

# Incorporation of glycine residues in even–even nylons disrupts their characteristic all-*trans* conformation

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(Received 15 May 1997; revised 27 August 1997; accepted 16 October 1997)

A series of regular polymers derived from the inclusion of glycine in even–even nylons (2,4, 2,6, 4,4 and 4,6) has been prepared by the active ester method. The structure and morphology of lamellar crystals have also been investigated by using transmission electron microscopy, selected-area electron diffraction and X-ray diffraction. The results indicate that at room temperature the structure of these nylons is different from the typical forms ( $\alpha$  and  $\beta$ ) of even–even polyamides. Observations described in this paper are complementary to previous work about the incorporation of glycine units in nylons derived from  $\omega$ -amino acids and indicate that glycine residues always tend to adopt their characteristic polyglycine II conformation. © 1998 Elsevier Science Ltd. All rights reserved.

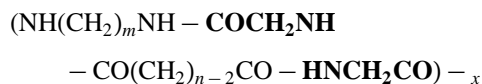
(Keywords: polyamides; nylons; glycine)

## INTRODUCTION

At room temperature even–even nylons are generally found in parallel sheets of hydrogen-bonded molecular chains which have an extended conformation<sup>1–4</sup>. These sheets can either stack together with a progressive shear (termed  $\alpha$ -phase<sup>5,6</sup>) or with a staggered shear (termed  $\beta$ -phase<sup>5,6</sup>), giving different triclinic unit cells. Another structure, the  $\gamma$ -form<sup>6,7</sup>, corresponds to a pseudo-hexagonal packing which is also organized in parallel sheets. In this case hydrogen bonds are established between amide groups which are tilted *ca.* 60° off the plane defined by the methylene carbons. This last form is seldom found in even–even polyamides. However, when hydrogen bonds cannot be well established between chains in their extended conformation (even–odd, odd–even and odd–odd nylons) this structure is favoured.

In recent years interest in the study of polymers which incorporate  $\alpha$ -amino acids has increased since they may have biodegradable properties<sup>8–11</sup>. In fact, some glycine-containing polyamides derived from nylon 6,6 and nylon 6 have been reported to be biodegradable<sup>12–14</sup>. Structural studies have been also carried out in polymers derived from glycine and different  $\omega$ -amino acids ( $\beta$ -alanine, 6-aminohexanoic acid, 11-aminoundecanoic acid and 12-aminododecanoic acid), which have been extensively studied<sup>15–19</sup>. The results show a new structure for these polymers (named nylons 2/*n*) which is related to the polyglycine II structure reported by Crick and Rich<sup>20</sup>. Thus, glycine residues adopt a characteristic conformation with their torsional angles  $\Psi$  (–NHCOCH<sub>2</sub>NH–) and  $\phi$  (–COCH<sub>2</sub>NHCO–) close to –145° (or +145°) and +77° (or –77°), respectively. This conformation gives rise to a hexagonal lattice with hydrogen bonds running in three different directions. Thus, the standard structure of nylons with a single hydrogen bond direction is no longer present.

Following this line glycine can be also sequentially incorporated in a nylon *m,n*, giving polymers with a regular sequence of amide groups in a head-to-tail and tail-to-head arrangement. These polymers can be represented by the general formula:



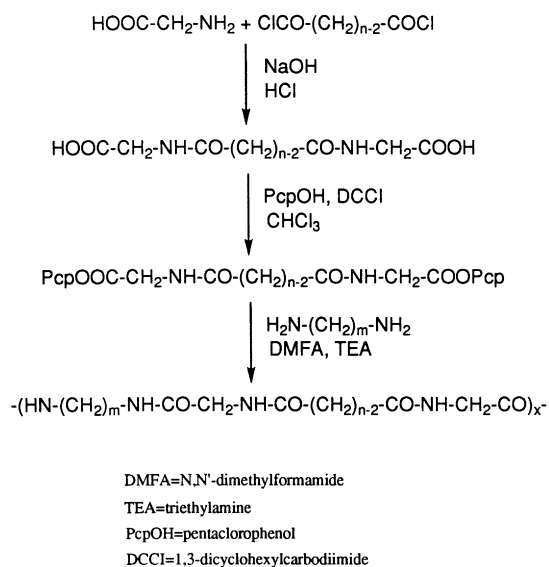
Note that the symmetry of the repeat unit causes adirectional molecular chains and so no distinction between a parallel or an antiparallel packing will exist, as is the case of nylons *m,n*. These new polymers can be synthesized by the polycondensation of a diamine and a special diacid which incorporates the glycine residues. Thus, we propose for simplification purposes the general denomination 'nylons *m,2/n/2*' in order to name them. In contrast to the previously studied nylons 2/*n*, their synthesis can be achieved with a high yield and a lower number of steps as described below. Thus, possible commercial applications can be envisaged. In this paper we study a group of polymers with an even lower number of methylenes (*m* = 2,4 and *n* = 4,6). As far as we know, it is the first time that the synthesis and structure of this kind of polymers have been investigated.

## EXPERIMENTAL

### Synthesis

All chemicals were ACS grade and were used as received. Solvents were purified and dried by standard methods<sup>21</sup>. Nylons 2,2/4/2; 4,2/4/2; 2,2/6/2 and 4,2/6/2 were synthesized by solution polycondensation of active esters following the three-step synthesis indicated in *Scheme 1*. The reaction between glycine and the appropriate diacyl chloride was conducted in a sodium hydroxide solution as described by Cleaver and Pratt<sup>22</sup>. The resulting diacids were activated

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Scheme 1

with pentachlorophenol using 1,3-dicyclohexylcarbodiimide as condensing agent<sup>23</sup>. Polymerizations were conducted at room temperature for a period of 5 days in a dimethylformamide solution. The total ester salt concentration was 1 g/ml, and 2.2 equiv. of triethylamine were added as proton acceptor. After addition, the solution turned gradually darker in color and more and more viscous in consistency. Polymers were precipitated from the reaction mixture by adding ethyl ether. The crude materials were washed successively with ethanol, water, ethanol and ethyl ether.

### Characterization

The chemical compositions of the polymers were ascertained by infrared and n.m.r. spectroscopies. The intrinsic viscosity of the polymers was determined with a Cannon-Ubbelohde microviscometer at a temperature of  $25.0 \pm 0.1^\circ\text{C}$ , using dichloroacetic acid as a solvent. Infrared absorption spectra were recorded from potassium bromide pellets with a Perkin-Elmer 783 spectrophotometer in the  $4000\text{--}500\text{ cm}^{-1}$  range. N.m.r. spectra were registered from solutions in deuterated trifluoroacetic acid using tetramethylsilane (TMS) as an internal standard. A Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz was used for  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. studies, respectively. Thermal behavior was investigated with a Perkin-Elmer DSC-4 equipped with a TADS data station at a heating rate of  $10^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. Temperature was calibrated using an indium standard ( $T_m = 492.75\text{ K}$ ).

### Structural methods

Crystallization experiments were carried out isothermally from diol solutions or from precipitation with *n*-butanol of dilute acid solutions. The crystals were recovered by centrifugation and were repeatedly washed with *n*-butanol.

For electron microscopy the crystals were deposited on carbon-coated grids and then shadowed with Pt-carbon at an angle of  $15^\circ$ . A Philips EM-301 electron microscope operating at either 80 or 100 kV for bright field and electron diffraction modes, respectively, was used. Electron diffraction diagrams were recorded by the selected area method on Kodak Tri-X films. The patterns were internally calibrated with gold ( $d_{111} = 2.35\text{ \AA}$ ).

X-ray diagrams were recorded under vacuum at room

**Table 1** Yields, elemental analysis, intrinsic viscosities and molecular weights estimations of nylons  $m,2/n/2$

Polymer	Yield (%)	Elemental analysis						$[\eta]^a$ (dl g <sup>-1</sup> )	$M_n^b$	$M_n^c$
		Carbon		Hydrogen		Nitrogen				
		Calc.	Found	Calc.	Found	Calc.	Found			
2,2/4/2	86	46.87	46.42	6.25	5.83	21.87	22.02	0.18	1200	1800
2,2/6/2	85	50.70	49.95	7.04	6.76	19.71	19.94	0.32	3500	5400
4,2/4/2	72	50.70	50.02	7.04	6.89	19.71	20.10	0.20	1500	3100
4,2/6/2	87	53.84	52.90	7.69	7.04	17.94	18.15	0.21	1600	2600

<sup>a</sup>Intrinsic viscosities measured in dichloroacetic acid at  $25^\circ\text{C}$

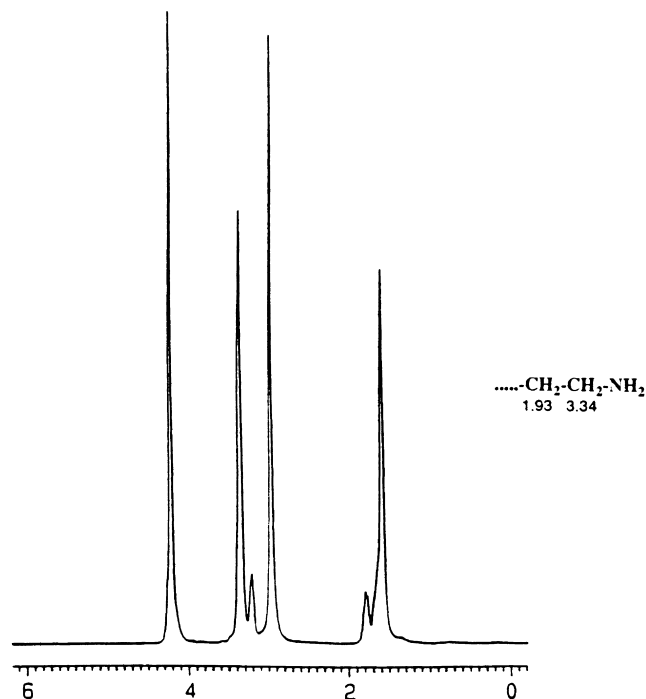
<sup>b</sup>Estimated by using the equation derived for nylon 6,6 (see Ref. 24)

<sup>c</sup>Determined from  $^1\text{H}$  n.m.r. spectroscopy

**Table 2**  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. chemical shifts (ppm) of nylons  $m,2/n/2^a$

	Polymer						
	<i>a</i>	<i>b</i>	<i>x</i>	<i>c</i>	<i>y</i>	<i>d</i>	<i>e</i>
$^1\text{H}$ n.m.r.							
2,2/4/2		3.80		4.36		3.12	
2,2/6/2		3.88		4.36		2.74	1.94
4,2/4/2	1.63	3.40		4.36		3.10	
4,2/6/2	1.58	3.43		4.33		2.80	1.85
$^{13}\text{C}$ n.m.r.							
2,2/4/2		41.34	172.27	45.46	179.21	31.98	
2,2/6/2		41.15	173.71	44.91	181.07	36.11	26.14
4,2/4/2	27.05	41.79	171.95	44.88	179.75	30.66	
4,2/6/2	27.42	41.65	173.84	42.93	181.86	36.35	26.17

<sup>a</sup>Assignments are given according to the labelled half repeat unit:  $-\text{CH}_2\text{ } a - \text{CH}_2\text{ } b - \text{NH} - \text{CO}_x - \text{CH}_2\text{ } c - \text{NH} - \text{CO}_y - \text{CH}_2\text{ } d - \text{CH}_2\text{ } e$ .



**Figure 1**  $^1\text{H}$  n.m.r. spectrum of nylon 4,2/4/2 in deuterated trifluoroacetic acid as representative of nylons  $m,2/n/2$ . Note the low intensity signals attributed to the terminal diamine units which were used to calculate their average molecular weight

temperature in a modified Statton camera (W. R. Warhus Wilmington DE) with a Ni-filtered  $\text{Cu K}\alpha$  radiation and were internally calibrated with calcite ( $d_B = 3.035 \text{ \AA}$ ). Patterns were recorded from either polymer powders or from mats of single crystals which were prepared by slow filtration of a crystal suspension on a glass filter.

## RESULTS AND DISCUSSION

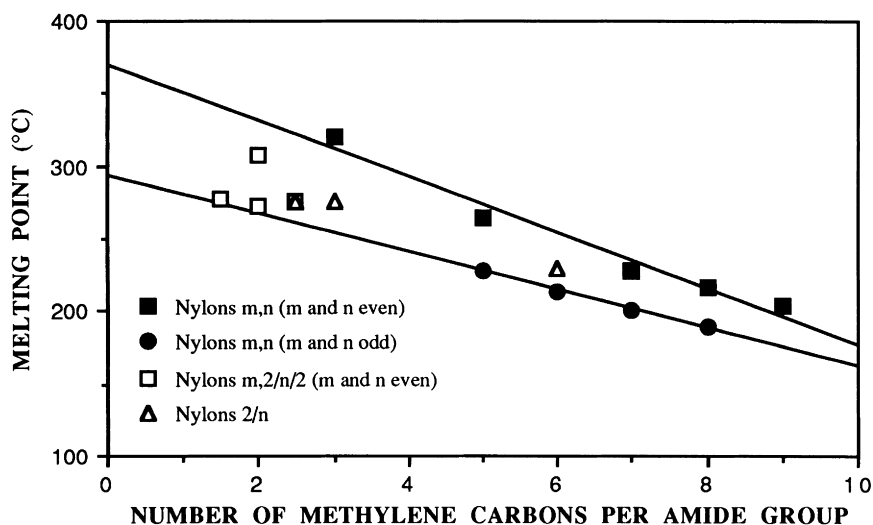
### Synthesis and characterization

The yields obtained in the synthesis of nylons  $m,2/n/2$  are relatively high (around 80%). However, their intrinsic

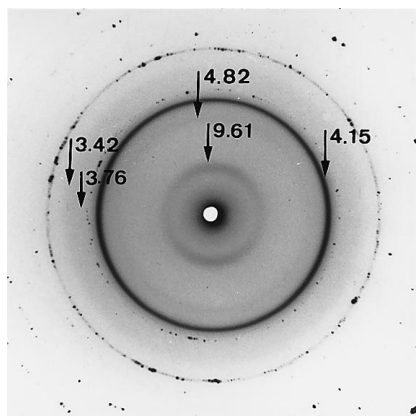
viscosities are low (*Table 1*), indicating reduced molecular weights. In fact an  $M_n$  value between 1200 and 3500, can be estimated using the Elias and Schumacher equation derived for nylon 6,6<sup>24</sup>. Precipitation of polymers at the incipient stages of polymerization is thought to be the cause of such results due to the high proportion of amide groups in the repeat unit. Thus, only strong acids such as formic, dichloroacetic or trifluoroacetic are good solvents for the polymers.

Data from n.m.r. spectroscopy are fully consistent with the anticipated chemical composition (*Table 2*). However, some additional low-intensity signals related with diamine terminal groups appear in both  $^1\text{H}$  and  $^{13}\text{C}$  spectra confirming the low molecular weight of these polymers. In agreement with the synthesis scheme no signals attributed to terminal diacid units could be detected. Furthermore the glycine methylene always appears as a single signal allowing us to assume that amine groups are the only kind of terminals. Thus, average molecular weights can be estimated from the integrated areas for protons of the different diamine units (*Figure 1*). These values are larger than those calculated from intrinsic viscosity using the expression derived from nylon 6,6<sup>24</sup>. It appears that the longer density of amide groups results in a more compact conformation in solution, probably due to intramolecular interactions between the peptide groups<sup>25</sup>.

Infrared spectra of all polymers show characteristic amide and methylene absorption bands. Signals arising from terminal pentachlorophenyl ester groups are not observed as expected from n.m.r. observations and in spite of the low molecular weight of the polymers. Thus, molecular weights could not be improved by thermal post-polycondensation as reported in related polymers<sup>19</sup>. A detailed study in the infrared spectra between 750 and 500  $\text{cm}^{-1}$  was performed. This region is highly sensitive to the conventional  $\alpha$  or  $\gamma$  structure of nylons. Two bands near to 695 and 568  $\text{cm}^{-1}$  appear but they do not fit with the expected ones for both the conventional  $\alpha$ -form<sup>26</sup> (690  $\text{cm}^{-1}$  (amide V) and 580  $\text{cm}^{-1}$  (amide VI)) and the  $\gamma$ -form<sup>27</sup> (630  $\text{cm}^{-1}$  (amide VI)). However, they agree with the characteristic absorptions found in the helical form II of polyglycine (696  $\text{cm}^{-1}$  (amide IV) and 563  $\text{cm}^{-1}$  (amide



**Figure 2** Melting points of nylons  $m,2/n/2$  versus number of methylene carbons per amide group. Melting temperatures of nylons  $m,n^1$  ( $\bullet$ ,  $\blacksquare$ ) and nylons  $2/n^{28}$  ( $\Delta$ ) are also indicated for comparison purposes. Note the different temperatures observed for the two isomers nylons 2,2/6/2 and 4,2/4/2 which may indicate an enhanced mobility of the adipoyl methylene groups in the solid state before melting. Note also that the melting temperatures for nylons  $m,2/n/2$  compare well with the previously reported data for nylons  $2/n$ . In particular the same temperature has been found for the two isomers nylons 4,2/6/2 and 2/5



**Figure 3** X-ray diffraction pattern of a sedimented mat of nylon 4,2/6/2 taken with the mat normal vertical. Although orientation is poor, probably due to the small dimension of the lamellar crystals, an equatorial and a meridional orientation can be observed for the more intense reflections which are, respectively, associated to the chain packing and to the repeat unit spacings. Rings arising from calcite calibration can also be observed

VI)). The infrared spectra show, also as a general trend in this zone, a methylene absorption band at  $720\text{ cm}^{-1}$  ( $\text{CH}_2$  rocking) whose intensity clearly increases according to the number of methylenes of the repeat unit.

Calorimetric analysis shows a single melting peak for all the polymers ( $277.2$ ,  $272.9$ ,  $306.9$  and  $275.2^\circ\text{C}$  for nylons 2,2/4/2, 4,2/4/2, 2,2/6/2 and 4,2/6/2, respectively) and indicates thermal decomposition since a stable baseline is not observed after fusion. Furthermore, no crystallization peak could be recorded when the samples were cooled from the melting point to room temperature. This decomposition is similar to the reported one for nylons 2/*n* with melting temperatures higher than  $270^\circ\text{C}$ <sup>28</sup>, and shows that thermal processing of this kind of polymer is not possible. It is interesting to note that the melting peaks of nylons *m*,2/*n*/2 fall in the range observed for nylons *m*,*n* with the same proportion between methylene carbons and amide groups<sup>1</sup>. However, as can be seen in *Figure 2*, the higher melting temperatures always correspond to the even–even nylons which are characterized by the extended conformations ( $\alpha$  and  $\beta$  structures) of their molecular chains.

Data obtained from X-ray diffraction patterns of sedimented mats indicate that a different structure from the  $\alpha$  and  $\beta$  forms of even–even nylons is obtained since their strong and characteristic reflections at spacings of 4.40 and 3.80 Å are not observed. On the contrary, an intense ring near 4.15 Å appears. This reflection may be determined by the intermolecular spacing in the pseudohexagonal arrangement characteristic of the  $\gamma$ -form or by the hexagonal lattice of the polyglycine II structure found in nylons 2/*n*. *Figure 3* shows the pattern of a sedimented mat of nylon 4,2/6/2 as representative. In addition to the 4.15 Å strong reflection, which has an equatorial orientation, another strong and diffuse reflection with a meridional or quasi-meridional orientation is observed. Its spacing increases with the number of methylenes of the repeat unit, and can be associated with the half of the repeat unit for each nylon. The reflections observed are summarized in *Table 3*. A tentative indexing is presented, related to that found in the  $\gamma$ -form and the polyglycine II structures of nylons *m*,*n* and 2/*n*, respectively. Note also that the reflections associated to the chain repeat length have practically the same spacing for the two isomers: nylons 4,2/4/2 and 2,2/6/2, which indicates that the molecular conformation is not strongly influenced by the relative length of the diamine and diacid residues. In all cases a unit cell with the chain axis parameter equivalent to only one repeat unit is sufficient to index all the observed reflections.

Suitable crystals for electron microscopy were obtained from nylons 4,2/4/2 and 4,2/6/2 by isothermal crystallization from 1,4-butanediol at  $120^\circ\text{C}$  and glycerine at  $133^\circ\text{C}$ , respectively. Nylon 4,2/4/2 gives elongated and small lamellar crystals (*ca.*  $0.4\ \mu\text{m}$ ) which in some cases appear bifurcated (*Figure 4b*), whereas crystals of nylon 4,2/6/2 have longer dimensions (*ca.*  $2\ \mu\text{m}$ ) and are oval-shaped (*Figure 4d*). Both kinds of crystal present serrated edges. This fact may be an indication of the absence of a single hydrogen bond direction, as discussed below. Polymers derived from ethylenediamine were more insoluble and thus crystallization experiments could only be done by precipitation with *n*-butanol of dichloroacetic acid (3:1) at  $98^\circ\text{C}$  (nylon 2,2/4/2) or with *n*-butanol and formic acid (5:1) at  $90^\circ\text{C}$  (nylon 2,2/6/2). Crystals of nylon 2,2/4/2

**Table 3** Measured and calculated X-ray diffraction spacings  $d_B$  (Å) for nylons *m*,2/*n*/2

Index	2,2/4/2		4,2/4/2		2,2/6/2		4,2/6/2	
	Calc. <sup>a</sup>	Measd. <sup>e</sup>	Calc. <sup>b</sup>	Measd. <sup>e</sup>	Calc. <sup>c</sup>	Measd. <sup>e</sup>	Calc. <sup>d</sup>	Measd. <sup>e</sup>
001	14.6	14.4 m	16.3	16.2 m	16.4	16.3 w	—	—
002	7.30	7.30 m	8.15	8.15 m	8.2	8.2 w	9.60	9.61 s
003	4.87	4.90 w	—	—	—	—	—	—
004	—	—	—	—	—	—	4.80	4.82 m
100, 010, $\bar{1}10$	4.22, 4.17, 4.17	4.21 vs	4.22, 4.15, 4.15	4.15 vs	4.15	4.15 vs	4.15	4.15 vs
101, 011, $\bar{1}11$	4.05, 4.01, 4.01	4.09 s	4.08, 4.02, 4.02	3.96 s	—	—	—	—
102, 012, $\bar{1}12$	3.65, 3.62, 3.62	3.57 m	—	—	3.70	3.72 s	3.81	3.76 m
103, 013, $\bar{1}13$	3.19, 3.16, 3.16	3.22 w	3.33, 3.30, 3.30	3.38 s	3.30	3.30 m	3.48	3.42 m
104, 014, $\bar{1}14$	—	—	2.93, 2.91, 2.91	2.92 m	2.92	2.93 w	—	—
105, 015, $\bar{1}15$	—	—	—	—	2.57	2.58 vw	—	—
120, $\bar{2}10$ , $\bar{1}20$	—	—	2.47, 2.42, 2.38	2.41 w	—	—	—	—

<sup>a</sup>On the basis of a monoclinic unit cell:  $a = 4.85\ \text{Å}$ ,  $b = 4.79\ \text{Å}$ ,  $c = 14.6\ \text{Å}$  and  $\gamma = 119.6^\circ$  for nylon 2,2/4/2

<sup>b</sup>On the basis of a monoclinic unit cell:  $a = 4.84\ \text{Å}$ ,  $b = 4.77\ \text{Å}$ ,  $c = 16.3\ \text{Å}$  and  $\gamma = 119.5^\circ$  for nylon 4,2/4/2

<sup>c</sup>On the basis of a monoclinic unit cell:  $a = 4.79\ \text{Å}$ ,  $b = 4.79\ \text{Å}$ ,  $c = 16.4\ \text{Å}$  and  $\gamma = 120^\circ$  for nylon 2,2/6/2

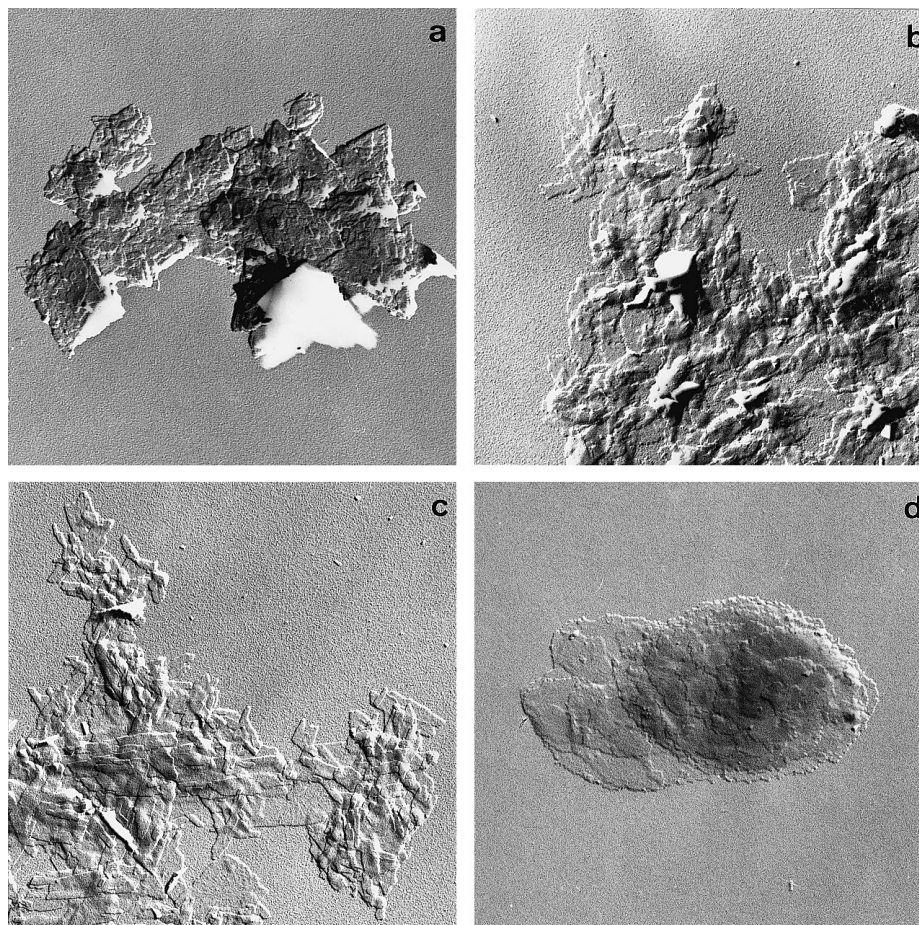
<sup>d</sup>On the basis of a monoclinic unit cell:  $a = 4.79\ \text{Å}$ ,  $b = 4.79\ \text{Å}$ ,  $c = 19.2\ \text{Å}$  and  $\gamma = 120^\circ$  for nylon 4,2/6/2

<sup>e</sup>Abbreviations denote intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak

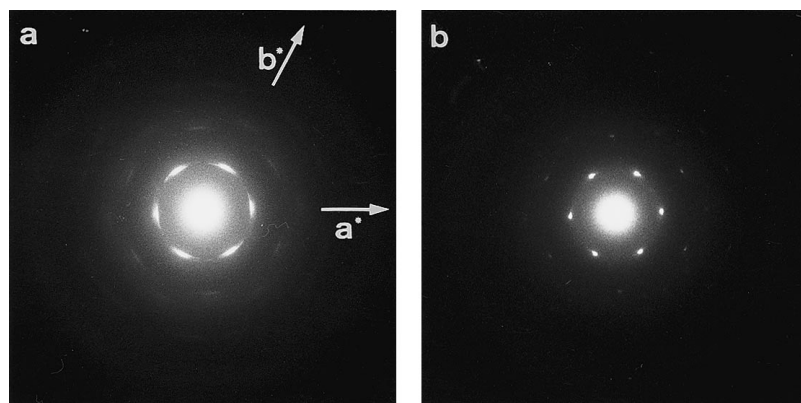
(Figure 4a) are small and have a lozenge shape. Often several sets of lozenges are superimposed giving rise to larger lozenges and triangular or starfish morphologies which may be interpreted as an epitaxial effect due to the presence of more than one hydrogen bond direction. Crystals of nylon 2,2/6/2 (Figure 4c) are elongated and frequently stack together giving also triangular aggregates. Sometimes these thin lamellae are split suggesting more than one main growth direction, as expected when hydrogen bonds run in two or three directions.

However, it is important to note that regular crystals with hexagonal or triangular morphologies could not be observed on this new family of polymers. These morphologies were characteristic of nylons 2/*n*<sup>15,16</sup>, and were explained as a consequence of their three- or six-fold molecular symmetry.

In all cases the thickness of the individual single crystals derived from the length of their shadows in the micrographs was in the 50–60 Å interval. This thickness is in agreement with the value found in nylons with a similar amide/



**Figure 4** Transmission electron micrographs of crystals of nylons: (a) 2,2/4/2 prepared by precipitation of a dilute dichloroacetic acid solution (1 mg/ml) with three volumes of *n*-butanol at 98°C; (b) 2,2/6/2 crystallized by precipitation of a dilute formic acid solution (1 mg/ml) with 5 vol. of *n*-butanol at 90°C; (c) 4,2/4/2 crystallized from a 1,4-butanediol solution (1 mg/ml) at 120°C; and (d) 4,2/6/2 prepared from a glycerine solution (1 mg/ml) at 133°C. Scale bar  $\times 25\ 300$



**Figure 5** Selected area electron diffraction pattern from crystals of nylons 2,2/4/2 (a) and 4,2/6/2(b). Note that the second pattern has an apparent 6mm symmetry

**Table 4** Measured and calculated electron diffraction spacings  $d_B$  (Å) for nylons  $m,2/n/2$ 

Index <sup>a</sup>	2,2/4/2		4,2/4/2		2,2/6/2		4,2/6/2	
	Calc.	Measd. <sup>b</sup>	Calc.	Measd. <sup>b</sup>	Calc.	Measd. <sup>b</sup>	Calc.	Measd. <sup>b</sup>
100	4.22	4.22 s	4.22	4.21 s	4.15	4.15 s	4.15	4.13 s
010	4.17	4.17 s	4.15	4.15 s	4.15	4.15 s	4.15	4.17 s
$\bar{1}$ 10	4.17	4.17 s	4.15	4.15 s	4.15	4.15 s	4.15	4.17 s
110	2.43	2.42 m	2.42	2.43 m	2.40	2.41 m	2.40	2.43 m
$\bar{2}$ 10	2.43	2.42 m	2.42	2.43 m	2.40	2.41 m	2.40	2.43 m
$\bar{1}$ 20	2.40	2.39 m	—	—	2.40	2.41 m	2.40	2.42 m
200	2.11	2.11 w	2.11	2.11 w	2.075	2.08 m	—	—
020	—	—	—	—	2.075	2.08 m	—	—
$\bar{2}$ 20	—	—	—	—	2.075	2.08 m	—	—

<sup>a</sup>On the basis of the monoclinic unit cells indicated in Table 3

<sup>b</sup>Abbreviations denote intensities: s, strong; m, medium and w, weak

methylene proportion<sup>29</sup> and indicates that molecular chains are folded within the lamellae.

Single crystals of each polymer were also subjected to electron diffraction. The patterns show an apparent  $mm$  symmetry and intense electron diffraction spots in the 4.12–4.15 Å interval as shown in Figure 5 and Table 4. Because of the small dimensions of the crystals only two orders could be observed. Note that the projected unit cells become an hexagonal one when the repeat unit is constituted by adipoyl residues. Thus, the length of the methylene segment in the diacid unit influences chain packing. Furthermore, the intensity of the spots approaches the  $6mm$  symmetry characteristic of nylons  $2/n$ .

The unit repeat lengths for all these  $m,2/n/2$  polymers studied are shorter than those derived by extrapolation of other nylons in the  $\alpha$  or  $\gamma$  structures. A shortening of about 0.7–0.9 Å with respect to the all-*trans* structure is observed in all cases (Table 5). This value is larger than the one expected for a  $\gamma$ -form, whereas it is similar to reported values for nylons  $2/n$ .

As illustrated in Figure 6a the introduction of glycine residues in a nylon  $m,n$  makes impossible the establishment of hydrogen bonds between molecular chains within a sheet when they have an extended conformation and no shear between molecular chains along the chain axis direction exists. However, an extended conformation may be possible in the particular case of nylons  $m,2/n/2$  with identical number of methylenes carbons in the diamine and the dicarboxylic units ( $m = n - 2$ ), since a shear of half repeat unit optimizes the hydrogen bonding geometry (Figure 6b). All the structural data (shortening of the repeat unit and packing spacings) indicate that this kind of conformation is not favoured even for nylons 2,2/4/2 and 4,2/6/2. On the other hand a  $\gamma$  conformation could improve the hydrogen bonding geometry (Figure 6c) and give also a good explanation for the non-hexagonal symmetry of the electron diffraction patterns. However, there are some considerations that make also this type of structure unlikely: (a) the experimental values of the repeat unit are shorter than the expected ones for a typical  $\gamma$ -form; (b) morphological observations of single crystals suggest that hydrogen bonds are established in at least more than one direction; (c) previous data on polymers (nylons  $2/n$ <sup>18</sup>) and model compounds<sup>30,31</sup> indicate that glycine residues tend to take a polyglycine II conformation. In this sense we have to consider that hydrogen bonds with good geometry could be established when glycine residues take their polyglycine II

conformation, and the diamine and the dicarboxylic units keep their characteristic  $\gamma$  conformation (torsional angles for bonds adjacent to the amide groups around  $\pm 120^\circ$ ). In the same way the shorter values of the chain repeat units could be well explained. Note also that hydrogen bonds result in only two directions when the two glycine residues of the repeat unit have opposite conformations (Figure 6d). It should be pointed out that different models with more than one hydrogen bond direction have also been reported for nylons without glycine residues. Thus, two hydrogen bond directions have recently been postulated for some even-odd nylons<sup>32–35</sup> as well as for the previous model on nylon 8 reported by Vogelson and Pearce<sup>36</sup>. Moreover, a three hydrogen bond directions scheme has been postulated for the pseudo-hexagonal phase normally found in some nylons above the Brill temperature<sup>37,38</sup>. This phase can also be obtained at room temperature by quenching from the crystallization temperature below the glass transition temperature as it has been reported by Atkins et al.<sup>39</sup> for nylon 8 chain-folded lamellar crystals.

The non-hexagonal morphology and the non-hexagonal  $mm$  symmetry of the electron diffraction pattern of nylons  $m,2/n/2$  could be also justified with the two hydrogen bonding scheme. The opposite conformation for the two glycine residues is also in agreement with the experimental data on the previously studied model compound, *N,N'*-bis-propylcarbamoyladipamide ( $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH-CO-CH}_2\text{-NH-CO-(CH}_2\text{)}_4\text{-CO-NH-CH}_2\text{-CO-NH-CH}_2\text{-CH}_2\text{-CH}_3$ )<sup>40</sup>. Work is in progress with similar polymers derived from diamine and dicarboxylic units with longer methylene segments. The results indicate that high molecular weights can be obtained and also that similar structures are present.

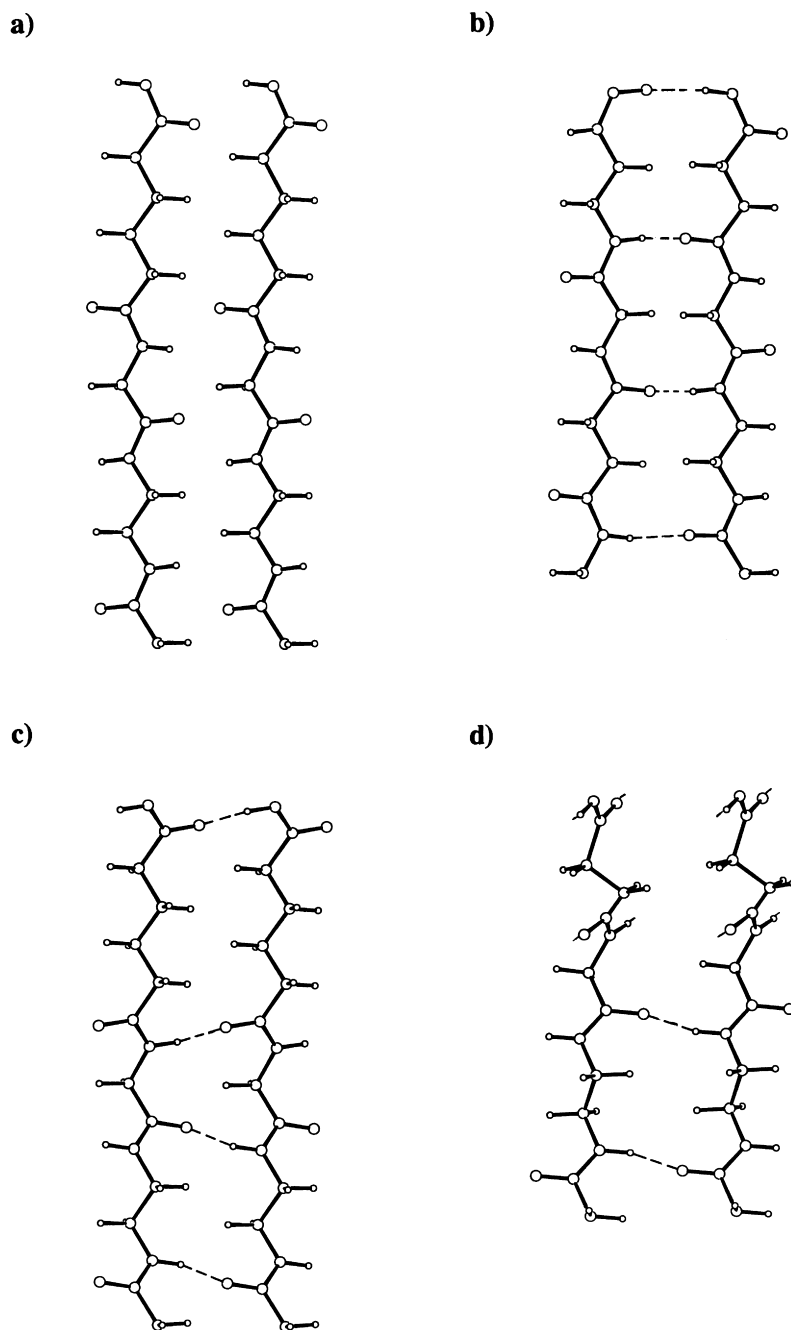
## CONCLUSIONS

The results presented in this paper about nylons  $m,2/n/2$  ( $m = 2,4$  and  $n = 4,6$ ) can be summarized as follows.

(1) Polymers can be obtained with high yields and moderate molecular weight by the active ester method.

(2) High melting temperatures together with thermal decomposition are found for all these polymers, which are characterized by a high amide/methylene ratio.

(3) These nylons can be crystallized in the form of chain-folded lamellae around 50–60 Å thick. Their morphologies are rather variable but serrated edges are always observed.



**Figure 6** Ball and stick representations of selected fragments of nylons  $m,2/n/2$ . (a) NH and CO groups cannot face correctly when molecular chains have an extended conformation and no shift exists between neighboring chains. (b) Only when  $n = m + 2$  can all the NH and CO groups face in order to establish hydrogen bonds. In this case, consecutive molecular chains with an extended conformation are shifted half a repeat unit in the chain axis direction. (c) Hydrogen bonds can be established between non-sheared molecular chains when they assume a  $\gamma$  conformation, due to the more planar disposition of the amide groups. Note that hydrogen bonds run in only one direction. (d) When glycine residues assume the polyglycine II conformation hydrogen bonds can also be established. In this case the glycine residues produce a rotation of approximately  $60^\circ$  between its NH and CO direction. This rotation is recuperative and the chain periodicity corresponds to only one repeat unit when consecutive glycine residues have opposite conformations. Note that hydrogen bonds appear in only two directions which form an angle of approximately  $120^\circ$

**Table 5** Comparison between the experimental repeat unit length<sup>a</sup> of nylons  $m,2/n/2$  and the expected values for an extended<sup>b</sup> or a  $\gamma$  conformation<sup>c</sup>

Nylon	Unit repeat length (Å)			Shortening <sup>d</sup> (Å/amide group)
	Experimental	Extended conformation	$\gamma$ conformation	
2,2/4/2	14.6	17.5	16.1	0.73
4,2/4/2	16.3	20.0	18.6	0.90
2,2/6/2	16.4	20.0	18.6	0.90
4,2/6/2	19.2	22.5	21.1	0.82

<sup>a</sup>Deduced assuming monoclinic unit cells

<sup>b</sup>Assuming an average increment of  $1.25 \text{ \AA}$  for every chain axis bond

<sup>c</sup>Assuming shortening of  $0.35 \text{ \AA}$ /amide group with respect the extended conformation, as usual in nylons

<sup>d</sup>With respect to the extended conformation

(4) A shortening between 0.7 and 0.9 Å per amide group with respect to the extended conformation is observed. Thus, the structure of these polymers is different from the all-*trans* conformation ( $\alpha$  and  $\beta$  forms) characteristic of even-even polyamides. Results indicate that glycine residues tend to adopt their polyglycine II conformation and so more than one hydrogen bond direction exists in the crystal.

(5) Molecular packing clearly deviates from the hexagonal one when the number of methylenes is low.

#### ACKNOWLEDGEMENTS

This research has been supported by a DGICYT Grant No. PB93-1067. L.F. acknowledges financial support from the Ministerio de Educación y Cultura. E.N. acknowledges financial support from the Department d'Ensenyament de la Generalitat de Catalunya.

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