
220	2.21		2.21 w E	
200	2.11		2.09 w E	

[a] On the basis of monoclinic cell: $a = 4.79$, $b = 5.67$, $c = 36.3$ Å and $\gamma = 61.8°$.
[b] Expansion for abbreviations as in Table 1.
[c] Electron diffraction data.
[d] X-ray diffraction data.

patterns and precludes the existence of a binary screw axis which relates the two chemical repeat units of the unit cell. This structure is different to the triclinic one observed in MPMD-6, and seems to be related to the pseudohexagonal γ form of nylons, in the sense that the c and c^* axes are not coincident. It is also interesting to note that the γ form is stabilized when long polymethylene segments are present due to the improved van der Waals interactions between their methylene groups. In the same way, the related nylon 5,10 [7] showed also a greater tendency to adopt a γ form than the nylon 5,6 [6]. The molecular conformation of the MPMD-10 monoclinic form is far away from all-*trans*, since shortening of a ca. 1.4 Å/amide group is observed. Thus, the torsional ψ_i angles of the diacid unit may be deviated towards 120° (as a conventional γ form [14]), in addition to the folding of the diamine moiety. The lamellar thickness of MPMD-10 crystals can be accurately deduced from the lamellar orders observed in the mat of sedimented crystals (Fig. 4(b) and Table 2). A lamellar thickness of 53 Å is found, and indicates that three chemical repeat units exist in the lamella. In comparison, four repeat units are deduced for MPMD-6 in agreement with the common feature of nylons [15], that the number of amide groups within the lamella decreases as the number of methylenes in the chemical repeat.

MPMD-10 gives also a structure similar to that found in MPMD-6 when fibers are annealed (120°C) under stress. Thus, non-meridional 00*l* reflections (17.72, 8.83 and 5.97 Å) are observed (Fig. 4(c)) in addition to the characteristic ones of the monoclinic structure. Unfortunately, fibers break before a complete structural transition is attained, and so the unit cell cannot be deduced due to reduced number of observed reflections. However, a cc^* angle of 39.7° is measured and a chain axis parameter of 39.7 Å can be deduced, which indicates a more extended conformation than the previous structure. Moreover, a shortening with respect to the all-*trans* conformation ($c = 41.8$ Å) and to the α-like phase ($c = 41.07$ Å) of nylon 5, 10 [7] is still found.

Three main conclusions can be derived from the present work. (a) A similar structure with a single hydrogen bond direction and non-coincident cc^* axes has been found in both polyamides. (b) The side methyl group of the MPMD units precludes the structure with two hydrogen bond directions postulated for nylons with odd diamine units. (c) When the number of methylenes of the diacid moiety increases a second structure with a shorter repeat unit, and a monoclinic unit cell seems to be favored. This behavior is similar to that found between the α and the γ structures of the conventional nylons.

Acknowledgements

This investigation has been supported by a research grant from CICYT (MAT97-1013). L.F. acknowledges financial support from the Ministerio de Educación y Cultura. We are also grateful to Dr. K. Gardner from the DuPont Company, who provided us the samples used for this study.

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