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Synthesis and Characterization of Polyamides *n*,3

Juana Eva Aceituno,[†] **Valya Tereshko,**[†] **Bernard Lotz,**[‡] **and Juan A. Subirana***,[†]

Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Spain, and Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg, France

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ABSTRACT: We have synthesized, by the active esters method, several polyamides (nylons) *n*,3 with *n* = 4−6, 8, 9, and 12. We have studied these polymers and another group of similar polymers obtained from carbon suboxide. The methods used involve IR and NMR spectroscopies, calorimetry, electron diffraction and microscopy, and X-ray diffraction. These polymers show structural polymorphism, in the sense that powder samples prepared directly after polymer synthesis have a poorly ordered structure that is different from that found in single crystals and oriented films. Single crystals have been obtained by solution crystallization; they usually have irregular shapes and borders. Electron diffraction of single crystals shows that the molecular chains pack in a quasi-hexagonal rectangular cell. Electron and X-ray diffraction of oriented films shows that the molecules pack in either an orthorhombic or a monoclinic unit cell, depending on the parity of *n*. The molecules are linked by a unique network of hydrogen bonds, with two spatial orientations that form an angle of about 120°. Such an organization is quite different from the usual α- and γ-forms of nylons.

Introduction

Polyamides containing malonamide residues (nylons *n*,3) are expected to have unique features due to the presence of a single methylene unit placed between two amide groups: $(CH_2)_nNHCOCH_2CONH$.

Paiaro et al.[1] have reported that for such polymers the length of a monomeric unit was shorter than the fully extended form. They interpreted this observation as indicating an inclination of the monomer units of the polymer chain with respect to the overall molecular orientation.

Besides their intrinsic interest, these polymers are isomers with nylons 2/*n* (copolymers of glycine and ω-amino acids) and 1,*n* (copolymers of diaminomethane and α,ω-dicarboxylic acids), which have been studied in detail in our laboratory.[2−5] Therefore, we decided to study the nylons *n*,3 more thoroughly. Comparative studies[6] have shown that this family of polyamides has some features in common with their isomers nylons 1,*n* and 2/*n*. However differences are also found. In particular, nylons *n*,3 appear to be polymorphic, as first observed[7] with nylon 8,3. Structural studies of model compounds[8,9] indicate that these polymers may have two H-bond directions in the crystalline state.

Experimental Section

Synthesis and Characterization. Solvents and chemicals were obtained from either Merck or Fluka and were used as received. Solvents were dehydrated when required with either sodium or a molecular sieve. Several starting products were tried to obtain the polymers by polycondensation. The best results were obtained by polycondensation of diphenyl malonate with *N*,*N*′-bis(trimethylsilyl)diamines, following the method described by Katsarava et al.[10] for similar polyamides. Diphenyl malonate was prepared as described by Parihar et al.[11] Details of the synthesis are given elsewhere.[12] In this way, polyamides *n*,3 with *n* = 4−6, 8, 9, and 12 were prepared. Samples prepared by the carbon suboxide method[1] were kindly given to us by Dr. Paiaro, with *n* = 4−6 and 8.

The intrinsic viscosity of the polymers was determined with a Cannon-Ubbelohde microviscometer at a temperature of 25.0 ± 0.1 °C. Dichloroacetic acid was used as a solvent. The density of polymer films was measured at 25 °C by the flotation method in a KBr solution.

Infrared absorption spectra were recorded from potassium bromide pellets with a Perkin-Elmer 783 spectrophotometer in the 4000−500 cm^{-1} range. NMR spectra were recorded from polymer solutions in trifluoroacetic acid/chloroform (1:1) using a Bruker AMX-300 spectrometer operating at 300.1 MHz for ^1H NMR and at 75.5 MHz for ^{13}C NMR. All chemical shifts are referenced to tetramethylsilane (TMS) used as an internal standard. Deuterated solvents were used in some cases.

Thermal behavior was investigated with a Perkin-Elmer DSC-4 equipped with a TADS data station at a heating rate of 10 °C/min in a nitrogen atmosphere. Temperature was calibrated using an indium standard. Themogravimetry was carried out in a Perkin-Elmer TGS-1 analyzer at a heating rate of 10 °C/min.

Structural Methods. Polymer crystals were obtained from dilute solutions [0.05−0.1% (w/v)] in polar polyfunctional alcohols. The polymers were dissolved at 170−233 °C, and the solutions were transferred to constant-temperature baths in the 80−160 °C interval for 2−5 h. Crystallization experiments were also carried out at room temperature from dilute solutions of the polymers in formic acid by the addition of an alcohol. The crystals were recovered by centrifugation and repeatedly washed with *n*-butanol.

For electron microscopy, 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 diagrams were recorded by the selected-area method on Kodak Tri-X films. The patterns were calibrated internally with gold (d_{111}= 2.35 Å). Polymer decoration was achieved by evaporating polyethylene onto the surface of single crystals, as described by Wittmann and Lotz.[13]

Oriented thin films suitable for electron diffraction were obtained from a hot solution (about 60 °C) of polymer that was allowed to evaporate slowly. Orientation was achieved by shearing the polymer film with a knife while the solution was evaporated. Carbon was then deposited over the film. A droplet of a 20% solution of poly(acrylic acid) in water was deposited over the most birefringent areas of the sample. The triple film was detached from its glass suport and transferred onto a water surface to dissolve the poly(acrylic acid) support. The polymer/carbon film was then recovered on a copper grid.

X-ray diagrams were recorded under vacuum at room temperature, and calcite (d_B = 3.035 Å) was used for calibra-

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[†] Universitat Politècnica de Catalunya.

[‡] Institut Charles Sadron.

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Table 1. Characterization of Polyamides *n*,3 Synthesized by the Carbon Suboxide Method

	elementary analysis									
	carbon		hydrogen		nitrogen					
polymer	calcd	found	calcd	found	calcd	found	[η] (dL g^{-1})	M_n[a]	T_m (°C)	T_g[b] (°C)
nylon 4,3	53.8	51.5	7.7	7.5	17.93	16.8	0.43	6000	275	73
nylon 5,3	56.4	53.9	8.3	8.0	16.5	15.4	0.39	5000	248	65
nylon 6,3	58.7	59.1	8.7	8.6	15.2	13.8	0.33	3500	241	50
nylon 8,3	62.2	60.7	9.5	9.5	13.2	12.9	0.71	15000	233	55

[a] Determined from the equation for nylon 6,6 in dichloroacetic acid at 25 °C.[14] [b] Values obtained in our laboratory by Xenopoulos et al.[16]

Table 2. Synthesis and Characterization of Polyamides *n*,3 Synthesized by the Active Esters Method

		elementary analysis									
		carbon		hydrogen		nitrogen					
polymer	yield (%)	calcd	found	calcd	found	calcd	found	[η][a] (dL g^{-1})	M_n[b]	X_n[c] (°C)	T_m (°C)
nylon 4,3	99.0	53.8	53.0	7.7	7.3	17.9	15.4		2500	15.2	276
nylon 5,3	85.5	56.4	54.8	8.3	7.5	16.5	13.8		3200	18.7	238
nylon 6,3	92.0	58.7	56.3	8.7	8.3	15.2	13.6		3300	17.9	248
nylon 8,3	95.0	62.2	61.0	9.5	8.8	13.2	11.9		5800	27.1	226
nylon 9,3	96.0	63.7	61.3	9.8	9.2	12.4	11.2	0.19	2500	10.5	226
nylon 12,3	91.0	67.1	65.2	10.5	10.1	10.4	9.9	0.35	3200	11.7	217

[a] Intrinsic viscosity measured in dichloroacetic acid at 25 °C. [b] Determined from ^{1}H NMR. [c] Average degree of polymerization, defined as the number of dicarboxylic acid units.

tion. A modified Statton camera (W. R. Warhus, Wilmington, DE) with Ni-filtered copper radiation of wavelength 1.542 Å was used for these experiments. Alternatively, a graphite monochromator was used in some experiments. Patterns were recorded from polymer powders, oriented films, and mats of single crystals. The latter were prepared by slow filtration of a crystal suspension on a glass filter.

Results

Characterization. Part of the experiments described in this paper were carried out with samples prepared from carbon suboxide. The main features of these samples are given in Table 1. A second series of samples was prepared by the active esters method; in general they had lower molecular weights, as shown in Table 2.

The molecular weights given in Table 1 were calculated from the intrinsic viscosity by using the formula[14] for nylon 6,6, a method that should only give approximate values. For the polymers obtained by the active esters method (Table 2), the molecular weights were determined from the NMR spectra, which clearly showed the presence of the terminal residues as is apparent in Figure 1. This method had already been used[4] with the polyamides 1,*n* and is described in detail elsewhere.[12] For most of the polymers of Table 2 it was not possible to determine the intrinsic viscosity, since the value of η_{sp}/c increased upon dilution, a feature that has already been observed in other polyamides.[15]

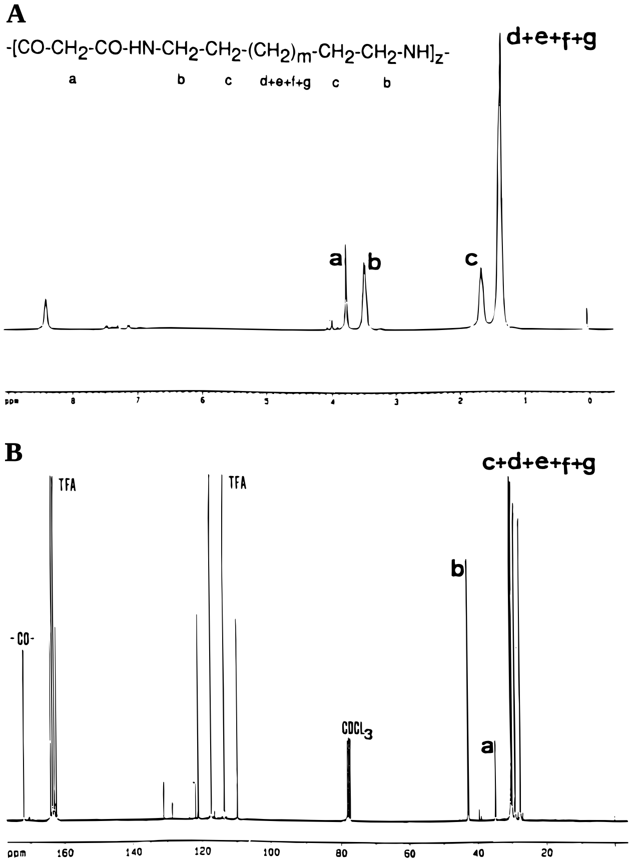

Figure 1. NMR spectra of nylon 12,3 disolved in trifluoroacetic acid/chloroform: (A) ^{1}H; (B) ^{13}C. The other polymers have similar spectra. The minor side peaks near the proton signals a and b are due to the methylene groups of the terminal units. They have been used to ascertain the molecular weights of the samples.

Infrared Spectra. The infrared spectra are given as supporting information (Figure 11). They were similar to those obtained from other polyamides and displayed no significant differences for the two types of samples studied. The positions of the main bands are also given in the supporting information as Table 8 and compared with those of other polyamides. In general, similar bands fall in the same range, but there are some striking differences. For example, the nylons *n*,3 have their amide B and amide VI bands located close to those of the γ-form of nylon 6, whereas for the isomeric nylons 1,*n*, these bands are near the position of the α-form of nylon 6. The amide II band of the nylons *n*,3 falls between the corresponding bands of nylon 6 in the α- and γ-forms, whereas the band for nylons 1,*n* is placed at a shorter wavenumber. Such systematic differences in the infrared spectra suggest original conformational and/or structural features. An unexpected shoulder at about 1720 cm^{-1} was found in all samples, a feature that is found neither in other polyamides nor in a nylon 4,3 dimer (E. Navarro, private communication).

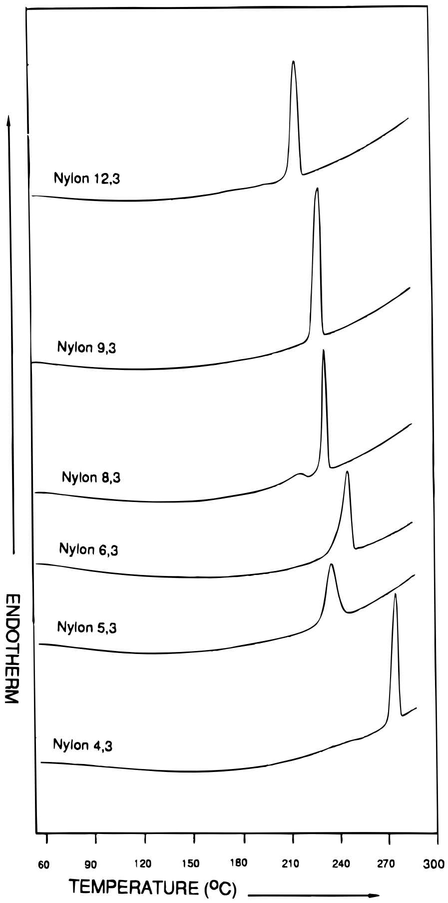

Figure 2. DSC traces for solution-crystallized nylons *n*,3 (prepared by the active esters method) obtained at a rate of 10 °C/min. These traces were carried out after a process of melting and cooling. In such a way, the multiple melting peaks that are usually observed[16] are not found, a fact that indicates that the crystals have a rather uniform size.

NMR Spectra. The chemical shifts of the more intense signals observed in the ^{1}H and ^{13}C NMR spectra of nylons 1,*n* are reported in Table 9 as supporting information. They are all in full agreement with the anticipated chemical composition. Furthermore, signals attributed to terminal groups can also be observed, which can be used for molecular weight determination.[4] The ^{1}H NMR spectra show a single signal for the methylene malonamide protons around 3.7 ppm, whereas the methylene protons next to the amino groups appear between 3.4 and 3.5 ppm, generally as a poorly resolved triplet. An example is given in Figure 1A. It should be noted that the intensity of the signal of the methylene malonamide protons decreases significantly when the spectra are recorded in a deuterated solvent, due to hydrogen/deuterium exchange of this methylene group.

^{13}C NMR spectra also present a single signal for the methylenes of the malonamide units, whereas the carbons of the diamine units show different signals in agreement with position effects (Figure 1B). Small peaks due to the terminal residues are also present.

Thermal Behavior. The thermal behavior of these polymers is similar to that of other polyamides. As a general trend, melting points increase as the density of amide groups increases. DSC curves usually show several melting peaks, probably due to the presence of imperfect crystals. Upon annealing, a single melting peak is found, as shown in Figure 2. The values for the melting temperatures are given in Tables 1 and 2. The value for nylon 5,3 in Table 2 and in Figure 2 is anomalously low, possibly due to the presence of some low molecular weight impurity. When compared with their isomers, the nylons 1,*n*[4] the nylons *n*,3 have a melting point lowered by about 10−20°C, depending on the length *n* of the monomer unit. On the other hand, as already reported,[4] the melting point of nylons *n*,3 is higher than that of most nylons *m*,*n*. Detailed melting curves and a calorimetry study of some of these polymers have been presented elsewhere.[16]

Table 3. Optimal Crystallization Conditions for Nylons *n*,3

nylon	solvent	concentration (mg/mL)	temperature (°C)
nylon 4,3[a]	1,4-butanediol	1	152
nylon 5,3[a]	1,4-butanediol	1	125
nylon 6,3[a]	1,4-butanediol	1	135
nylon 8,3[a]	HCOOH/EtOH (3:1)	0.5	room temperature
	HCOOH/EtOH (2:1)	0.33	room temperature
	HCOOH/EtOH (3:2)	0.4	room temperature
	HCOOH/BuOH (2:1)	0.33	room temperature
nylon 9,3[b]	1,4-butanediol	1	79
	ethylenglicol	1	25
	ethylenglicol	1	90
	N,N′-dimethylacetamide	1	160
nylon 12,3[b]	1,4-butanediol	1	117
	1,4-butanediol	1	121

[a] Synthesized by the carbon suboxide method. [b] Synthesized by the active esters method.

Studies with Single Crystals. Suitable crystals for electron microscopy were obtained for most polymers from diol solutions under the conditions described in Table 3. In nylon 8,3 it was not possible to prepare suitable crystals from a diol solution; instead a mixture of formic acid/alcohol was used. The crystals obtained are shown in Figures 3 to 5. In all cases the approximate thickness of the crystals is about 50−60 Å. Their edges are irregular.

The morphology of the crystals varies for the different polymers and depends on the crystallization conditions. Nylons 5,3 and 6,3 frequently form thin, elongated crystals, as shown in Figure 3. In nylon 6,3, a continuous straight line runs through the center of some of the crystals obtained. This line may indicate either a change in fold plane orientation or a twin plane. Crystals of the other polymers have, in general, ill-defined shapes and are less elongated. The crystals of nylons 4,3 have a lozenge shape. Often several sets of lozenges are superimposed with their long axes at about 60° to each other, giving rise to an overall apparent X or starfish shape, as shown in Figure 4. The size and shape of the crystals may vary in different preparations, as illustrated in Figure 5.

In summary, the lack of a well-defined morphology in the crystals obtained from nylons *n*,3 may be influenced by the low molecular weight of the samples used, with end groups interfering with regular crystal growth. However, this effect is most likely due to the molecular organization of hydrogen bonds, as will be discussed in the following.

Decoration of the crystals with polyethylene did not indicate any clear preferential orientation of the folds on the lamellar surface, as shown in Figure 6 for a crystal of nylon 6,3. However, differences in the density of the decoration (of lateral versus central parts of the crystal) suggest the existence of growth sectors. Similar

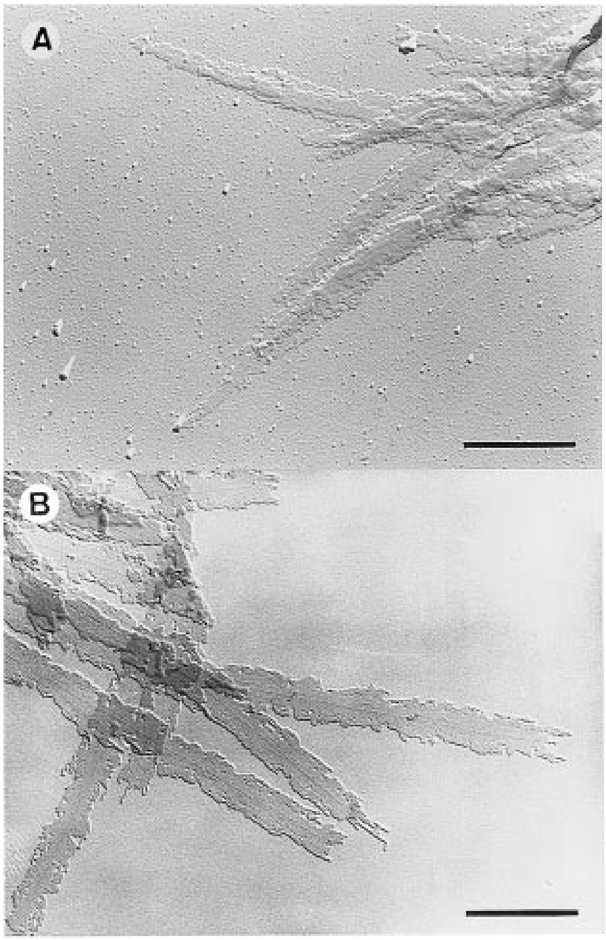

Figure 3. Transmission electron micrographs of crystals prepared in a butanediol solution of nylons: (a) 5,3 (grown at 125 °C); (b) 6,3 (grown at 135 °C). Both polymers were prepared by the carbon suboxide method. A scale bar of 1 μm is shown.

results were found with crystals from the other materials studied.

Single crystals of each polymer were subjected to electron diffraction. Nearly identical patterns were obtained in all cases, as shown in Figure 7 and in Table 10 (the latter is included in the supporting information). The electron diffraction pattern is quasi-hexagonal, but in such an equatorial projection in fact corresponds to a centered rectangular cell. The largest spacing corresponds to the 200 reflection, which is oriented perpendicular to the long axes of the elongated crystals. The actual values differ slightly for each individual nylon, but no clear trend was detected in these variations. Therefore, we decided to use a single average unit cell for all of the samples studied, with dimensions 8.32 (±0.05) × 4.71 (±0.02) Å^2. The observed values differ from the calculated values by 1% or less, except for a couple of reflections in the whole set that differ by 2%.

Deviation from hexagonal symmetry is also apparent from the intensity of the reflections. In a hexagonal pattern the reflections indexed as 420 and 510 would be equivalent to 130. Here the latter are either very weak or not observed, as shown in Figure 7.

Diffraction from oriented films to be presented in the following indicates that when n = odd the unit cell is truly orthorhombic, but when n = even the unit cell is monoclinic, with a monoclinic angle β of about 101°. From the monoclinic unit cell observed in fibers, it would be expected (assuming that the fold surface is 001) that the molecular chains would be inclined by 11° relative to the electrom beam and that some of the reflections found in patterns such as Figure 7 should not be observed. However, it is common experience that they do appear for such small tilts as a result of either wrinkling/shearing of the crystals themselves or the nonplanarity of the carbon support film. Alternative but less likely explanations would involve either multiple twinning in the crystal (a possibility hardly compatible with the structure of molecular models discussed elsewhere)[18] or the presence of yet another, orthorhombic, crystal modification.

Mats of single crystals were also studied by X-ray diffraction. In most cases it was difficult to obtain adequate orientation and stacking of the crystals. No suitable mat could be prepared from nylons 5,3 and 8,3. Some small angle reflections could be measured from mats of nylons 4,3, 9,3, and 12,3, from which the lamellar thickness could be estimated. The values obtained are given in Table 4. On the other hand, a well-oriented mat could be prepared from nylon 6,3. Its X-ray diffraction pattern showed many sharp reflections, an observation that indicates that the thickness of the crystals is rather constant and therefore folding at the surface of the lamellae must be rather regular, a question that has been analyzed in detail elsewhere.[19]

Studies with Oriented Films. Oriented films were studied by both electron (thin films) and X-ray diffraction (thicker films). Practically identical results were obtained from polymers prepared by both synthetic methods. Examples of the patterns obtained are shown in Figures 8 and 9. From such patterns, the unit cells given in Table 5 were determined from the measured X-ray diffraction arcs listed in Table 11 (supporting information). The electron diffraction patterns from thin films agreed with the unit cells determined by X-ray diffraction. When n = odd (Figure 9), the diffraction patterns appear to be orthorhombic, although the possibility that they are monoclinic, with β close to 90°, cannot be excluded. When n = even, the patterns are monoclinic, as is clearly apparent from Figure 8. When such patterns were indexed, it was possible to find suitable unit cells with the monoclinic angle formed between c and either of the two axes (4.71 or 8.32 Å) of the rectangular unit cell found by electron diffraction of single crystals. The unit cells given in Table 5 were chosen for two reasons: (1) The agreement between observed and calculated values was slightly better when the angle was formed between c and the long side of the rectangular unit cell. (2) Most importantly, the symmetry of the molecule suggested by model studies[8,9] required that the monoclinic angle be formed between c and the long side of the rectangular unit cell. Further studies on model compounds to clarify this organization in detail are in progress.[18]

Before we present the data obtained for each polymer, some general features of the patterns should be discussed. Since the patterns are obtained from stroked films, which may display some double orientation, some expected reflections may appear to be very weak or absent. Some of the differences found between the X-ray and electron diffraction patterns appear to be related to such variations in the degree of double orientation.

All patterns show a clear, but diffuse, off-meridional arc at about 2.1−2.2 Å, which in some cases cannot be

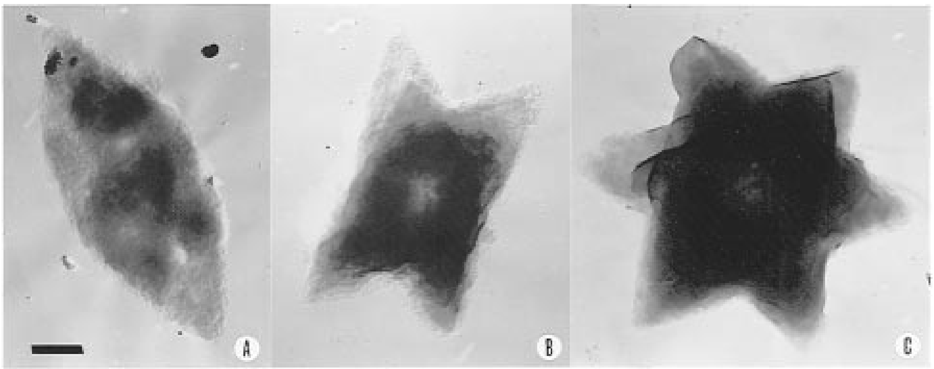

Figure 4. Transmission electron micrographs of nylon 4,3 crystals obtained in butanediol at 152 °C: (A) single crystal; (B and C) crystals showing approximate 60° rotations. A scale bar of 1 μm is shown.

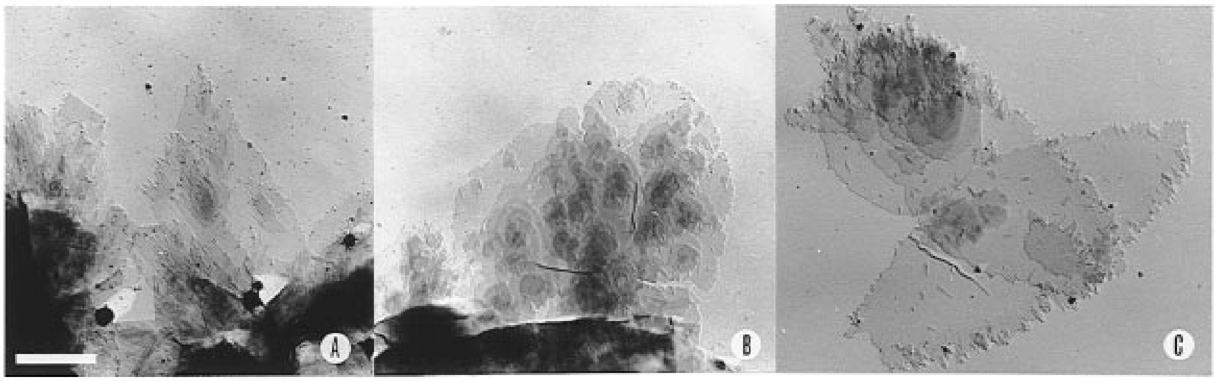

Figure 5. Transmission electron micrographs of nylon 9,3, illustrating the changes in morphology observed. The crystals were obtained (A) in ethylene glycol at room temperature, (B) in ethylene glycol at 90 °C, and (C) in formic acid/methanol (1:1) at 89 °C. A scale bar of 1 μm is shown.

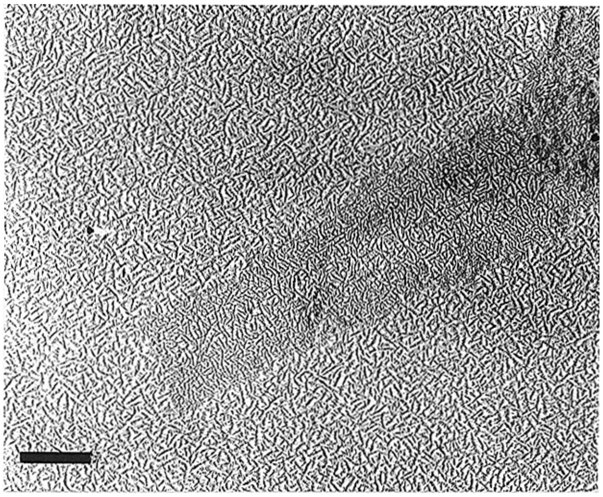

Figure 6. Electron micrograph of nylon 6,3 crystals grown in 1,4-butanediol at 135 °C. The crystals were decorated with polyethylene[13] and shadowed with Pt/C at an angle of 15°. Scale bar: 1 μm.

indexed as a well-defined diffraction spot. Diffraction in this region is due to the zig-zag nature of the CH_2 chain and should appear even when the samples are poorly oriented.

Another peculiar but general feature of the X-ray diffraction patterns is that, in some samples of all the polymers studied, an additional meridional reflection with medium intensity appears at 0.77 ± 0.01 times the 002 spacing. We cannot account for the presence of such a reflection on either structural or instrumental grounds. In the pattern shown in Figure 9 such a reflection is not visible, but it has been observed in other samples of nylon 5,3.

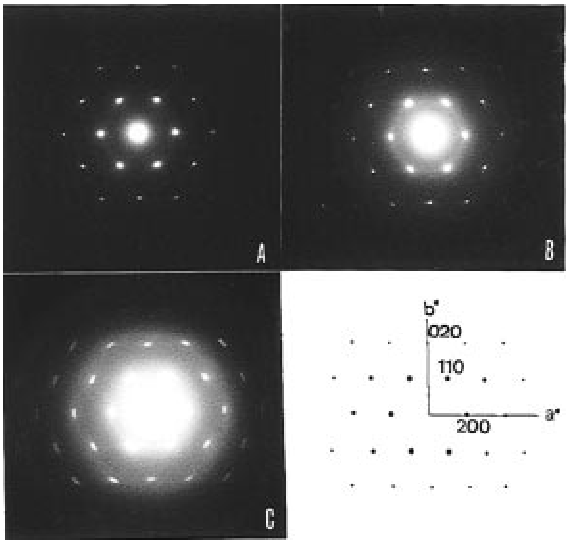

Figure 7. Selected-area diffraction patterns from crystals of nylons (A) 4,3, (B) 8,3, and (C) 9,3. A diagram of the reciprocal rectangular net is also shown, in which the most prominent diffraction spots are indicated.

Table 4. Low-Angle Spacings (Å) in Oriented Samples of Nylons *n*,3

nylon	4.3	5.3	6.3	8.3	9.3	12.3
oriented film		88	86	streak	106	streak
mat	61.5		56.5		59.5	71

We will now proceed to describe in detail the results obtained for each polymer. For nylon 4,3, we could not prepare a sample suitable for X-ray diffraction, and the unit cell was determined from the electron diffraction pattern shown in Figure 8. The unit cell dimensions are given in Table 5. The pattern is clearly monoclinic,

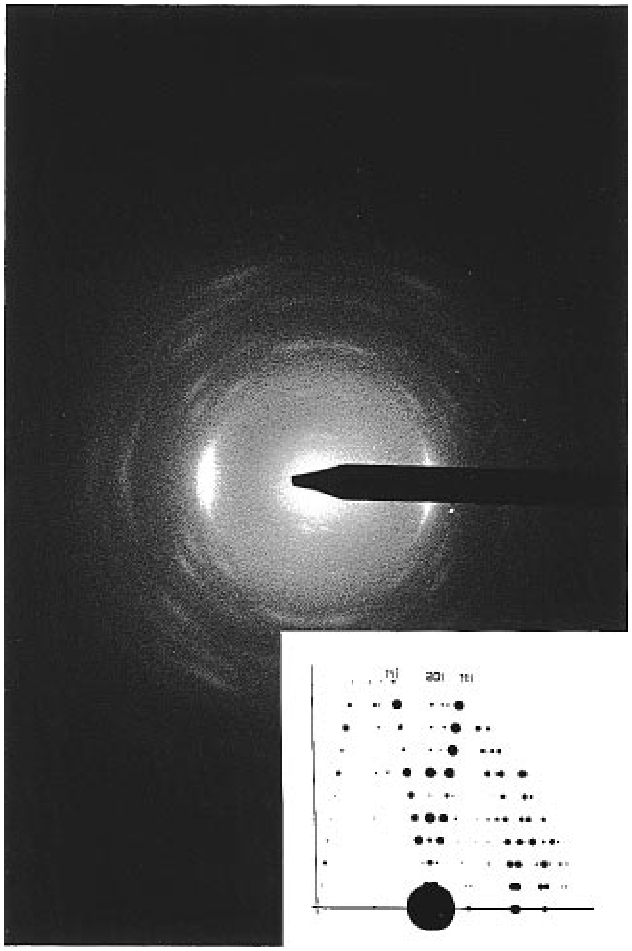

Figure 8. Electron diffraction pattern obtained from an oriented film of nylon 4,3. A scheme of the monoclinic pattern prepared with the program CERIUS[21] is also shown. The intensities of the spots are only approximate since a preliminary model was used to obtain the simulated pattern.

and a value of *c* equal to twice the monomeric unit length is found. On the equator, the 310 and 020, as well as the 400 and 220, arcs have spacings slightly different from those measured in the electron diffraction patterns from single crystals. It appears, therefore, that the unit cell is slightly different in fibers than in single crystals, with $a \sin\beta$ greater and *b* smaller, both by about 2%, so that no change in density results from this change in dimensions. Such a difference in unit cells with $a \sin\beta = 8.47$ Å and $b = 4.62$ Å was also found in nylons 5,3 and 6,3, i.e., in the nylons with a shorter repeat unit.

The X-ray diffraction pattern for nylon 5,3 is presented in Figure 9. In each layer line there is only a pair of arcs that correspond to the superposition of the 20*l* and 11*l* reflections that have similar spacings; there is no evidence for a monoclinic structure. All measurements agree very well with the calculated spacings, except for the off-meridional arcs in the electron diffraction pattern. In this region, two arcs are found in unexpected positions, which may indicate a distortion of the unit cell in the films used for electron diffraction. On the other hand, the deviation of the 002 reflection from its calculated value may be due to the presence of strong diffuse instrumental scattering in this region.

In nylon 6,3, the equatorial spacings are again different from those found in single crystals. Equatorial dimensions similar to those determined for nylons 4,3 and 5,3 are found here. The measured spacings given in Table 11 (supporting information) agree rather well with those calculated from the unit cell given in Table 5. In nylons 8,3 and 9,3, the calculated and measured spacings also agree rather well. In nylon 8,3, although the pattern is clearly monoclinic, no 20*l* reflections are visible, whereas some of these reflections are apparent in the other nylons with *n* = even, as shown in Table 11 (supporting information). In nylon 9,3, the 020 and 220 reflections are not clearly visible, and we cannot exclude the possibility that fibers from this compound might tend to adopt a hexagonal, less well ordered pattern, perhaps due to the greater freedom of the nine CH_2 groups present, when compared with nylon 5,3, which is clearly orthorhombic.

The unit cell dimensions of nylon 12,3 were difficult to determine. All reflections were used to define the best unit cell given in Table 5. Comparison of the calculated and measured values shows that the 00*l*

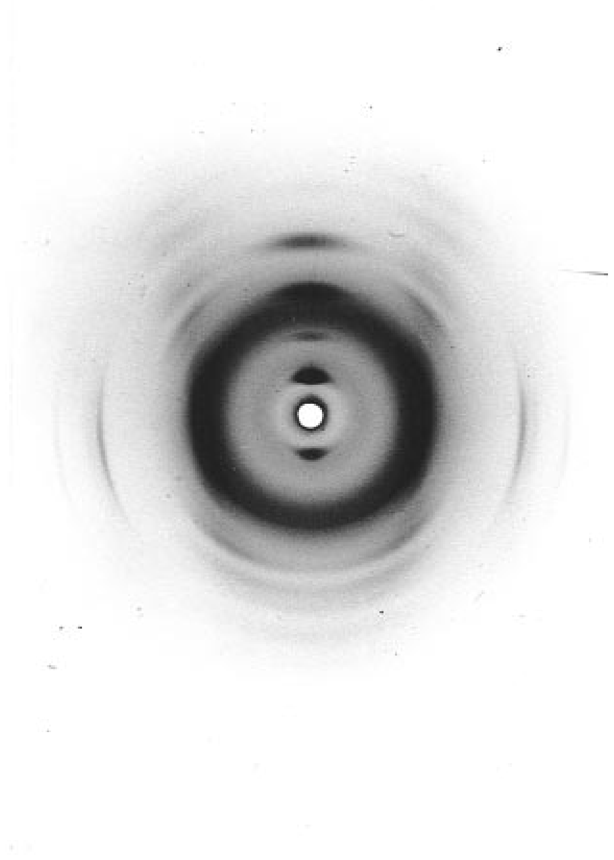

Figure 9. X-ray diffraction pattern (orthorhombic) from an oriented film of nylon 5,3. The film was tilted slightly, so that reflections in the upper half of the pattern are more intense.

Table 5. Summary of the Main Crystallographic Data for Nylons *n*,3[a]

polymer	*a* (Å)	*b* (Å)	*c* (Å)	α (deg)	β (deg)	γ (deg)	density (g L^{-1}) exp	density (g L^{-1}) calcd
nylon 4,3	8.65	4.62	20.40	90	102.5	90		1.324
nylon 6,3	8.60	4.62	25.70	90	100.4	90	1.139	1.218
nylon 8,3	8.50	4.71	30.70	90	101.7	90	1.133	1.171
nylon 12,3	8.48	4.71	41.30	90	101	90	1.068	1.100
nylon 5,3	8.47	4.62	22.40	90	90	90	1.177	1.289
nylon 9,3	8.32	4.71	32.70	90	90	90	1.145	1.173

[a] Parameters related to chain packing ($a \sin\beta$, *b*) were determined from electron diffraction data. The remaining parameters were calculated from X-ray diffraction patterns of oriented films as described in the text, with the exception of nylon 4,3, for which only electron diffraction data were available.

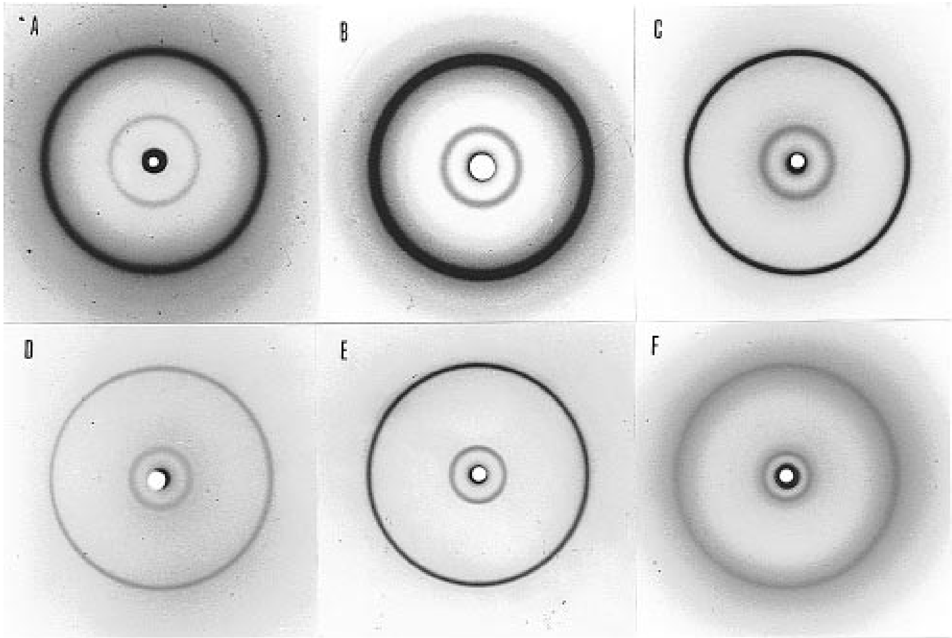

Figure 10. X-ray diffraction patterns obtained from polymer powders of nylons prepared by the active ester method: (A) 4,3; (B) 5,3; (C) 6,3; (D) 8,3; (E) 9,3; (F) 12,3. The patterns from powders of nylons prepared by the carbon suboxide method are practically identical.

Table 6. Molecular Unit Length (*c*/2) of Nylons *n*,3 in the Solid State (Å)

nylon	oriented films	powder X-ray	powder X-ray (ref 1)
4,3	10.15	10.0	9.8
5,3	11.2	11.1	10.9
6,3	12.85	12.5	12.1
8,3	15.35	14.7	14.0
9,3	16.35	16.0	15.3
12,3	20.65	19.1	18.5
Δ[a]	1.30	1.15	1.09

[a] Δ represents the average increase in molecular length for each CH_2 unit.

Table 7. Contribution of Atomic Groups to the Size (Å) of the Monomer Unit along the Chain Direction in Different Polyamides

nylon	CONH	CH_2
α-form	2.26	1.27
γ−form	1.86	1.27
1,n[a]	1.92	1.25
n,3 films (n = odd)	1.82	1.27
n,3 films (n = even)	1.98	1.27
n,3 powder[b]	2.00	1.15−1.20
n,3 powder[b] (ref 1)	2.19	1.09

[a] Calculated for n = even from the values given by Franco et al.[4] [b] For n,3 powders, the values measured by us and those given by Paiaro et al.[1] are both given. For these calculations it is assumed that the repeat units are tilted, as discussed in the text. The calculated contribution of methylene groups in the powder sample varies depending on whether the value for nylon 12,3 is included.

experimental spacings are all smaller than the calculated values. This is especially true for the electron diffraction spacings. A smaller *c* value (about 40.8 Å) would give better agreement for the 00*l* reflections, but then the off-meridional reflections would show poor agreement with the calculated values. These different estimates of the *c* value must be taken into consideration for the discussion presented in the following.

The polymer films were also studied by low-angle X-ray diffraction. The results obtained are given in Table 4. Only in the case of nylons 5,3 and 9,3 was a well-defined low-angle spot visible. In the latter case a spacing of 106 Å was determined, which is considerably greater than the 59.5 Å lamellar spacing found in single crystals. The same is true for nylon 6,3, although in this case the low-angle spacing at about 86 Å is much more diffuse. In nylons 8,3 and 12,3 a diffuse streak was only visible, which might indicate the presence of lamellae, but with very variable thickness. In any case, these observations indicate that, upon annealing, lamellar crystals are formed in the films, but their long period is greater than that found in mats of single crystals.

Powder Diffraction. After synthesis and purification, the polymers appeared as powders, which were also studied directly by X-ray diffraction. Usually only two diffraction rings were observed, as shown in Figure 10. The outer ring (at about 4.1 Å) is determined by the intermolecular spacing in a quasi-hexagonal arrangement, whereas the inner ring appears to correspond to the molecular unit length. The spacings measured for the inner rings are given in Table 6. Spacings smaller than those obtained from oriented films are found. Paiaro et al.[1] found even smaller spacings, which, for comparison purposes, are also given in Table 6.

From the values given in Table 6, it is possible to determine the average increase, Δ, in molecular unit length that corresponds to each methylene group. The values obtained are given in Table 7. For oriented films Δ is 1.30 Å, but when a smaller *c*/2 value is chosen for nylon 12,3 (as discussed in the previous section), this value decreases to 1.27 Å, which corresponds to the trans,trans conformation of the methylene units in an extended polymer chain. On the other hand, the corresponding value for powders is significantly shorter, particularly in the data reported by Paiaro et al.[1] This decrease in the value of Δ was interpreted[1] as indicating that in powders the methylene zig-zag is oriented at an angle with respect to the overall molecular orientation, but it could equally well indicate a monoclinic geometry of the unit cell. In any case, this comparison of pristine and recrystallized states of the nylons *n*,3 further demonstrates the structural polymorphism of these polymers.

Discussion

A striking feature of the polymers described in this paper is their polymorphism. While all single crystals show the same rectangular cell in projection, as determined by electron diffraction, oriented films have a slightly different cell geometry for low values of *n*, as shown in Table 5. The molecular unit length of these polymers also takes different values, depending on the conditions of preparation of the samples, as shown in Table 6. In Table 7 we compare the contributions of different atomic groups to the length of the monomeric units. In oriented films the chains appear to be approximately parallel to the stretching direction, since the contribution of each CH_2 group is 1.27 Å, as in polyethylene. On the other hand, in the poorly crystallized powder samples (especially those studied by Paiaro et al.)[1], the contribution of each CH_2 group is much lower, which indicates that stretches of the repeat unit may be tilted relative to the overall chain orientation or the *ab* plane of the unit cell. Given the poor quality of the powder patterns, it is not possible to determine their structure in detail. Therefore, we will concentrate on the structures of oriented films and lamellar crystals.

The unit cells given in Table 5 are quite different from those found in the conventional α- and γ-forms of nylons. No evidence for a fully stretched, all-trans α-form has been found under any conditions, a fact that is not surprising taking into account the conformational features of the malonamide unit. The presence of a single methylene between two amide groups does not allow an all-trans conformation of the malonamide unit, as has been shown in low molecular weight model substances.[8,9]

The family of nylons *n*,3 represents one group of polymers in which isolated methylene groups are placed between two amide units. In our laboratory, we have also studied two other groups of polymers, nylons 2/*n* and 1,*n*, which also have isolated methylene groups between two amide units. In a preliminary analysis,[20] it was shown that the conformation of the methylene–diamide unit varies significantly in each case, due to the different orientation of the amide groups with respect to the central methylene unit. In all cases, deviations from an all-trans conformation are found.

The nylons 2/*n* are copolymers of glycine and ω-amino acids: all of the amide units have the same orientation along the molecular chain, which has an N-terminal and a C-terminal end. These polymers form 3-fold or 6-fold helices,[2] similar to the poly(glycine) II helix.

In the nylons 1,*n* an isolated methylene unit is linked to two nitrogen atoms of the amide units. As a result, the peptide units tend to orient themselves in opposite directions.[5] For n = odd, a helical organization of polymer chains is present. For n = even, parallel sheets of hydrogen-bonded molecules are formed.[4] Since the conformation around the peptide group is folded considerably, these polymers are quite different from the α- and γ-forms of nylons, which have most or all of their main chain bonds approximately in the trans conformation.

In the case of the nylons *n*,3 studied in this paper, Paiaro et al.[1] proposed a model based on the inclination of the polymer chains to interpret the data obtained from poorly ordered crystals in pristine powder samples. However, in oriented films and single crystals, the polymer chains are not inclined, as indicated by their diffraction patterns. The average rise per methylene group (1.27 Å, Table 7) coincides in value with that of a straight poly(methylene) chain. Furthermore, the model proposed by Paiaro et al.[1] is based on an unlikely conformation of the malonamide unit with torsion angles that do not coincide with those found in model compounds.[8,9] The unit cell of such model compounds is very similar to that found in nylons *n*,3, so it is likely that the organization of polymer and model compounds is similar, with the hydrogen bonds organized (in *c* axis projection) along the two diagonals of the unit cells given in Table 5 and the two hydrogen-bond directions at approximately 120°. Such a model will be analyzed in detail elsewhere,[18] where alternative models will be also analyzed and excluded. This organization of hydrogen bonds is compatible with the lack of well-defined faces in the lamellar crystals presented in Figures 3–5. In elongated crystals, such as those shown in Figure 3 for nylons 5,3 and 6,3, hydrogen bonds would be oriented at 60° on either side of the major growth direction.

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Supporting Information Available: Figure 11 and Tables 8–11 (15 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Paiaro, G.; Pandolfo, L.; Busico, V.; Corradini, P. *Eur. J. Polym. Sci.* **1988**, *24*, 99.
(2) Bella, J.; Puiggalí, J.; Subirana, J. A. *Polymer* **1994**, *35*, 1291.
(3) Puiggalí, J.; Subirana, J. A. In *The Polymeric Materials Enclyclopedia*; Salomone, J. C., Ed.; CRC Press: Boca Raton, FL, in press.
(4) Franco, L.; Navarro, E.; Subirana, J. A.; Puiggalí, J. *Macromolecules* **1994**, *27*, 4284.
(5) Alemán, C.; Franco, L.; Puiggalí, J. *Macromolecules* **1994**, *27*, 4298.
(6) Puiggalí, J.; Aceituno, J. E.; Franco, L.; Lloveras, J.; Prieto, A.; Vidal, X.; Xenopoulos, A.; Fernández-Santín, J. M.; Subirana, J. A. *Prog. Colloid Polym. Sci.* **1992**, *87*, 35.
(7) Aceituno, J. E.; Subirana, J. A. In *Electron Microscopy EUREM 92*; López-Galindo, A.; Rodríguez-García, M. I., Eds.; Publicaciones de la Universidad de Granada: Granada, 1992; Vol. 2, p 375.
(8) Tereshko, V.; Navarro, E.; Puiggalí, J.; Subirana, J. A. *Macromolecules* **1993**, *26*, 7024.
(9) Navarro, E.; Puiggalí, J.; Subirana, J. A. *Macromol. Chem. Phys.* **1995**, *196*, 2361.
(10) Katsarava, R. D.; Kharadze, D. P.; Avalishvili, L. M.; Zaalishvili, M. M. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 585.
(11) Parihar, D. L.; Sharma, S. P.; Verma, K. K. *J. Chromatogr.* **1967**, *27*, 276.
(12) Aceituno, J. E. Ph.D. Thesis, Universitat Politècnica de Catalunya, Barcelona, Spain, 1995.
(13) Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Part B: Polym. Phys.* **1985**, *23*, 205.
(14) Elias, H. G.; Schumacher, R. *Makromol. Chem.* **1964**, *76*, 23.
(15) Hornsby, P. R.; Tung, J. F. *Polymer* **1994**, *35*, 3799.
(16) Xenopoulos, A.; Wunderlich, B.; Subirana, J. A. *Eur. Polym. J.* **1993**, *29*, 927.
(17) Abu-Isa, I. *J. Polym. Sci. Part A: Polym. Chem.* **1971**, *9*, 199.
(18) Puiggalí, J.; Aceituno, J. E.; Subirana, J. A. Manuscript in preparation.
(19) Subirana, J. A.; Aceituno, J. E. *Makromol. Chem., Macromol. Symp.*, in press.
(20) Bella, J.; Subirana, J. A. *Polym. Prepr.* **1992**, *33*, 276.
(21) *CERIUS*; Molecular Simulations, Inc.: Burlington, MA, 1993.

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