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Incorporation of glycine residues in even–even polyamides. Part II: Nylons 6,10 and 12,10

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Abstract

Sequential copolymers of glycine and nylons 6,10 and 12,10 have been prepared by incorporating single glycine units at both ends of the diamine. These polymers have been obtained by interfacial polymerization and subsequently characterized by infrared and n.m.r. spectroscopies together with thermal analysis. The structure and morphology of lamellar crystals have also been investigated by X-ray diffraction and transmission electron microscopy, both imaging and diffraction. Additional data have been obtained from uniaxially oriented fibres. Results described in this paper complete previous studies on the incorporation of glycine units in nylons derived either from ω-amino acids or from diamines and diacids. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyamides; Nylons; Glycine

1. Introduction

At room temperature, lamellar crystals of even–even nylons are usually composed of chain-folded, hydrogen-bonded sheets which can stack together in two different ways giving either the α or the β-phase. It has been found that some even–even nylons crystallize in the α- form [1,2] and others in the β-form [3,4]. Some nylons have been found in both structures, being the ratio of α to β-phase variable with crystal preparation [1,5–7]. This is the case of nylons 6,10 [5] and 12,10 [6], which are related to the nylons reported in the present article. In contrast, the γ-form, which corresponds to a pseudohexagonal packing of parallel sheets with hydrogen bonds established between amide groups tilted about 60° off the methylene carbon plane, is seldom found at room temperature in even–even polyamides.

As was discussed previously, in a series of papers published over the last few years, certain sequential copolymers of glycine and ω-amino acids (nylons 2/*n*) [8–12] assume a new structure related to the polyglycine II [13], which is characterized by a three-dimensional network of hydrogen bonds. Thus, glycine residues adopt a particular conformation with their torsional angles φ (–CONHCH$_2$CO–) and Ψ (–NHCH$_2$CONH–) close to $+77°$ (or $-77°$) and $-145°$ (or $+145°$), respectively. Following along this line, in an earlier article [14] we studied the nylons indicated in Scheme 1, which were named as nylons *m*,2/*n*/2, since they may be considered as the result of the polymerization of a diamine and a modified diacid which incorporates two glycine residues at either side. Note that alternatively they could be named nylons 2/*m*/2,*n* since they may be also synthesized from a diacid and a diamine which incorporates both glycine residues. The previous work was carried out with polymers characterized by $m = 2, 4$ and $n = 4, 6$, with a high density of amide groups. Their synthesis gave polymers with moderate molecular weight, low solubility and poor thermal stability. Results from X-ray diffraction and electron microscopy indicated that the characteristic sheet structure of even–even nylons was disrupted by the incorporation of glycine residues. In particular, they showed the following features: (i) glycine residues tend to take the typical polyglycine II conformation, where a rotation of 60° is produced between their NH and CO directions; (ii) the two glycine residues of the repeat unit have opposite conformations and so the rotation induced by each residue is recuperative; and (iii) a lattice with two hydrogen bond directions at about 120° is derived.

The present article deals with the study of nylons 2/6/2,10 and 2/12/2,10 in order to: (i) obtain polymers with sufficiently high molecular weight to have fibre and film-forming properties; (ii) obtain easy processing materials,

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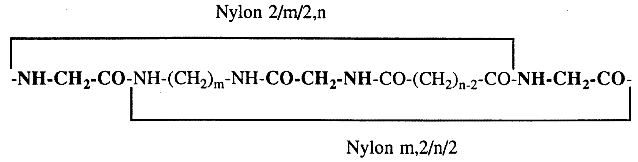


$$-NH-CH_2-CO-NH-(CH_2)_m-NH-CO-CH_2-NH-CO-(CH_2)_{n-2}-CO-NH-CH_2-CO-$$

Scheme 1.

since the melting point decreases as the methylene content increases; and (iii) study the effect of glycine residues in nylons with long methylene segments. In contrast, the study of polymers which contain α-amino acids has gained interest since they may have biocompatible and biodegradable characteristics [15–23]. Thus, different studies have been reported about the incorporation of α-amino acids in nylons [17,20–23]. In particular, the introduction of glycine in nylons 6,6 and 6 has been reported to give biodegradable materials [7,21–23].

In addition, copolymers of nylons 2/12/2,10 and 12,10 have also been prepared to improve the processing of samples, in a similar way to the random 2/6 and 2/12 copolymers previously studied in our laboratory [12].

2. Experimental

All chemicals were ACS grade or higher and were used as received. Solvents were purified and dried by appropiate standard methods [24].

2.1. Synthesis

Standard melt polycondensation methods for preparing *m,n* polyamides are inadequate for the synthesis of glycine copolymers, since they degrade during polycondensation and yield a deeply coloured solid. Thus, these polymers were prepared by interfacial polymerization between the sebacic acid and a diamine which incorporates the glycine residues. This monomer was synthesized in solution applying the widely known methodology developed for the synthesis of peptides [25] and indicated in Scheme 2a.

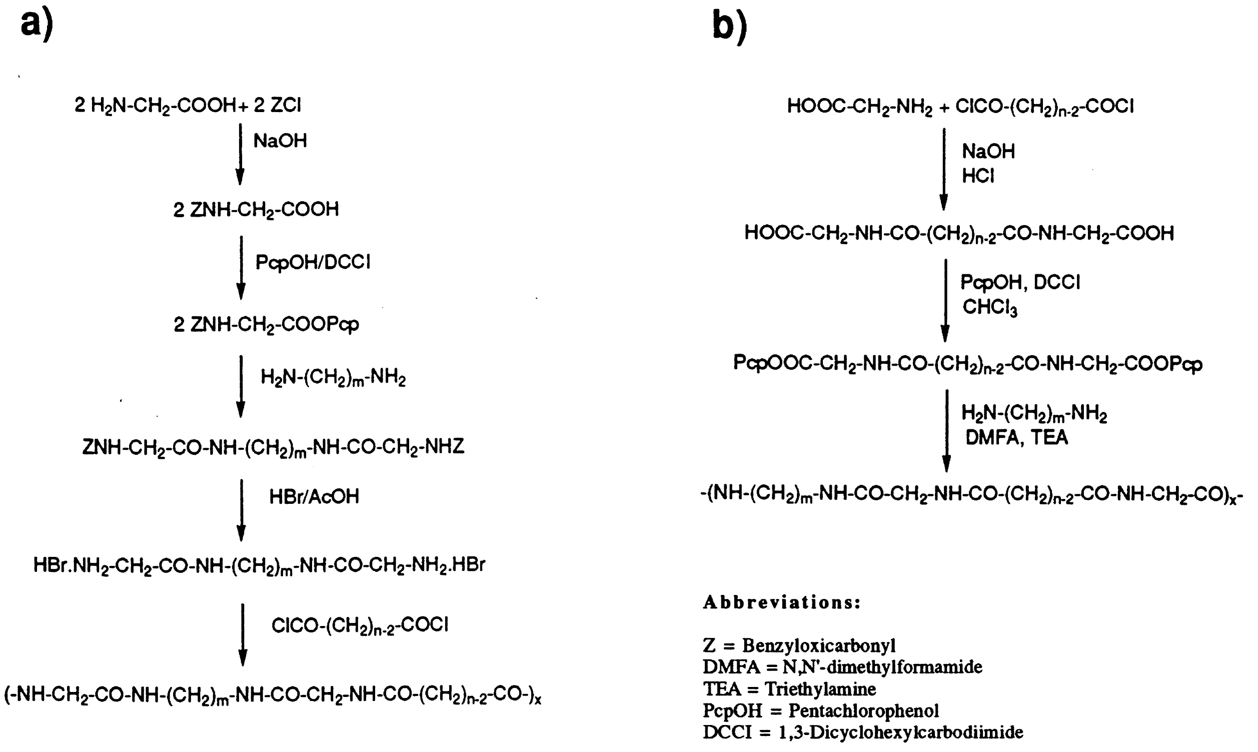
Glycine was carbobenzoxylated according to the general Zervas [26] method and recrystallized from ethyl acetate with a yield of 70%.

N-carbobenzyloxy-glycine pentachlorophenyl ester was prepared according to published procedures [27] and then crystallized from isopropanol, resulting a 72% yield of the pure substance.

2.2. Coupling reaction

A mixture of the diamine (1,6-hexamethylendiamine or 1,12-dodecamethylendiamine, 0.05 mol) and *N*-carbobenzyloxy-glycine pentachlorophenyl ester (0.1 mol), dissolved in ethyl acetate (50 ml), was stirred at room temperature for 12 h. The precipitate was filtered and washed several times with ethyl acetate. The yields for the 1,6-hexamethylendiamine and 1,12-dodecamethylendiamine derivatives were 90% and 88%, respectively.

Elemental analysis: calculated for $C_{26}H_{34}N_4O_6$: C



Abbreviations:

Z = Benzyloxicarbonyl
DMFA = N,N'-dimethylformamide
TEA = Triethylamine
PcpOH = Pentachlorophenol
DCCI = 1,3-Dicyclohexylcarbodiimide

Scheme 2.

62.65%, H 6.83%, N 11.24%; found, C 62.63%, H 6.90%, N 11.82%.Calculated for $C_{32}H_{46}N_4O_6$: C 65.98%, H 7.90%, N9.62%; found, C 65.03%, H 7.94%, N 9.74%.Melting points: 176°C and 174°C for $C_{26}H_{34}N_4O_6$ and $C_{32}H_{46}N_4O_6$, respectively.

2.3. Removal of the protecting group

The protected monomer (0.02 mol) was dissolved in 150 ml of glacial acetic acid containing 20% HBr. The initial vigorous evolution of carbon dioxide ceased after about 30 min after standing for 30 min at room temperature, the precipitate obtained was filtered, washed with ethyl ether and finally dried in a vacuum desiccator. The yields were 75% and 83% for 1,6-hexamethylendiamine and 1,12-dodecamethylendiamine, respectively.

Elemental analysis: calculated for $C_{10}H_{24}N_4O_2Br_2$: C 30.63%, H 6.12%, N 14.29%; found: C 30.27%, H 6.43%, N 13.98%.Calculated for $C_{16}H_{36}N_4O_2Br_2$: C 40.35%, H 7.57%, N 11.77%; found: C 39.97%, H 7.63%, N 11.88%.Melting points for $C_{10}H_{24}N_4O_2Br_2$ and $C_{16}H_{36}N_4O_2Br_2$ were 178 and 180°C, respectively.

2.4. Polymerizations

Interfacial polymerization was carried out following the method described in the literature for the synthesis of nylon 6,10 [28] (Scheme 2a). Approximately 0.01 mol of the diamine were dissolved in 30 ml of water (1,6-hexamethylenediamine derivative) or 30 ml of a mixture of water and acetone (1,12-dodecamethylendiamine derivative, due to its insolubility in water). To the diamine solution 0.04 mol of sodium hydroxide was slowly added to scavenge the HCl produced by the reaction and also to neutralize the HBr from the salt of the diamine. On the other hand, 2.13 ml (0.01 mol) of sebacic acid were dissolved in 70 ml of carbon tetrachloride. This solution was added to the other one and a film was formed at the interface immediately. For nylon 2/12/2,10 the film was collected, washed with water, ethanol and acetone and finally dried in a stove at 40°C. For nylon 2/6/2,10, the two-phase system was stirred because a firm film is not obtained at the interface. After addition was complete stirring was continued for 30 min. The polymer which precipitated was isolated by filtration.

Copolymers of nylon 2/12/2,10 and 12,10 were also synthesized by interfacial polymerization by the reaction of different proportions of *N*,*N*′-diglycyl-dodecanediamine dihydrobromide and 1,12 dodecamethylendiamine with sebacoyl chloride. Thus, nylons with 10 and 40% of glycine nominal content (molar percentage assuming that both diamine and diacid are equivalent to one amino acid) were synthesized. Note that glycine units are not randomly distributed along the polymer chain since they will always be placed between a diamine and a diacid unit, and consequently glycine blocks are excluded.

2.5. Characterization

The chemical constitution of the polymers was ascertained by infrared and n.m.r. spectroscopies and elemental analysis. Infrared absorption spectra were recorded from potassium bromide pellets in a Perkin–Elmer 783 spectrophotometer in the 4000–5000 cm^{-1} range. n.m.r. spectra were registered from polymer solutions in deuterated trifluoracetic acid using a Bruker AMX-300 spectrometer operating at 300.1 MHz for ^1H n.m.r. and at 75.5 MHz for ^{13}C n.m.r.. The intrinsic viscosity of the polymers was determined by measurements with a Cannon–Ubbelohde microviscometer in dichloroacetic acid solutions at 25 ± 0.1°C. Thermal behavior was investigated with a Perkin–Elmer DSC-4 equipped with a TADS data station at heating and cooling rates of 20°C/min in a nitrogen atmosphere. Temperature was calibrated using an indium standard.

2.6. 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.

Samples for transmission electron microscopy were made by placing drops of crystal suspension on carbon-coated copper grids and then shadowed with Pt-carbon at an angle of 15°. Crystals were examined in both imaging and diffraction modes, using a Phillips 301 TEM operating at 80 or 100 kV, respectively. Electron diffraction diagrams were recorded by the selected area method on Kodak triX films and the patterns were internally calibrated with gold ($d_{111} = 2.35$ Å). Some crystals were decorated with polyethylene vapour, following the Wittmann and Lotz polyethylene decoration technique [29].

Wide- and low-angle X-ray diffraction patterns were obtained, under vacuum at room temperature, using a Ni-filtered CuK_a radiation from a modified Statton camera (W. R. Warhus Wilmington DE). Calcite ($d_B = 3.035$ Å) was dusted onto selected samples for calibration purposes. Diagrams were recorded from either polymer powders, sedimented crystal mats or fibres. Mats of single crystals were prepared by slow filtration of a crystal suspension on a glass filter. Fibres were obtained by extrusion from the melt and then annealed at 120°C.

3. Results and discussion

3.1. Synthesis and characterization

Previous synthesis of related polymers was carried out using the active-ester method depicted in Scheme 2b.

Table 1
Spectroscopic and calorimetric data for 2/*m*/2,*n* polymers[a]

Polymer	IR data (cm^{-1})	^{1}H NMR data (ppm)	^{13}C NMR data (ppm)	Calorimetric data[b] T (°C), ΔH (kJ/mol), χ(%)
2/6/2,10	3298 (amide A), 3088 (amide B), 2928 and 2855 (CH$_2$ stretching), 1641 (amide I), 1551 (amide II), 723 (CH$_2$ rocking), 699 (amide IV), 565 (amide VI)	4.36 (2H, –NH-CH_2-CO–) 3.47 (2H, –NH-CH_2-CH$_2$–) 2.64 (2H, –CO-CH_2-CH$_2$–)	183.10 (–CO-CH$_2$-CH$_2$–) 173.20 (–CO-CH$_2$-NH–) 45.27 (–NH-CH$_2$-CO–) 43.21 (–NH-CH$_2$-CH$_2$–) 36.79 (–CO-CH$_2$-CH$_2$–)	T_f (*230.5*, 261.5), ΔH_f (39.9) T_c (166.1), ΔH_c (− 19.2) χ (38)
2/12/2,10	3300 (amide A), 3090 (amide B), 2925 and 2853 (CH$_2$ stretching), 1644 (amide I), 1556 (amide II), 722 (CH$_2$ rocking), 699 (amide IV), 562 (amide VI)	4.36 (2H, –NH-CH_2-CO–) 3.46 (2H, –NH-CH_2-CH$_2$–) 2.60 (2H, –CO-CH_2-CH$_2$–)	183.18 (–CO-CH$_2$-CH$_2$–) 173.50 (–CO-CH$_2$-NH–) 45.24 (–NH-CH$_2$-CO–) 43.78 (–NH-CH$_2$-CH$_2$–) 36.92 (–CO-CH$_2$-CH$_2$–)	T_f (244.5), ΔH_f (38.4) T_c (212.2), ΔH_c (− 30.2) χ (43)
2/12/2,10 (10%)[c]	3318 (amide A), 3102 (amide B), 2914 and 2843 (CH$_2$ stretching), 1640 (amide I), 1544 (amide II), 722 (CH$_2$ rocking), 688 (amide V), 582 (amide VI)	4.36 (2H, –NH-CH_2-CO–) 3.46 (2H, –gly-NH-CH_2-CH$_2$–) 3.56 (2H, –seb-NH-CH_2-CH$_2$–) 2.55 (2H, –gly-CO-CH_2-CH$_2$–) 2.75 (2H, –dod-CO-CH_2-CH$_2$–)	183.2 (–gly-CO-CH$_2$-CH$_2$–) 181.6 (–dod-CO-CH$_2$-CH$_2$–) 173.5 (–CO-CH$_2$-NH–) 45.2 (–NH-CH$_2$-CO–) + (–seb-NH-CH$_2$-CH$_2$–) 43.8 (–gly-NH-CH$_2$-CH$_2$–) 36.9 (–gly-CO-CH$_2$-CH$_2$–) 35.6 (–dod-CO-CH$_2$-CH$_2$–)	T_f (173.4), ΔH_f (29.2) T_c (160.2), ΔH_c (− 13.0) χ (33)
2/12/2,10 (40%)[c]	3312 (amide A), 3085 (amide B), 2915 and 2842 (CH$_2$ stretching), 1640 (amide I), 1557 (amide II), 722 (CH$_2$ rocking), 683 (amide IV + amide V), 562 (amide VI)	4.36 (2H, –NH-CH_2-CO–) 3.46 (2H, –gly-NH-CH_2-CH$_2$–) 3.56 (2H, –seb-NH-CH_2-CH$_2$–) 2.60 (2H, –gly-CO-CH_2-CH$_2$–) 2.76 (2H, –dod-CO-CH_2-CH$_2$–)	183.2 (–gly-CO-CH$_2$-CH$_2$–) 181.6 (–dod-CO-CH$_2$-CH$_2$–) 173.5 (–CO-CH$_2$-NH–) 45.2 (–NH-CH$_2$-CO–) + (–seb-NH-CH$_2$-CH$_2$–) 43.8 (–gly-NH-CH$_2$-CH$_2$–) 36.9 (–gly-CO-CH$_2$-CH$_2$–) 35.6 (–dod-CO-CH$_2$-CH$_2$–)	T_f (*216.7*, 240.1), ΔH_f (27.4) T_c (169.1), ΔH_c (− 24.7) χ (31)

[a] Abbreviations: gly, glycine; seb, sebacic acid; hex, hexamethylendiamine; dod, dodecamethylendiamine. χ denotes crystallinity.
[b] When double melting peaks are observed the peak with a lower heat of fusion is indicated in italics
[c] Molar glycine percentage in copolymers obtained as described in the text

Polymers had a moderate molecular weight, so an alternative synthesis, by interfacial polymerization, was used for nylons 2/6/2,10 and 2/12/2,10. Although this process has two additional steps (Scheme 2a) the global yield is similar. Further, nylon 2/6/2,10 was synthesized by both methods. As expected, the sample prepared by interfacial polymerization had a higher intrinsic viscosity (0.50 dl/g in front of 0.38 dl/g). In contrast, interfacial polymerization seems appropiate for 2/*m*/2,*n* nylons, because of the lower hydrolysis rate of sebacoyl dichloride. This was not the case for the previous polymers where for instance, succinyl dichloride should be used.

The organic solvent (toluene, carbon tetrachloride or methylene dichloride) and proton aceptor (NaOH, Na$_2$CO$_3$ or diamine excess) to be used were optimized in order to increase the molecular weight of the polymer. The polymerization yield was high (about 80%) and intrinsic viscosities, around 0.50, were obtained, so that excellent film and fibre forming properties were found.

Infrared spectra of all polymers show characteristic methylene and amide absorption bands (Table 1). It is worth noting the presence of two bands near 699 and 565 cm^{-1} (or 562 cm^{-1} for nylon 2/12/2,10) in the conformationally sensitive region of 750–500 cm^{-1}. These absorption bands do not fit with those expected for both the conventional α-form [30]: 690 cm^{-1} (amide V) and 580 cm^{-1} (amide VI) and the γ-form [31]: 630 cm^{-1} (amide VI). However, they agree with the characteristic absorptions found in the helical form II of polyglycine: 696 cm^{-1} (amide IV) and 563 cm^{-1} (amide VI).

Data from n.m.r. spectroscopy are fully consistent with the anticipated chemical composition. All the signals are summarized in Table 1. The ^{1}H n.m.r. spectra of nylons 2/6/2,10 and 2/12/2,10 show a single signal for the glycine protons around 4.36 ppm, whereas the methylene protons next to the amide groups appear, also as single signals, around 3.47 (–NH-CH_2–) and 2.64 (–CO-CH_2–) ppm. The ^{13}C n.m.r. spectra also present well differentiated signals for the methylene of the glycine unit (45.27 ppm) and the methylenes next to the amide group in the diamine and carbonyl segments (43.21 and 36.79 ppm, respectively). Nylons 2/12/2,10 (10%) and 2/12/2,10 (40%) present different ^{1}H and ^{13}C spectra to those of nylon 2/12/2,10, since new signals arising from –CH$_2$CH$_2$NHCOCH$_2$CH$_2$- sequences appear (Fig. 1). For random copolymers, the ^{1}H spectrum was used in order to determine the molar composition. Thus, the copolymer composition was calculated from area I_1 of the methylene protons of glycine and areas I_2, I_3 and I_4, I_5 of the methylene protons representative of diamine and diacid units, following the simple

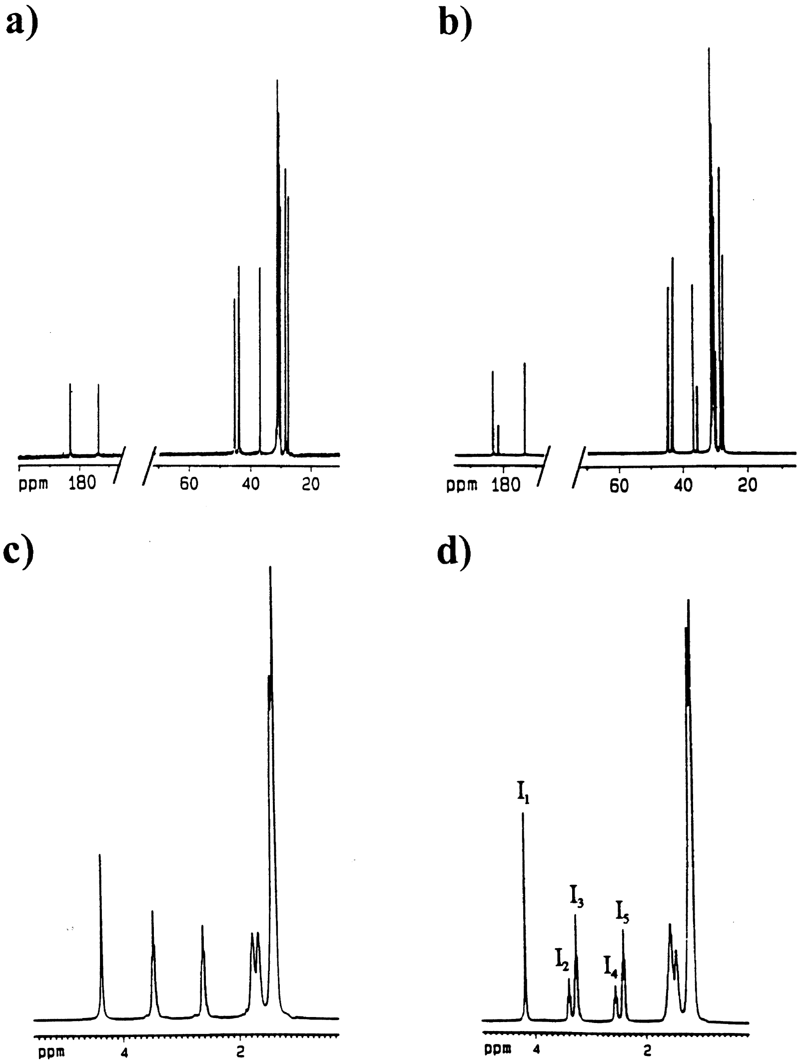


Fig. 1. ^{13}C-n.m.r. spectra of: (a) nylon 2/12/2,10; (b) nylon 2/12/2,10 (40%). ^{1}H-n.m.r. spectra of: (c) nylon 2/12/2,10; d) nylon 2/12/2,10 (40%). The labelled signals have been used in order to determine the molar percentage of glycine, as described in the text. Polymers were dissolved in deuterated trifluoracetic acid and tetramethylsilane was used as internal reference. Assignment of the main signals is given in Table 1.

relation:

$$\%\mathrm{Gly} = \frac{2I_1}{2I_1 + I_2 + I_3 + I_4 + I_5} 100$$

Results compare well with the feed ratios within 5% deviation (11.2% and 37.4%).

Calorimetric data are also summarized in Table 1. In general, single or double melting peaks are observed. Melting temperatures of nylons 2/*m*/2,*n* are higher than the related nylons *m*,*n* (223°C and 188°C for nylons 6,10 [5] and 12,10 [6], respectively) caused by the increased amide/methylene ratio. In contrast, random copolymers melt, as expected, at lower temperatures than the homopolymers. Thus, nylons 2/12/2,10 (10%) and 2/12/2,10 (40%) melt at lower temperatures than nylons 12,10 and 2/12/2,10. Crystallinities around 40% could be estimated for all nylons from their experimental heat of fusion and the group contributions reported by Van Krevelen [32]. Nylon 2/6/2,10 was not stable through fusion since the sample, after the heating run, showed a dark coloration and an important weight loss. However, nylons 2/12/2,10 were thermally more stable, probably due to their lower melting temperature. In this sense, their stability increases when the glycine content is reduced. Thus, a second heating run reproduced the first runs for nylons 2/12/2,10 (40%) and 2/12/2,10 (10%).

3.2. Structural characterization

Crystals suitable for electron microscopy were obtained from nylon 2/6/2,10 by isothermal crystallization from dilute solutions (0.1% (w/v)) in 1,4-butanediol or glycerine. Their morphology varies depending on the conditions used for preparation of the samples. Thus, long (about 6 μm) sheaves, which appear folded over themselves, were obtained from 1,4-butanediol at 136°C (Fig. 2a). Shorter oval-shaped crystals were found when crystallization was conducted in glycerine solutions at 178°C (Fig. 2b). These

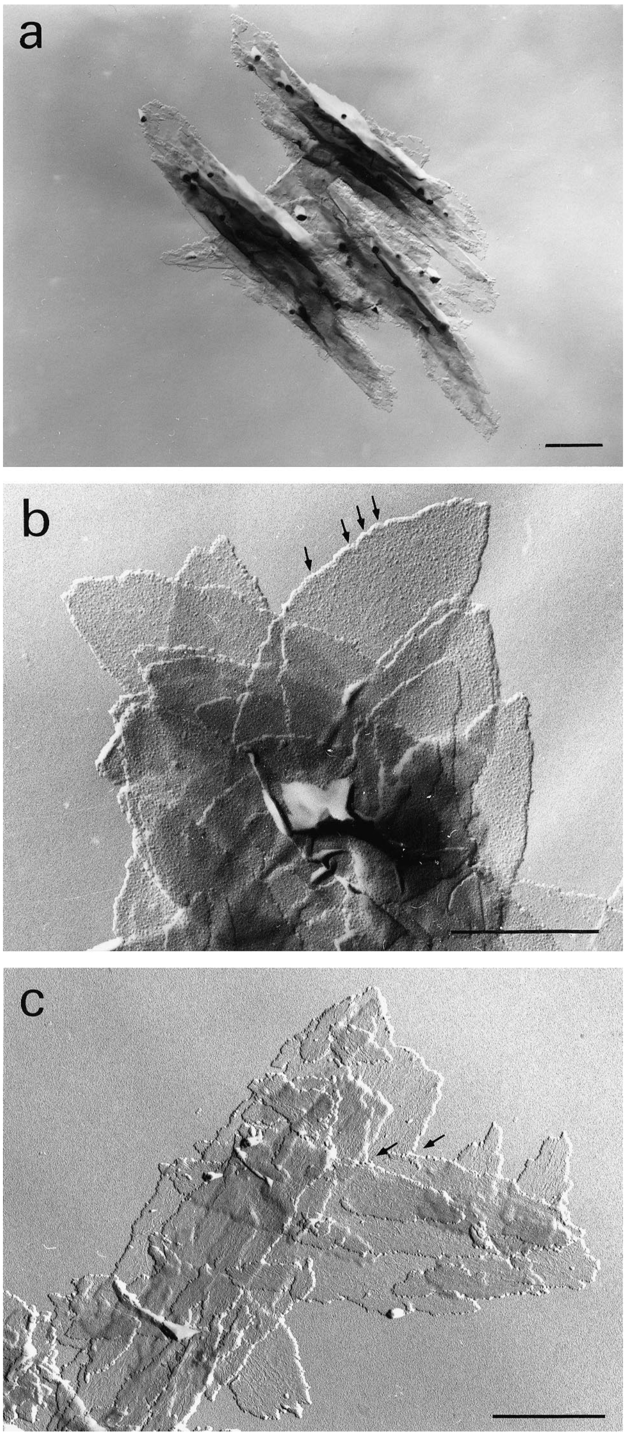


Fig. 2. Transmision electron micrographs of lamellar crystals of: (a) nylon 2/6/2,10 prepared from a 1,4-butanediol solution (0.5 mg/ml) at 136°C; (b) nylon 2/6/2,10 crystallized from glycerine solution (1 mg/ml) at 178°C. Arrows indicate irregular edges in the oval-shaped crystals; (c) nylon 2/12/2,10 prepared by precipitation of a dilute formic acid solution (0.1% (v/w)) with four volumes of *n*-butanol at 78°C. Crystals appear frequently bifurcated as indicated by arrows. Scale bars: 1 μm.

lamellae show a maximum width of 1 μm and a thickness about 60 Å, as estimated by the measurement of their Pt/C shadows in the micrographs.

Isothermal crystallization of nylon 2/12/2,10 in the same solvents renders small and thick crystals without any defined morphology. However, single crystals are formed when the polymer is precipitated from formic acid (0.1% (w/v)) by adding four volumes of *n*-butanol at 70°C. These crystals (Fig. 2c) are elongated (3 μm long and not more than 1.5 μm wide) and thicker (about 80 Å) than nylon 2/6/2,10 crystals. Note also that the lamellae frequently grow in two different directions.

Crystals of both nylons are characterized by having serrated edges, which indicates a disordered crystalline growth. Further, it was not possible to obtain a regular disposition of polyethylene bars in decoration experiments carried out by following the Wittmann and Lotz method [29]. In all cases the polyethylene fibrils appeared randomly distributed on the crystal surface as an indication of an irregular folding habit.

Electron diffraction patterns from both nylons show a quasihexagonal symmetry with a basic spacing of 4.15 Å (Fig. 3, Table 2). Up to four orders of this reflection can be seen in the original picture, which indicates that the crystal structure is well preserved up to near 1 Å resolution. It is worth noting that these electron diffraction patterns show many more reflections than those previously reported for nylons m,2/n/2 ($m = 2, 4$, $n = 4, 6$), probably caused by the larger crystal dimensions. Although the diagrams are clearly hexagonal in spacings, they are not in intensity since at most an *mm* symmetry could be observed. Both nylons were indexed according to a primitive cell of parameters: $\alpha_p = \beta_p = 4.79$ Å and $\gamma = 120°$.

X-ray diffraction diagrams were recorded from either powder samples, sedimented crystal mats or fibres prepared from the melt. All the diffraction patterns are characterized by well-defined reflections, which demostrate crystalline order; the most intense appearing at 4.15 Å spacing. This reflection has an equatorial orientation in both mats (Fig. 4) and fibres (Fig. 4 Fig. 5) in agreement with the electron diffraction data. It is worth noting that the two intense and characteristic spacings (about 4.40 and 3.80 Å) of extended conformations (α and β forms) cannot be observed whatever the preparation conditions. Both nylons can be indexed (Table 3 Table 4) according to hexagonal unit cells, where the *c* (chain axis) parameter varies in agreement with the unit repeat length (26.9 and 34.3 Å for nylons 2/6/2,10 and 2/12/2,10, respectively). In addition, a lamellar thickness of about 55 Å could be deduced from the low-and wide-angle diffraction pattern of sedimented crystals of nylon 2/6/2,10. The high number of lamellar orders observed in the patterns indicate that the lamellar width must be fairly constant and that the neigbouring lamellae in the stacking diffract coherently, as found in other nylons [33]. On the contrary, for nylon 2/12/2,10 no additional reflections to those indexed as 001 (found also in the fibre patterns) were detected in the low-angle region. This fact may be attributed to a rather variable thickness for this kind of crystal obtained by precipitation techniques.

Table 2
Measured and calculated electron diffraction spacings d_B (Å) for nylons 2/6/2,10 and 2/12/2,10

Index[a]	2/6/2,10 calc	meas*d*[b]	2/12/2,10 calc	measd[b]
100	4.15	4.15 vs	4.15	4.15 vs
110	2.40	2.40 s	2.40	2.41 s
200	2.07	2.09 s	2.07	2.08 s
210	1.57	1.58 m	1.57	1.52 m
300	1.38	1.39 m	1.38	1.40 m
220	1.20	1.19 m	1.20	1.19 m
130	1.15	1.15 w	1.15	1.15 m
400	1.04	1.02 w	1.04	1.06 w

[a] On the basis of a projected unit cell of parameters: $a_p = b_p = 4.79$ Å and $\gamma = 120°$

[b] Abbreviations denote intensities: s, strong; m, medium; and w, weak

We could not prepare good fibres from nylon 2/6/2,10 because of its high melting point and the decomposition that takes place after fusion. Thus, the fibres obtained were very brittle and slightly yellowish. However, some orientation is detected in their X-ray fibre patterns, so the 002 reflection appears on the meridian with a slightly shorter spacing than the corresponding one in powder and mat patterns, probably due to some distortion in the chain conformation. Better fibres, without any appreciable coloration, were obtained from nylon 2/12/2,10. In a similar way to nylon 2/6/2,10 the fibres coming directly from the melt show a shorter 002 spacing (about 16 Å in front of 17.1 Å). However, all reflections result in agreement with powder patterns (Table 4) when the fibres are annealed under stress at 140°C. This fact indicates that some rearrangement of the molecular conformation is produced.

X-ray diffraction data show that the unit repeat lengths of nylons 2/6/2,10 and 2/12/2,10 are shortened from the values estimated for an extended conformation (0.78 and 0.80 Å/amide group, respectively). Moreover, this shortening is also larger than expected for the pseudohexagonal phase of nylons, since values around 0.35 Å/amide group are reported for a γ-form [34]. On the contrary, a similar shortening has been found in polymers where glycine residues take their polyglycine II conformation (nylons 2/n) [35]. The deviation of a 6 *mm* symmetry of the electron diffraction patterns may be interpreted as an indication that the two glycine residues of the repeat unit have opposite conformations, giving rise to a lattice where amide groups are oriented only in two directions (Fig. 6). Reported diffraction data on a related model compound constituted by an adipoyl unit linked to two glycinamide residues are also in agreement with this assertion [36].

It is clear that a three-fold helix will be generated when: (i) both glycine residues take the same chirality and the polyglycine II conformation; and (ii) the diamine and dicarbonylic moieties take their extended (α form) or quasiextended (γ form) conformations. In this case a lattice with three equivalent hydrogen bond directions is expected, in disagreement with the non-hexagonal morphologies exhibited by the single crystals. However, an explanation based on the reduced number of repeat units (less than three) that

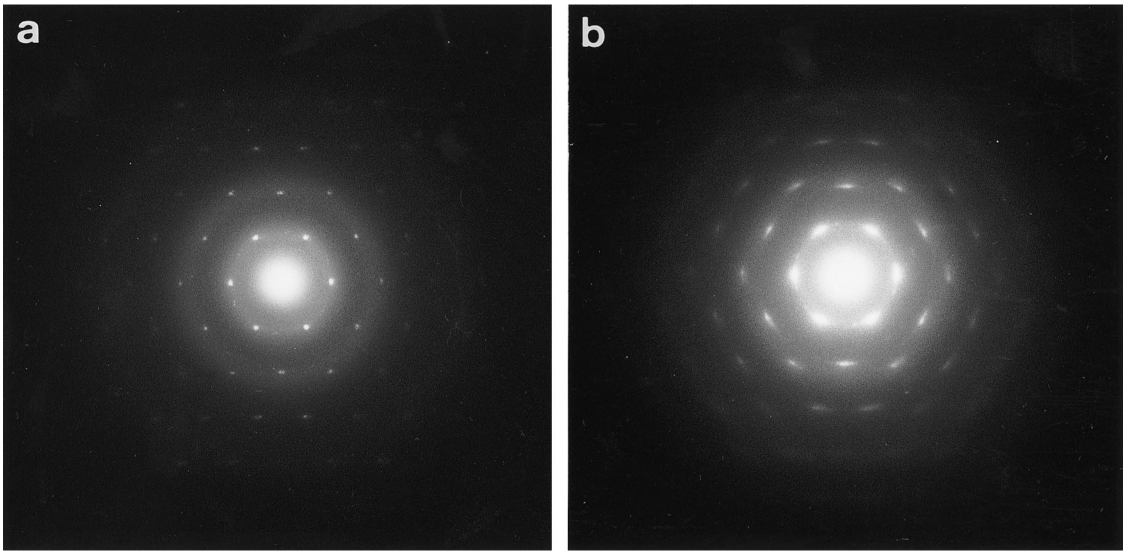


Fig. 3. Selected-area electron diffraction patterns from crystals of nylons 2/6/2,10 (a) and 2/12/2,10 (b). The electron diffraction pattern of nylon 2/12/2,10 was obtained from the crystals prepared from glycerine, since 1,4-butanediol preparations give much more arched reflections.

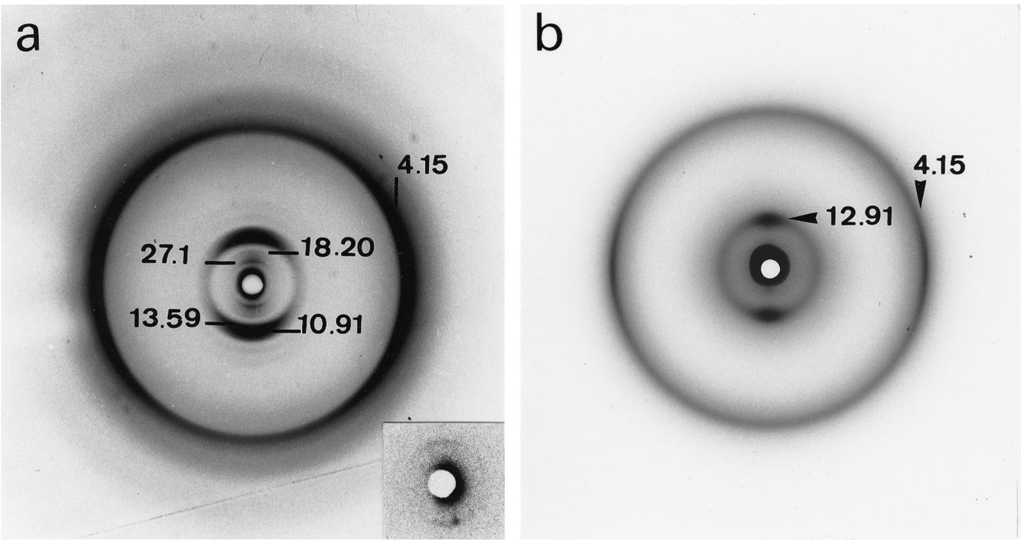


Fig. 4. (a) X-ray diffraction pattern of a sedimented mat of nylon 2/6/2,10 taken with the mat normal vertical. Note the different lamellar orders observed in the meridian as well as the strong reflection in the equator. In the low-angle pattern (inset) the spacing at 55 Å represents the lamellar stacking periodicity. (b) X-ray fibre diffraction pattern of nylon 2/6/2,10, which shows a fair orientation. Moreover, only a meridional reflection at 12.90 Å and an equatorial reflection at 4.15 Å could be detected. Representative spacings are indicated in Angstroms.

fits in the lamellar thickness cannot be excluded. The serrated edges, the irregular folding and the lamellar growth in two directions (Fig. 2c) point to a lattice with more than one hydrogen bond direction.

The processing of nylon 2/12/2,10 is improved when the glycine content is reduced. Thus, very good fibres (Fig. 5b) were obtained at 40% molar content of glycine, resulting in an X-ray diffraction pattern in close agreement with the regular 2/12/2,10 polymer (Fig. 5a). When the glycine content is reduced the structure approaches that found in nylon 12,10. Thus, at 10% of glycine the fibre pattern (Fig. 5c) shows two equatorial reflections with spacings similar to those observed in the extended form of nylon 12,10 (Fig. 5d). Moreover, an excellent agreement (spacings and intensities) is also found between their meridional reflections.

4. Conclusions

The results of the present study can be summarized as

Table 3
Measured and calculated X-ray diffraction spacings d_B (Å) for nylon 2/6/2,10

Index	Cal.[a]	Powder Measd.[b]	Mat Measd.[b]	Fibre Measd.[b]
1º lamellar order	54.5		55[c] s M	
001, 2º order	26.9, 27.25	26.9 w	27.10 s M	
3º order	18.17		18.20 m M	
002, 4º order	13.45, 13.62	13.50 s	13.59 s M	12.90 s M
5º order	10.90		10.91 s M	
003, 6º order	8.97, 9.08	9.00 w	9.23 w M	
7º order	7.78		7.81 w M	
9º order	6.05		6.18 w M	
100	4.15	4.15 vs	4.15 vs E	4.15 vs E
104	3.53	3.50 w	3.53 s	
106	3.05	3.08 w	3.01 w	
109	2.42	2.42 w	2.46 w	

[a] On the basis of a hexagonal unit cell with parameters: $a = b = 4.79$ Å, $c = 26.9$ Å and $\gamma = 120°$
[b] Abbreviations denote intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. Orientations: M, meridional; E, equatorial.
[c] Observed only in the low angle patterns.

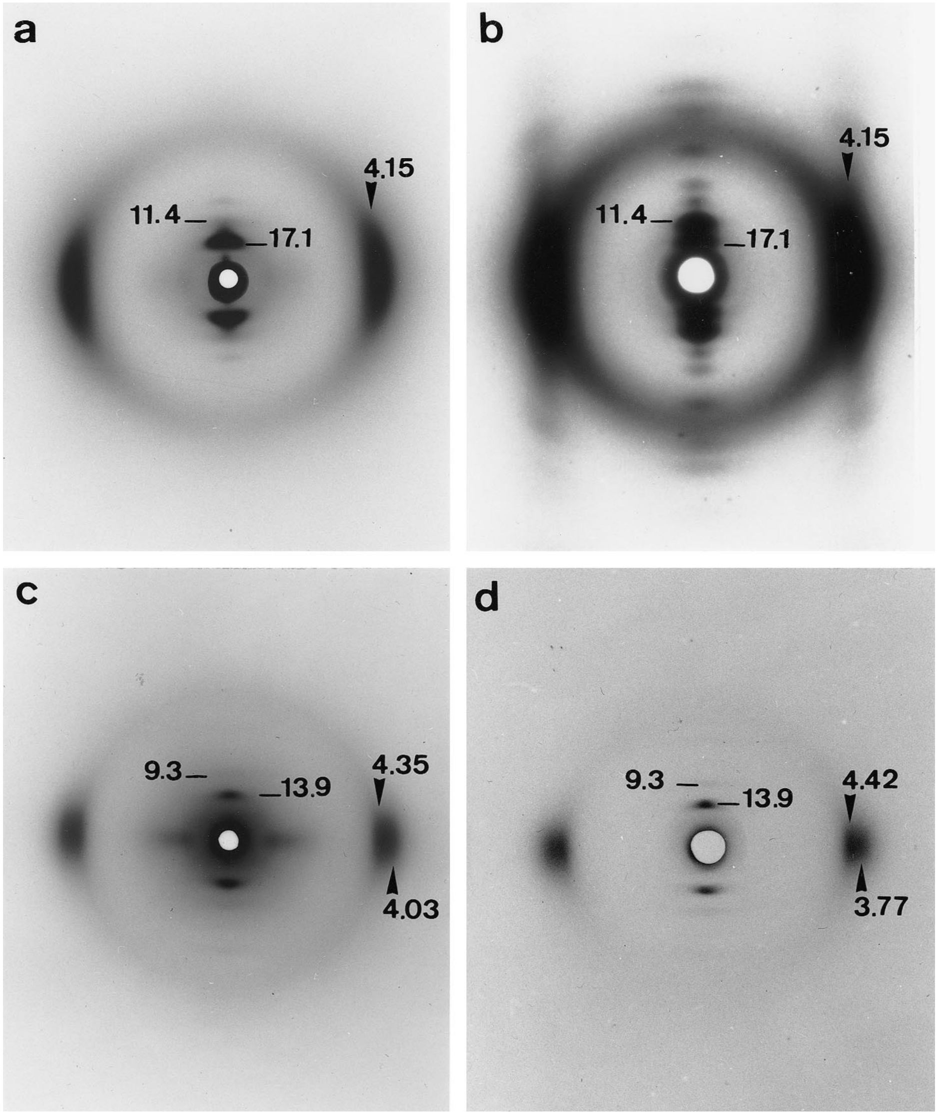


Fig. 5. X-ray fibre diffraction patterns of nylon 2/12/2,10 with different glycine molar content: (a) 50%; (b) 40% and (c) 10%. The fibre diffraction pattern of nylon 12,10 (0% glycine) is given in (d) for comparison purposes. Representative spacings are indicated in Angstroms.

Table 4
Measured and calculated X-ray diffraction spacings d_B (Å) for nylon 2/12/2,10

		Powder	Annealed fibre
Index	Cal.[a]	Measd.[b]	Measd.[b]
001	34.3	34 m	34 m M
002	17.15	17.14 vs	17.1 vs M
003	11.43	11.51 m	11.4 m M
004	8.57	8.27 vw	8.40 w M
005	6.86	6.90 w	6.82 vw M
100	4.15	4.15 vs	4.15 vs E
103	3.90	3.90 s	
104	3.73	3.71 m	
105	3.55	3.51 w	
106	3.35	3.29 w	
108	2.98	3.03 w	
10,10	2.69	2.66 w	
110	2.40	2.40 w	

[a] On the basis of a hexagonal unit cell with parameters $a = b = 4.79$ Å; $c = 34.3$ Å; and $\gamma = 120°$

[b] Abbreviations denote intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. Orientations: M, meridional; and E, equatorial.

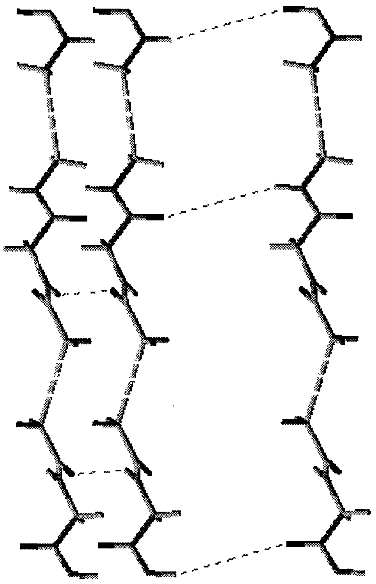


Fig. 6. Lateral view of three hydrogen bonded chains. The molecular chain on the left is at a different level in the view direction. For simplification purposes the intermediate methylenes of both diamine and dicarbonylic moieties have been removed. Moreover, the separation distance between molecular chains has been increased to clarify the representation. Note that each glycine residue produces a rotation of ca. 60° between their NH and CO directions. This rotation is recuperative when the two glycine residues have opposite conformations. In this case, all amide groups point in only two directions. Diamine and dicarbonylic moieties have been represented assuming that they take a γ conformation, in order to improve the hydrogen bond geometry. Oxygen atoms are in black.

follows:

1. Polymers and copolymers have been prepared, by interfacial polymerization, with high yields and adequate molecular weight to give film and fibre-forming materials. Moreover, polymers derived from 1,12-dodecamethylendiamine have a sufficiently low melting point to be stable through fusion, so that processing from the melt can be carried out.
2. The incorporation of glycine residues in nylons 6,10 and 12,10 disrupts their α-structure. The experimental results indicate a hexagonal packing, where hydrogen bonds are established in more than one direction in space. The conformation of glycine residues introduces a rotation of approx. 60° between consecutive amide groups.
3. Fibre-forming properties and processing can be improved when the glycine content is reduced. Structures ranging from the pseudohexagonal packing to the α-sheet structure are obtained depending on the glycine content.

Acknowledgements

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