Polymer 41 (2000) 5437–5441

polymer

A sheet structure in an alternate copolymer of 4-aminobutyric acid and α-isobutyl-L-glutamate

M.T. Casas, J. Puiggalí*

Departament d'Enginyeria Química, ETS d' Enginyers Industrials, Universitat Politècnica de Catalunya, Diagonal 647, Barcelona 08028, Spain

Received 23 June 1999; received in revised form 3 September 1999; accepted 7 October 1999

Abstract

An alternating copolyamide derived from 4-aminobutyric acid and α-isobutyl-L-glutamate has been synthesized by the active ester method, and subsequently characterized. The structure and morphology of lamellar crystals have been investigated by using transmission electron microscopy. Additional data have been obtained from uniaxially oriented films by using X-ray diffraction. Experimental results agree with an orthorhombic unit cell of parameters $a = 4.88$, $b = 14.0$ and the chain axis $c = 10.5$ Å. A sheet structure with intermolecular hydrogen bonds was deduced taking also into account infrared dichroism data. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyamides; Glutamates; Nylons

1. Introduction

During the last years, it has been demonstrated that nylon 3 derivatives, with an alkoxycarbonyl group attached to the backbone β carbon of the repeating unit, adopt helical arrangements similar to those found in polyα-amino acids. Thus, different works on the helical structures of poly(α-alkyl β-L-aspartate)s $[-(NHCH(COOR)CH_2CO)_n-]$ have been published [1–4]. In the same way, investigations on substituted β-amino acid oligomers also demonstrated their capability to give helical arrangements [5,6].

Substituted γ-amino acid oligomers are just beginning to be intensively investigated. The reported results show that a helical conformation with intramolecular hydrogen bonds appears to be stabilized. This conformation is related to that previously indicated for poly(α-benzyl γ-L-glutamate) [8], a nylon 4 derivative, which had a 5_2 helix according to X-ray and electron diffraction data.

In this work, we undertake the study of the regular copolymer constituted by 4-aminobutyric acid and α-isobutyl-L-glutamate units. This polymer may be considered as a nylon 4 derivative where the half of the repeating units are stereoregularly substituted in the backbone γ carbon by isobutyloxycarbonyl groups. The main purpose of this research is to know if it is possible to have a helical conformation with intramolecular hydrogen bonds when the ratio of lateral groups is reduced to the half.

2. Experimental

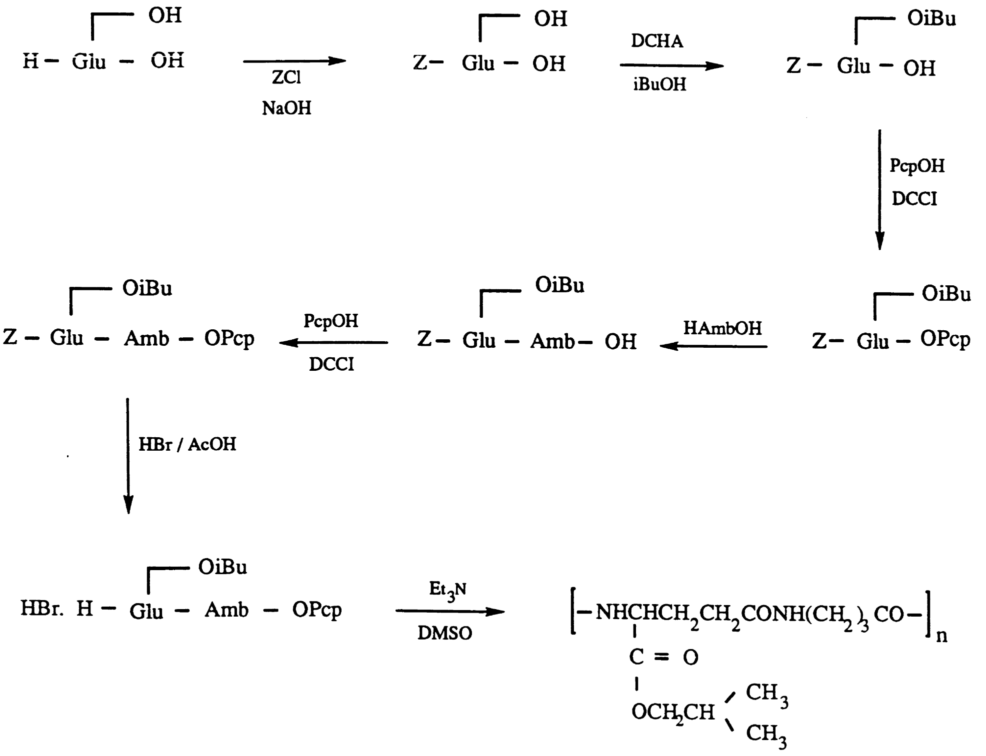
The polymer was synthesized by the active ester method using pentachlorophenylic derivatives and following the steps indicated in Scheme 1. Selective esterification of glutamic acid was carried out according to the procedure described by Nefkens et al. [9]. The coupling reaction between the glutamic derivative and the aminobutyric acid was done using 2-hydroxypyridine as catalyst. All intermediates were recrystallized and their structures verified by standard chemical procedures. Polymerization was conducted in a dimethyl sulfoxide solution at room temperature with a monomer concentration of 1 g/ml. Triethylamine (2.2 eq.) was added in order to liberate the amino groups and to neutralize the acidic substances generated during polymerization. After 5 days the polymer was recovered by precipitation with ethyl ether and extensively washed with water, ethanol and ethyl ether. The polymer was obtained with a 75% yield and an intrinsic viscosity of 0.92 dl/g, which was measured in a dichloroacetic acid solution at 25°C.

The chemical structure of the polymer was ascertained by ^{13}C NMR with a Varian XL-200 spectrometer. δ (ppm) from deuterated trifluoroacetic acid solutions: 179.84 and 179.45 (NHCO), 174.83 (COO), 76.42 (OCH_2), 55.28 (NHCH), 42.44 ($NHCH_2$), 33.98 and 33.12 ($\mathit{C}H_2CO$), 29.52 ($\mathit{C}H(CH_3)_2$), 26.40 ($\mathit{C}H_2CH_2CO$) and 19.32 (CH_3). In addition, no trace of transpeptidation was detected, i.e. no γ-isobutyl glutamate units were apparent. The degree of racemization during polymer synthesis was determined by

---

* Corresponding author. Fax: +34-934017150.
E-mail address: puiggali@eq.upc.es (J. Puiggalí).

PII: S0032-3861(99)00754-5



Abbreviations:

Z: Benzyloxycarbonyl
DCHA: Diciclohexylamine
PcpOH: Pentachlorophenol
DCCI: Diciclohexylcarbodiimide
iBuOH: Isobutanol
HAmbOH: 4-Aminobutyric acid
AcOH: Acetic acid
Et_3N: Triethylamine
DMSO: Dimethyl sulfoxide

Scheme 1.

measuring the optical rotation of a hydrolyzed sample. We found less than 2% of D-amino acid after correction of the blank value and thus racemization can be considered negligible. A density of 1.15 g/cm^3, measured at 25°C in an aqueous solution of KBr, and a melting temperature of 228°C also characterize the sample.

Crystallization experiments were carried out from dilute polyol solutions (0.1% w/v) at temperatures between 40 and 150°C. For electron microscopy, the crystals were deposited on carbon-coated grids and then shadowed with Pt-carbon at an angle of 15°. Decoration experiments were carried out by using polyethylene and following the Wittmann and Lotz technique [10]. A Philips EM-301 electron microscope operating at either 80 or 100 kV for bright field and electron diffraction modes, respectively, was used. Oriented films for X-ray diffraction were obtained either from stroking a concentrated formic acid solution over a mica surface or stretching a melt pressed film. X-ray patterns were recorded under vacuum at room temperature in a modified Statton camera (W.R. Warhus, Wilmington, DE) with Ni-filtered Cu K_α(radiation. Patterns were internally calibrated with gold or calcite for electron or X-ray diffraction, respectively. A Perkin–Elmer Model 783 spectrophotometer equipped with a gold polarizer was used to determine the infrared dichroism of oriented films. Infrared spectra showed characteristic amide and ester absorption bands: 3274 (amide A), 3058 (amide B), 1725 (CO, ester), 1627 (amide I), 1534 (amide II) and 695 cm^{-1} (amide V).

3. Results and discussion

Different crystal morphologies were attained depending on the crystallization conditions (Fig. 1). In general, needle-like crystals were obtained from diol solutions as hexanediol (Fig. 1a) or 2-methyl-2,5-pentanediol in the 40–120°C

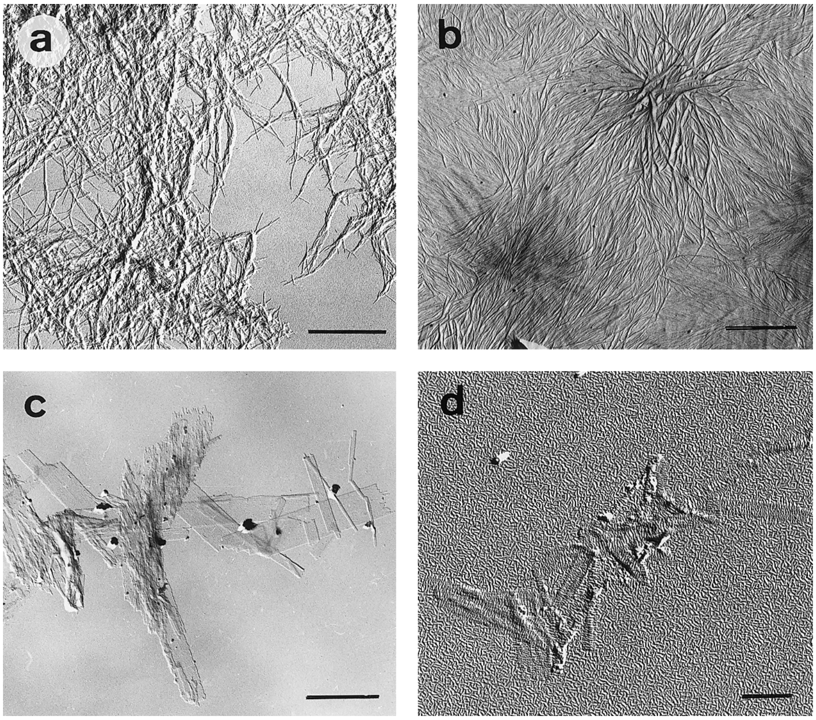


Fig. 1. Transmission electron micrographs of: (a) ribbonlike crystals obtained from hexanediol at 40°C; (b) film constituted by spherulitic aggregates prepared from a glycerine solution at 100°C; (c) lathlike single crystals obtained from glycerine at 150°C; (d) polyethylene decoration of the last crystals. Scale bars 1 μm.

temperature interval. Thin films were obtained in crystallizations from grlycerine at low temperatures (Fig. 1b), whereas well-developed crystals could be attained at temperatures near 150°C (Fig. 1c). These single crystals have a highly preferred growth direction as manifested by their aspect ratio (length/width > 10) and appear frequently to be broken, probably as a consequence of the separation centrifugation process. Note that the front edges are consequently serrated, whereas the lateral growth faces are very regular. In some cases, the front faces appear steeped (see arrow in Fig. 1c) in agreement with an orthorhombic morphology. As can also be seen in Fig. 1c the width dimension of the crystals is variable (0.15–0.60 μm). However, a rather homogeneous thickness (45–50 Å) can be estimated from the shadows of the crystals in the micrographs.

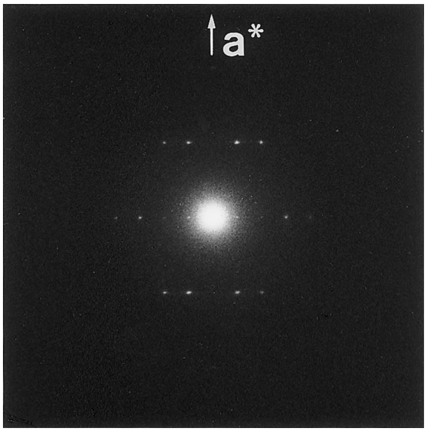


Fig. 2. Electron diffraction pattern of single crystals obtained from glycerine. a^* is oriented along the direction of maximum crystal elongation.

The electron diffraction patterns of isolated crystals

Table 1
Measured and calculated diffraction spacings (Å) for different samples of the copolymer

Index[a]	Calculated	Single crystal[b,c]	Oriented film[b,d]
010	15.0	15.0 m	15.0 vs E
020	7.5	7.5 w	7.5 vw E
030	5.00	5.00 s	5.00 w E
110	4.64	4.63 vs	4.62 vs E
120	4.09	4.09 s	4.09 m E
040	3.75	3.75 m	3.75 w E
200	2.44	2.44 vw	
001	10.5		10.5 s m
011	8.60		8.60 s off M
111	4.24		4.24 s off M
121	3.81		3.80 m off M
002	5.25		5.22 s M
012	4.96		4.92 s off M
022	4.30		4.40 m off M
003	3.50		3.52 w M
013	3.41		3.38 w off M

[a] On the basis of a orthorhombic cell of parameters: $a = 4.88$, $b = 15.0$ and $c = 10.5$ Å.

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

[c] Electron diffraction data.

[d] X-ray diffraction data.

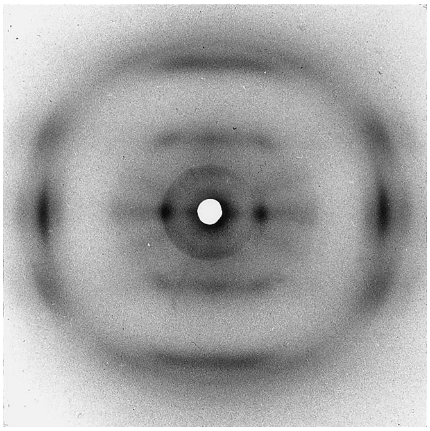


Fig. 3. X-ray diffraction pattern of an oriented sample obtained by stretching a polymer film at a temperature near fusion.

exhibit a *mm* symmetry and confirm their single-crystal character (Fig. 2). These *hk*0 patterns can be indexed as a primitive rectangular cell of parameters $a = 4.88$ and $b = 14.0$ Å (Table 1). The meridional spot at 2.44 Å (200 reflection) is oriented along the maximum crystal elongation and indicates, together with the results that will be discussed below, that intermolecular hydrogen bonds are established along the preferred growing direction, a fact that is usual in polyamides with a sheet structure. Furthermore, the diffraction patterns show that the molecular chains are perpendicular to the basal crystal faces and are folded as a consequence of their high molecular weight and the reduced lamellar thickness. Polyethylene decoration (Fig. 1d) allows us to ascertain the folding habit in the crystal surface. Thus, the regular striations perpendicular to the long faces of the crystals can be interpreted as an indication that the molecular chains are folded parallel to the long axis of the crystals and consequently along the hydrogen bonding direction.

Similar X-ray diffraction spacings were measured, either from powder or oriented samples coming from different preparation conditions (polymerization medium, crystallizations from polyol solutions, stroking of concentrated formic acid solutions or stretching of film samples near their melting temperature). Thus, no evidence of polymorphism could be detected. Fig. 3 shows the best oriented X-ray diffraction pattern of the copolymer, which agrees with an orthorhombic unit cell (Table 1) having the same *a* and *b* parameters as deduced from electron diffraction and a $c = 10.5$ Å. Note the equatorial orientation for the reflections observed in the electron diffraction patterns and the meridional orientation for the 00*l* reflections. A density of 1.17 g/cm^3, close to the experimental value of 1.15 g/cm^3, is calculated with the deduced cell parameters and a unit cell containing two molecules. Only *h*00 (with *h* odd) systematic absences could be inferred from electron and X-ray diffraction data. Consequently, expected space groups are reduced to a monoclinic $P2_111$ and an orthorhombic $P2_122$ taking also into account that an inversion center or a mirror plane symmetry are not possible due to the chiral L constitution of the glutamic unit. The two molecules of the unit cell are then related by a screw binary axis parallel to the crystal *a*-axis direction.

The values of the *a* and *b* crystallographic parameters indicate a molecular conformation where the isobutyl groups point along a single direction (*b*), i.e. a 1_1 or a 2_1 helical symmetry. It is worth noting that the 5_2 helical conformation postulated for substituted γ-amino acid derivatives [7,8] (equivalent to a 5_4 helix for the copolymer)

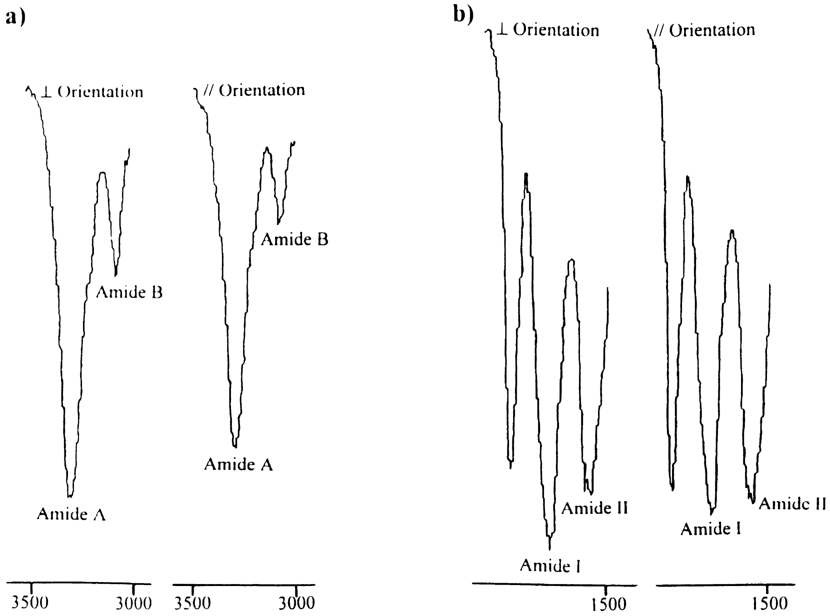


Fig. 4. Infrared spectra obtained with polarized light of an oriented film. Parallel and perpendicular orientations of the electric vector to the direction of stretching are indicated. Only 3500–3000 (a) and 1750–1500 cm^{-1} (b) regions of the spectra are shown.

has to be now discarded. The reduced diffraction data and the elevated number of torsional angles that define the unit repeat preclude a detailed conformational analysis. However, a 1_1 molecular symmetry can be deduced since a 2_1 helix has also to be rejected due to both the non $00l$ systematic absences and the short value of the a parameter that precludes the packing between helices with a great diameter. In addition, the infrared dichroism presented in Fig. 4 shows that hydrogen bonds are approximately perpendicular to the stretching direction and consequently a sheet structure with intermolecular hydrogen bonds (along the *a*-direction) may be postulated. The experimental value of the repeat unit length (10.5 Å) is much shorter than that found for nylon 4 [11] (12.25 Å) and shows the main effect of the isobutyl substituent. Thus, the molecular conformation has to be deviated from the extended one in order to obtain a compact structure and favorable Van der Waals interactions between neighboring layers. A similar observation has also recently been reported for a copolymer constituted by a quiral amino acid (L-alanine) and a non-substituted ω-amino acid (11-amino undecanoic acid) [12]. The value of 4.88 Å for the a parameter seems to indicate that hydrogen bonds are established between parallel molecular chains, a fact that may be feasible due to the non extended molecular conformation. However, we think that the antiparallel arrangement characteristic of the sheet structure of nylons [13] and polypeptides [14] explains better the folding habit observed from the polyethylene decoration of single crystals. In this sense, the halving of the *a*-axis dimension may be explained assuming a statistical packing in which consecutive antiparallel-chain sheets are stacked with a random displacement of $\pm\frac{1}{2}\times 4.88$ Å in the *a*-direction. This packing is equivalent to one in which each chain site is occupied by one half of an "up-chain" and one half of a "down-chain". The statistical arrangement would be likely when the intersheet interactions were similar for the two displacements and has already been reported in the literature for some polymers constituted by L-alanine [12,15]. Only the orthorhombic $P2_122$ space group is in agreement with a statistical distribution of up- and down-chains and the diffraction data. Note that this primitive cell defines the direction in which isobutyl groups point up. That is to say, the same direction for the antiparallel chains of a sheet, since thay are related by a binary axis parallel to the *b*-axis, and an opposite one for the chains of consecutive sheets.

In summary, the sheet structure with intermolecular hydrogen bonds characteristic of nylon 4 is maintained when isobutiloxycarbonyl groups are attached to the γ carbon atoms of alternating units. However, structural differences related to the molecular conformation and packing can be found. Thus, conformation deviates from the extended one and packing changes from a monoclinic unit cell to an orthorhombic one in order to improve Van der Waals interactions.

Acknowledgements

This research has been supported by CICYT (MAT97-1013).

References

[1] Fernández-Santín JM, Aymamí J, Rodríguez-Galán A, Muñoz-Guerra S, Subirana JA. Nature (London) 1984;311:53.
[2] Muñoz-Guerra S, Fernández-Santín JM, Alegre C, Subirana JA. Macromolecules 1989;22:1540.
[3] Bella J, Alemán C, Fernández-Santín JM, Alegre C, Subirana JA. Macromolecules 1992;25:5225.
[4] López-Carrasquero F, García-Alvarez M, Navas JJ, Alemán C, Muñoz-Guerra S. Macromolecules 1996;29:8449.
[5] Apella DH, Christianson LA, Karle IL, Powell DR, Gellman SH. J Am Chem Soc 1996;118:13071.
[6] Seebach D, Overhand M, Kühle FNM, Mastinioni B, Obere L, Hommel U, Widmer H. Helv Chem Acta 1996;79:913.
[7] Hintermann T, Gademann K, Berhard J, Seebach D. Helv Chem Acta 1998;81:983.
[8] Puiggalí J, Muñoz-Guerra S, Rodríguez-Galán A, Alegre C, Subirana JA. Makromol Chem Macromol Symp 1988;20/21:167.
[9] Nefkens GHL, Nirvard R. Recl Trav Chim Pay B 1964;83:199.
[10] Wittmann JC, Lotz B. J Polym Sci Polym Lett Ed 1985;23:200.
[11] Bellinger MA, Waddon AJ, Atkins EDT, Macknight WJ. Macromolecules 1944;27:2130.
[12] Paredes N, Rodríguez-Galán A, Puiggalí J. Polymer 1996;37:4175.
[13] Xenopoulos A, Clark ES. In: Kohan MI, editor. Nylon plastics handbook, Munich, Vienna: Hanser, 1995 chap. 5.
[14] Fraser RDB, MacRae TP. Conformation in fibrous proteins, New York: Academic Press, 1973.
[15] Arnott S, Dover SD. J Mol Biol 1967;30:201.