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Extended-Chain and Threefold Helical Forms of Poly(glycyl-β-alanine)

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ABSTRACT: An X-ray and electron diffraction study on the crystal structure of the polyamide poly(glycyl-β-alanine) is reported. Two well-defined forms were characterized by these techniques. Form I is a structure made of hydrogen bonded sheets where the chains are in the fully extended conformation. Its unit cell is orthorhombic with parameters a = 9.51 Å, b(chain axis) = 16.95 Å, c = 15.20 Å. Form II is a hexagonal lattice of 7 × $^3/_2$ helices with parameters a = 4.79 Å, c = 22.2 Å. In this case, chains are intermolecularly linked by hydrogen bonds, giving a structure similar to that described for polyglycine II. This type of helix had not yet been described for a polymer not a genuine polypeptide. While form II is found in samples prepared under a wide range of conditions, form I has only been detected in films obtained by epitaxial crystallization of the polymer on hydroquinone.

Introduction

Aliphatic polyamides represent a wide spectrum of polymers, which embraces synthetic polyamides as well as polypeptides and proteins, which can be regarded as nylon 2 derivatives. The crystalline structure of all these polymers has been extensively studied, and a considerable body of information now exists on this topic.[1,2] Due to the presence of amide groups in the backbone extensive hydrogen bonding occurs; these interactions play a decisive role in determining the crystal structure of these polymers. It is in fact the number of methylene units separating the amide linkages that accounts for the major structural differences observed among polyamides.

Both nylons and polypeptides have in common a structure made of hydrogen bonded sheets: their regular stacking generates the three-dimensional crystal. In the case of synthetic polyamides sheets consist of fully extended planar zigzag chains whereas β-sheet structures of polypeptides are characterized by a more or less pleated conformation. On the other hand, crystalline structures made of chains in helical conformation have been traditionally considered as exclusive of polypeptides and proteins. Among these structures the well known α-helix and the threefold helical structure of polyglycine II[3] stand out as the most prominent. Until recently the capability of polyamide chains to arrange themselves into helices appeared to be specific for backbones that contained only two main-chain carbon atoms per monomer unit. Recently we showed that it is possible to obtain a conformation similar to the helix in some nylon 3 derivatives.[4]

In the present work we describe a structural study of the copolyamide poly(glycyl-β-alanine). This polymer may be regarded as a modified nylon 3 in which one methylene unit has been removed from every other residue. We observe that this apparently slight change in the chemical constitution of the chain has a profound effect on the structural behavior of the polymer. Two well-defined crystalline forms are obtained in samples crystallized by epitaxial procedures. Form I has the conventional hydrogen bonded sheet structure characteristic of synthetic polyamides, where chains are completely extended. Form II is a threefold helical structure quite similar to that reported for polyglycine II. This crystalline dimorphism is envisaged as the logical consequence of the chemical constitution of this copolyamide, intermediate between a nylon and a polypeptide; it represents a departure from the usual crystalline behavior of this kind of polymer.

$$-(NHCH_2CONHCH_2CH_2CO)_n-$$

Experimental Section

Poly(glycyl-β-alanine) used in this work was prepared by polycondensation of the glycyl-β-alanine pentachlorophenyl ester bromhydrate. The reaction was carried out in dimethyl sulfoxide at room temperature for a period of 5 days. Trimethylamine was used as proton acceptor. An intrinsic viscosity of 0.19 $dL \cdot g^{-1}$ was measured for the purified polymer in dichloroacetic acid at 25 °C. A number-average molecular weight of 6000 is estimated for this sample when end amide groups are measured with either the Van Slyke[5] or the 2,4-dinitrofluorobenzene method.[6] Additional experiments of polycondensation were performed by using other solvents and modifying either the temperature or time of reaction, but polymers of lower molecular weight were obtained. These polymers were used only for X-ray powder analysis in order to compare samples prepared under different conditions. Samples of the polymer to be used for X-ray diffraction were washed with volatile alcohols or water and then dried under vacuum. X-ray powder diagrams were recorded under vacuum at room temperature in a modified Statton camera (W. R. Warhus, Wilmington, DE) with graphite-filtered copper radiation.

Samples for electron microscopy were prepared by epitaxial crystallization from a concentrated solution of the polymer following the technique developed by Wittmann and Lotz for polyethylene, polyesters, and polyamides.[7-9] Best results were achieved when hydroquinone was used as solvent substrate. The procedure was basically as follows: a film of poly(glycyl-β-alanine) of a few hundred angstroms thick was prepared by evaporating a dilute solution of the polymer in formic acid on a glass slide. Some small crystals of hydroquinone were deposited onto the film, and the preparation was then heated in order to melt the hydroquinone and dissolve the polymer. Crystallization of the mixture was done by cooling it slowly to room temperature. The hydroquinone crystallizes first, giving crystals for the epitaxial growth of the polymer, which occurs next. Hydroquinone was then throughly removed by washing with ethanol. Selection of areas appropriate for electron microscopy was made under the polarizing optical microscope. Such areas were covered with a thin carbon film, floated off on water, and picked up on copper grids. An Hitachi HU11CS electron microscope has been used for the electron diffraction work. Tilting of the specimen was achieved by using a set of specimen holders with fixed tilts.

Density measurements were carried out by flotation in mixtures of water and 25% potassium iodide solution.

Results

We have found that poly(glycyl-β-alanine) can adopt two well-defined crystalline structures, named form I and form II by analogy with the two well-known modifications of polyglycine to which they are closely related.

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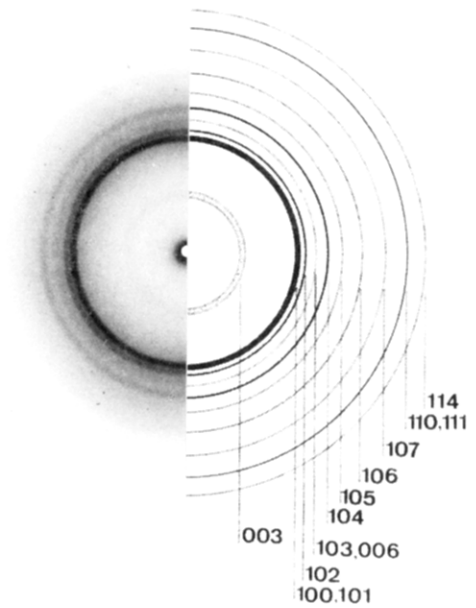
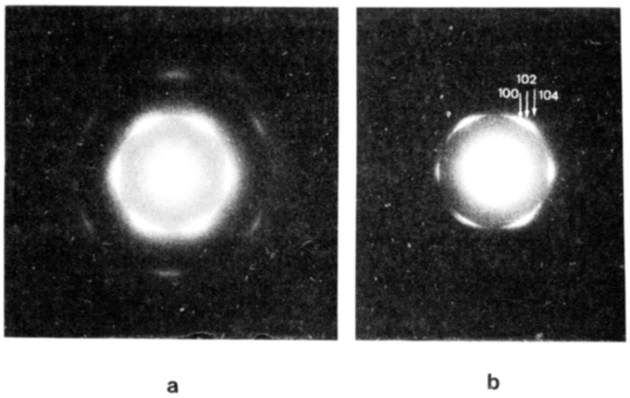


Figure 1. X-ray powder diagram of form II. All rings seen in the original picture are included in the scheme. The strongest ring is centered around 4.12 Å, and it is composed of two overlapping reflections indexed as (100) and (101) (see text).

Form II. The usual laboratory methods used for stretching polymers fail to orient poly(glycyl-β-alanine), and only powder X-ray diagrams are available. A ring pattern as shown in Figure 1 is recorded from a sample prepared by adding 10 volumes of water to a 1% solution of the polymer in formic acid. This type of diagram is the one obtained whatever treatment is applied to the sample. In contrast to polyglycine, neither the conditions used for polymerization nor the nature of the solvent from which the sample is recovered affects the crystalline structure adopted by the polymer. A hexagonal lattice with $a = 4.79$ Å, and $c = 22.2$ Å accounts for all the observed reflections. The weak and rather diffuse ring with a spacing of 7.4 Å is thus interpreted as corresponding to the third order of the axial repeat of the structure. The prominent ring with a spacing centered around 4.12 Å contains in fact the two overlapping reflections 100 and 101 with respective spacing at 4.15 and 4.09 Å as it becomes clear from diagrams recorded with much longer camera length. The 102 reflection is also fairly outlined and intense. The three next following rings are less defined, and according to the proposed cell have to be indexed as 103, 104, and 105. The rest of rings except that labeled as 110, 111 are diffuse and poorly seen, even in the original picture. They have been named with indexes giving the best fitting figures for the observed spacings, but some contribution from other overlapping reflections cannot be however completely excluded.

A film of poly(glycyl-β-alanine) prepared by epitaxial crystallization on hydroquinone provides single-crystal electron diffraction data that are consistent with and help to ascertain those obtained by X-rays. The electron diffraction diagram shown in Figure 2a indicates an hexagonal packing with a basic spacing of 4.15 Å. It corresponds to the projection down the c axis of the lattice defined above. Chains in this sample are therefore aligned parallel to the electron beam; i.e., they have crystallized with their axis normal to the surface of the substrate, which is, incidentally, a highly unusual orientation of polymers in epitaxial crystallization. Diagrams containing *hkl* reflections, i.e., giving information on the c axis periodicity, can be recorded if the specimen is tilted in the microscope. The diagram shown in Figure 2b was taken with a specimen tilted 30° around the a^* axis. Reflections indexed on the basis of the X-ray powder pattern as 102, 103, and 104 are now observed, in addition to the 100 ones, which are still prominent. Note that this diagram provides strong support for the indexing of these reflections since their location is as expected from a row of 101 reflections upon tilting of the specimen. All data collected from both X-ray and electron diffraction are listed in Table I as well as the corresponding calculated lattice spacings for this crystalline form II. A close similarity is found between these data and those reported for the hexagonal modification of polyglycine (polyglycine II)[3] with the exception of the c axis repeat distance, as would be expected from the different chemical sequence. This suggests that a similar molecular arrangement should be followed in both cases. According to point notation a $7 \times {}^3/_2$ helix is here proposed for the conformation of the chain in form II. The translation height for the glycyl-β-alanyl residue would be 7.4 Å, a spacing that is observed as a faint diffuse reflection in powder X-ray diagrams of this form. If it is assumed that the glycyl residue is arranged in this helix nearly as it is in polyglycine II with a translation height of 3.1 Å, a height of 4.3 Å is left for accomodating the β-alanyl residue. This



a b

Figure 2. Electron diffraction diagrams from a film of form II grown on hydroquinone: (a) diagram recorded with the film normal to the electron beam; (b) diagram recorded with the film tilted 30° around the a^* axis. Note the position of the row of 101 reflections at spacings consistent with the proposed structure. The 103 reflection is also detected in the original picture.

Table I
Observed and Calculated Spacings, *d* (Å), for Form II of Poly(glycyl-β-alanine)[a]

			electron diffraction[c]	
hkl	calcd	powder X-ray[b]	film normal to electron beam	film tilted 30°
003	7.40	7.42 vw		
100	4.15	4.15[d] vs	4.15	4.15
101	4.08	4.09[d] s		
102	3.89	3.91 s		3.91
103, 006	3.61, 3.70	3.64 w		3.65
104	3.30	3.30 s		3.33
105	3.03	3.05 w		
106	2.76	2.78 w		
107	2.51	2.55 vw		
110, 111	2.39, 2.38	2.39 m	2.39	
114	2.20	2.20 vw		

[a] Reflections are indexed on the basis of an hexagonal lattice with $a = b = 4.79$ Å and $c = 22.2$ Å. [b] Abbreviations used: vw, very weak; w, weak; m, medium; s, strong; vs, very strong. [c] Only spacings corresponding to first-order reflections of electron diffraction diagrams are included. [d] These two rings appear resolved in low-angle X-ray diagrams.

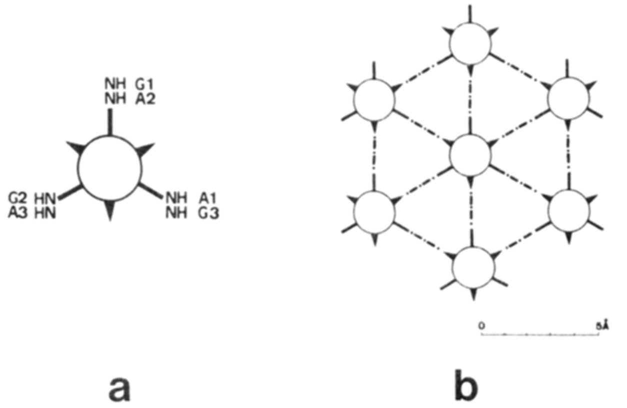


Figure 3. (a) Scheme of the projection of the helix of poly(glycyl-β-alanine) in form II down the chain axis. Only the location of groups responsible for hydrogen bonds are shown. The helix contains three residues glycyl-β-alanyl in two turns. G is glycyl, A is β-alanyl, and numerals refer to the number of the residues along the turn. Filled triangles stand for carbonyl groups. (b) Scheme of the projection of the lattice along the c axis showing seven chains. A polyglycine II-like structure with a = 4.79 Å is generated when helices are intermolecularly linked by hydrogen bonds along the 100 directions.

translation height is 0.5 Å shorter than that corresponding to β-alanyl in poly(β-alanine) (nylon 3) where chains are known to be in a fully extended zigzag conformation. NH and CO groups become approximately located around the helix axis, as indicated in the projection drawn in Figure 3a. A hexagonal lattice of a = 4.79 Å results when such helices are linked by hydrogen bonds, as shown in the scheme of Figure 3b. The calculated density for such a structure is 1.44 g·mL^{-1}, in good agreement with the observed value (1.43 g·mL^{-1}). More detailed features of this structure will be considered in the discussion.

Form I. A second crystalline modification of poly(glycyl-β-alanine) has been sometimes detected in samples prepared by epitaxial crystallization upon rapid cooling. Attempts to obtain this form by different methods have systematically failed. Examination with the polarizing optical microscope of a film grown on hydroquinone under such conditions reveals the occurrence of highly birefringent areas, which give an electron diffraction diagram as shown in Figure 4. It corresponds to the normal projection along the c axis of an orthogonal lattice of parameters a = 9.51 Å and b = 16.95 Å. A hydrogen bonded sheet structure of the type commonly found in nylons fits this lattice well. This interpretation implies that the film is doubly oriented so that sheets are lying parallel to its surface. The 16.95-Å spacing arises therefore from the chain axis repeat distance, which should consist of two glycyl-β-alanyl units. In fact an average rise per interatomic bond of 1.21 Å is precisely defined by the 1,14,0 reflections. This figure indicates that chains in this crystalline form are in a nearly fully extended planar conformation. On the other hand the 9.51-Å periodicity is clearly demonstrative of an antiparallel arrangement of the chains within the sheets. Such an arrangement is reasonably predicted for this polymer since it is unique in allowing all hydrogen bonds to be formed perfectly.

Given the double orientation obtained by epitaxial crystallization, information on the intersheet distance can only be gained by tilting the specimen around either the a or the b axis. The diagram obtained from a specimen that has been tilted 30° around the chain axis (b axis) is shown in Figure 5a. The strong reflection on the equator

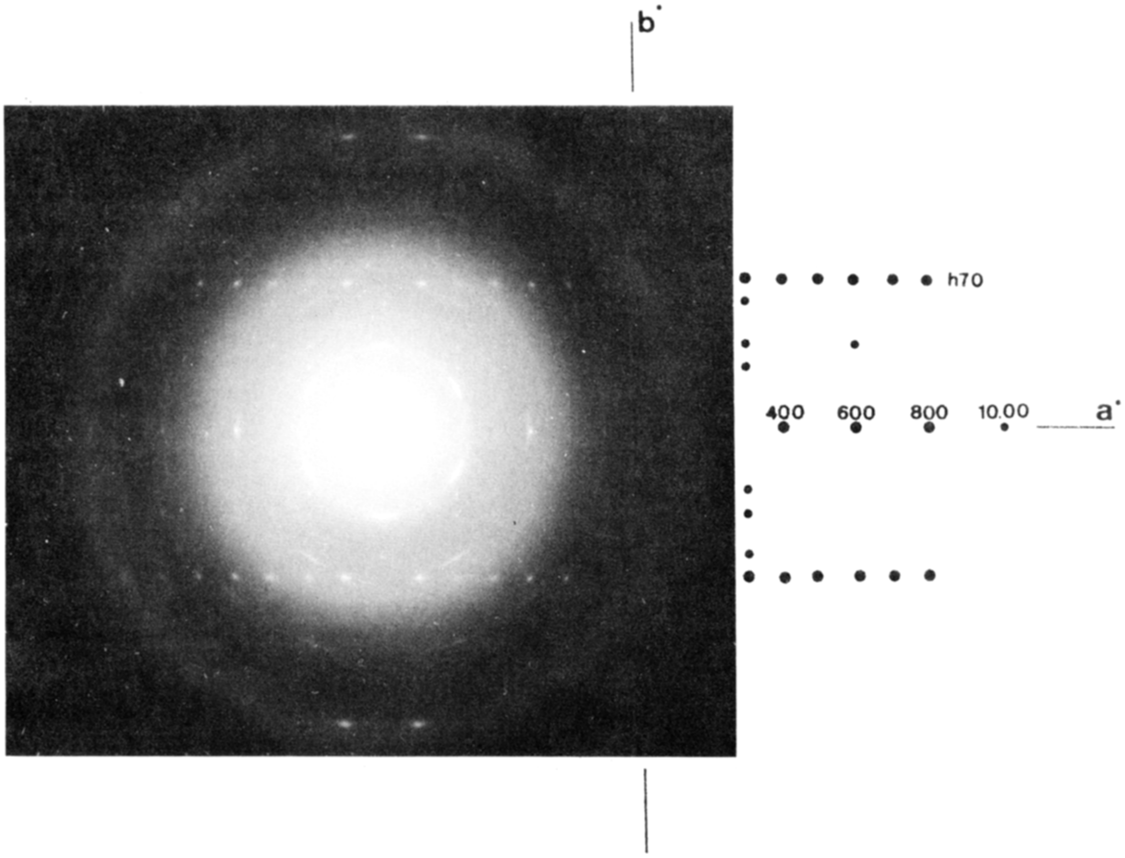


Figure 4. (a) Electron diffraction diagram of a sample of poly(glycyl-β-alanine) containing form I. The sample was prepared by epitaxial crystallization on hydroquinone as described in the text. A significant contribution of form II is still observable in this diagram. (b) Corresponding indexing of the diffraction spots. Reflections arisen from form II have not been included in this scheme. Parts a and b are not superimposed.

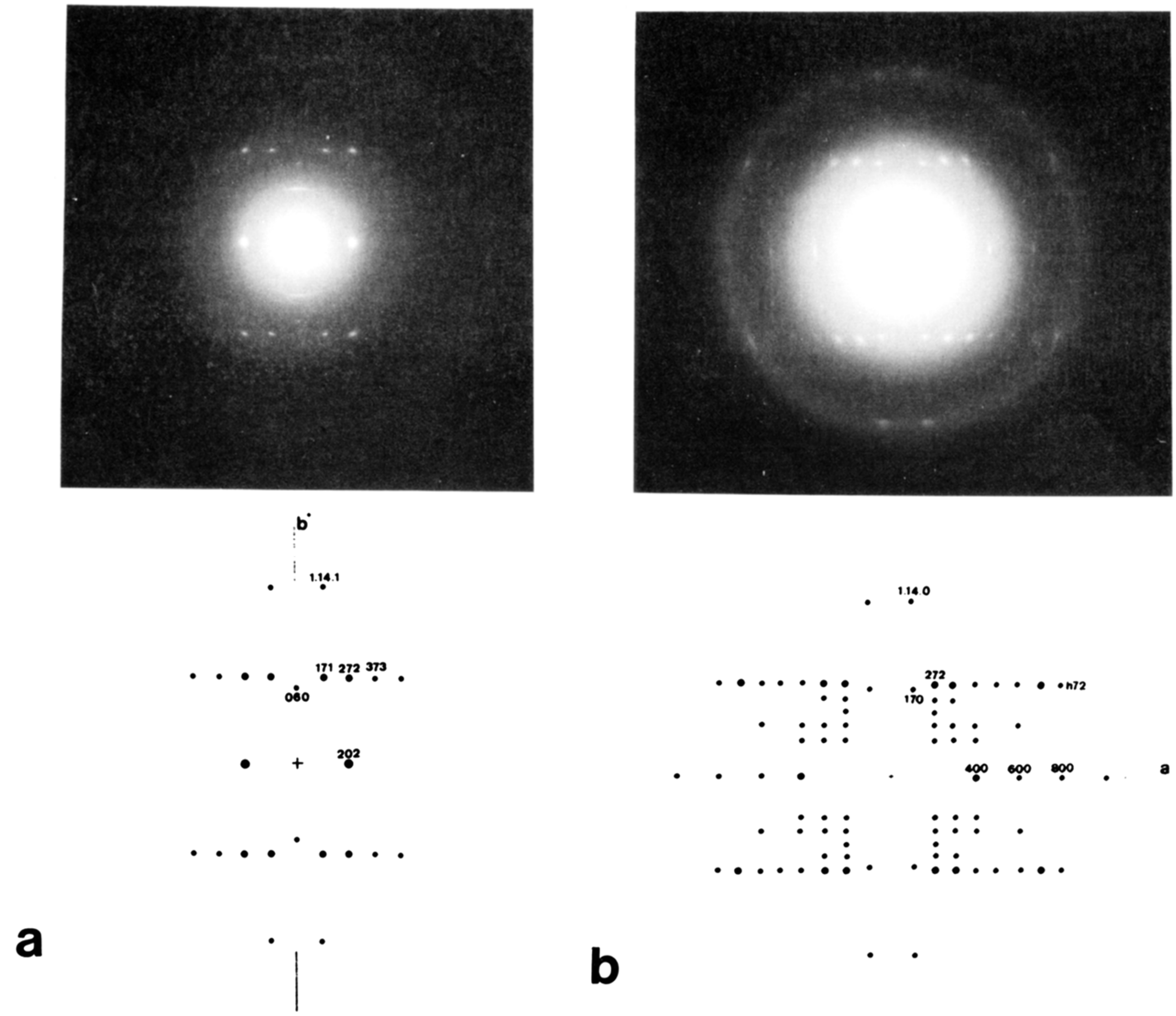


Figure 5. Electron diffraction diagrams of form I recorded for two distinct tilted orientations of the sample with respect to the electron beam: (a) 30°, tilting axis is the *b* axis; (b) 20°, tilting axis is the *a* axis. Reflections arising from *hk*0 planes are still present in diagram b (compare with diagram in Figure 4). Contribution of such types of reflections to spots 472 and 572, causing misalignment of the *h*72 row, is also detected.

with a spacing of 4.05 Å has to be indexed as 202 by analogy with other layered structures of polyamides, which suggests an intersheet distance of 3.80 Å, and a *c* repeat of four times this distance. Tilting the sample 20° around the *a* axis a diagram (Figure 5b) is in turn obtained that contains *h72* reflections consistent with such interpretation. A drawing of the model of the structure proposed for form I of poly(glycyl-β-alanine) is presented in Figure 6. The orthorhombic unit cell contains eight chains and its parameters are *a*(hydrogen-bond direction) = 9.51 Å, *b*(chain axis) = 16.95 Å, and *c* = 15.20 Å. A triclinic unit cell containing only two chains and with parameters a = 9.51 Å, b = 16.95 Å, c = 6.17 Å, α = 43.3°, β = 58.2°, γ = 90° could be also considered, but it does not reflect the true symmetry of the lattice. It should be noted that no sign of lattice symmetry other than orthorhombic has been detected along our observations in the electron microscope for different up and down positions of the samples. Arguments in support of the proposed structure will be discussed in detail in the next section.

Discussion

Form II is the crystalline modification usually observed and by far the most stable. On the contrary, form I is very elusive and was only found as the minor constituent in samples prepared by epitaxial crystallization.

The crystal structure proposed for form II follows basically the model described by Crick and Rich[3] for the hexagonal modification of polyglycine II. The projection of this structure down the *c* axis would be viewed as drawn in Figure 3b. Chains are packed in an hexagonal lattice so that each one is hydrogen bonded to its six nearest neighbors with an interchain distance of 4.79 Å fixed by such hydrogen bonds which are nearly perpendicular to the chain axis. The lattice is therefore linked by an infinite network of hydrogen bonds running from one cell to the next one along three directions at an angle of 120° one to each other. A threefold screw helix appears to be a plausible conformation for the chain of poly(glycyl-β-alanine) packed in such hexagonal structure. An axial repeat of 22.2 Å with a residue translation height of 7.4 Å is consistent with the available diffraction data and defines a helix containing three residues per two turns. Since no asymmetric carbon exists in the backbone, either left-handed or right-handed helices are equally probable. The helix sense must be however the same for every chain within a given crystallite in order to enable the formation of all hydrogen bonds. The possibility of inverting an individual

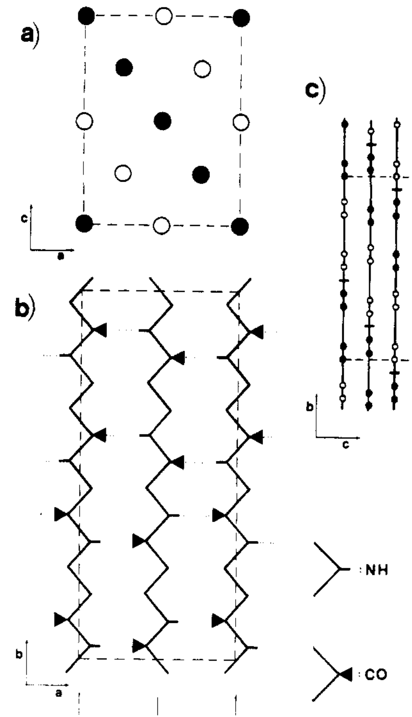


Figure 6. Model for the structure of form I of poly(glycyl-β-alanine). The unit cell is orthorhombic with a = 9.51 Å, b = 16.95 Å (chain axis), and c = 15.20 Å and contains eight chains. (a) Projection along the b axis. The black and white circles represent antiparallel chains. (b) A view normal to the ab plane of the unit cell showing the arrangement of hydrogen bonds between chains within a sheet. Only the first sheet has been drawn. (c) A projection of the structure along the a axis. Successive sheets are displaced along the b axis by a distance $b/4$. In this case the drawing scale has been reduced to half, and black and white circles represent carbonyl groups in opposite directions along the a axis.

chain in the lattice may be further considered. When a chain is turned upside down, groups responsible for the formation of hydrogen bonds once again occupy nearly the same heights, provided that the helix sense is maintained. All hydrogen bonds can be remade, and the new structure may have characteristics similar to those exhibited by the original lattice. The unit cell is now doubled and contains two chains. As no diffraction evidence is found, calling for larger lattice dimensions, a unit cell based on the simplest arrangement consisting of parallel helices has been assumed here.

Poly(glycyl-β-alanine) takes up this arrangement as it allows strong interactions between helices. It is in fact the hexagonal array of hydrogen bonds that imposes the existence of a threefold screw axis in the helix. This structure is generally referred to as polyglycine II, as it was first described for this polypeptide. It was also reported later for poly(L-proline)[10] and poly(hydroxy-L-proline)[11] as well as for certain sequential polypeptides made of glycine, proline, and alanine.[2,12] This is, on the other hand, the type of helix adopted by the polypeptidic chains in the three-strand rope of collagen.[13,14] To our knowledge, poly(glycyl-β-alanine) is the first polymer that is not entirely a polypeptide with this particular conformation.

A structure made of hydrogen bonded sheets is proposed for the other crystalline modification of poly(glycyl-β-alanine), namely form I. Chains within the sheets are arranged in antiparallel fashion to conform with the a dimension of 9.5 Å. This feature is common to all polyamides derived from ω-amino acids. Since a mean rise of 1.21 Å per interatomic bond along the backbone is measured, chains must have the fully extended conformation common to poly(β-alanine) and other higher polyamides. This figure is reduced to 1.16 Å in the β-sheet structure of polypeptides, where chains are in a pleated conformation. Polyglycine is unique in having a "rippled" sheet structure, where chains are less contracted than is usual in polypeptides but without achieving the completely extended conformation.[15] Hence the β-alanyl residue appears to impose the planar zigzag conformation to the entire chain of poly(glycyl-β-alanine).

The next point to be considered is the stacking of the sheets. An intersheet distance of 3.80 Å has been estimated from electron diffraction diagrams recorded from tilted samples, a value that is in the range usually found for polyamides, whereas a figure of 3.45 Å is observed in the sheet structure of polyglycine. Further, the diffraction data suggest that successive sheets are shifted by exactly half of the interchain distance along the a axis. This mode of stacking has been previously reported for the layered structures of other closely related polymers, such as the β-form of the poly(L-alanine)[16] and the two crystalline modifications of poly(β-alanine).[17,18] Taking into account such displacement, two alternative arrangements of layers may arise according to the relative upside-down orientation adopted by them. Although no experimental evidence exists to favor a definitive choice, a lattice similar to that described for the form I of poly(β-alanine)[17] is here preferred; in such a model the shift along the a axis happens in the same sense for every sheet. Finally we have to consider the arrangement of the layers along the chains axis (b axis). In this regard, reflections indexed as 1,14,1 and 171 in the diagram of Figure 5a are highly significant for they impose a repeat along the c axis four times the value of the intersheet distance. A fixed displacement of $b/4$ between successive layers generates a structure with such a repeat value and that is of the type described for the α-form of nylon 66.[19] As seen in Figure 6c, interactions between polar groups within neighboring sheets are minimized. Moreover a favored alignment of amide groups along the 170 direction is found in this structure. Such a location for these groups would be responsible for the high intensities exhibited by the $h7l$ rows of reflections present in every diagram of form I.

Conclusion

Poly(glycyl-β-alanine) may be envisaged as a polymer derived from nylon 3 where one peptide group for every β-alanyl residue has been inserted in the chain. Alternatively, it can be looked at as a polypeptide containing one additional methylene for every other peptide unit. These two alternative ways of considering the polymer, as nylon or polypeptide, are reflected in its crystalline structural behavior as a well-defined dimorphism. Form I adopts the common sheet structure of nylons, whereas form II is a threefold screw helix packed in an hexagonal lattice that has strong similarities with polyglycine II.

The results reported in this paper reveal that we are dealing with a new class of polyamides capable of taking up crystal structures reserved so far for polypeptides and proteins. It is also the case for poly(α-isobutyl L-aspartate)[4] where the presence of the pending carboxylate group in the chain of nylon 3 forces it to arrange in a helix of similar characteristics to the α-helix of polypeptides. Helical structures are anyway a departure from those commonly exhibited by synthetic polyamides, and presumably they will exhibit properties closer to those of α-polypeptides and proteins.

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Registry No. Poly(glycyl-β-alanine) (SRU), 100047-32-3; glycyl-β-alanine pentachlorophenyl ester (homopolymer), 100047-31-2.

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Onset of Chain Folding in Low Molecular Weight Poly(ethylene oxide) Fractions Crystallized from the Melt

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ABSTRACT: The nucleation theory approach to chain folding is herein extended to the case of short chains and employed to predict the undercooling at which a chain of specified length will exhibit f folds per molecule, where $f = 1, 2, 3, \ldots$. The extensive data of Kovacs and co-workers on low molecular weight poly(ethylene oxide) fractions, which clearly exhibit once-, twice-, three-times-, and four-times-folded ($f = 1$ through $f = 4$) crystals, are successfully interpreted in terms of the treatment. It would thus appear for this system that the frequently posed question of which factors control the onset of chain folding with increasing molecular weight and undercooling has been answered.

It is known that many high polymers consisting of flexible chains with sufficiently regular chemical chain units crystallize from the melt and dilute solution in the form of lamellar structures where each lamella (or single crystal) exhibits chain folding.[1-4] In a number of respects, our understanding of this phenomenon is in a relatively satisfactory state. For example, kinetic nucleation theory[4,5] predicts the initial lamellar thickness $l_g{}^*$ as a function of undercooling ΔT for high molecular weight polymers, including fractions. This holds for single crystals formed from dilute solution,[4] and recent synchrotron experiments that eliminate the effects of isothermal thickening have shown that it applies equally well to polyethylene when crystallized from the melt.[6] Progress has also been made on the basis of the same theoretical framework in understanding the kinetic processes by which chain folds are incorporated into the crystals as they are being formed, including a description of the overall kinetics of growth[4,7,8] as a function of ΔT. This state of affairs was attained in part because of the recognition of three regimes of crystallization (commonly denoted I, II, and III)[4,7-9] and also because of the introduction of the concept of reptation.[10,11] The latter allows one to understand not only the molecular weight dependence of the growth rate[11] but also how portions of the long molecules in a relatively high molecular weight fraction can be reeled from the entangled melt onto the substrate, allowing the formation of chain-folded clusters.[7,8,10,11] Further, one knows from the "Gambler's Ruin"[12,13] and related calculations[14] that there are definite topological constraints on nonadjacent reentry in high molecular weight polymers that require (for vertical stems) close to two-thirds "tight" folds, i.e., a lamellar surface with two-thirds adjacent or very near adjacent reentry type folds that have no amorphous character in the traverse between the stems. However, there does not appear up to now to be a treatment of the onset of chain folding in low molecular weight fractions. It is the purpose of this paper to outline such a treatment and apply it to the extensive and carefully executed data of Kovacs and co-workers on poly(ethylene oxide) (PEO) fractions crystallized as single crystals from the melt.[15-20] It will emerge that the data yield to a straightforward treatment that provides a clear insight into the physics of the onset of chain folding at low molecular weights. Specifically, we shall herein successfully predict the number of folds per molecule f that will appear in PEO lamellae crystallized from the melt at a specified undercooling ΔT^* for samples consisting of short molecules of length l_0.

Figure 1 (upper diagram) shows schematically how in the experiments of Kovacs and co-workers the growth rate G of a PEO fraction of fixed length l_0 varies with the undercooling ΔT. We choose to measure the undercooling for a given fraction consisting of molecules of length l_0 from the extended-chain melting point T_m appropriate to that fraction. Curves of the type shown define experimentally for each l_0 the undercooling $\Delta T^*{}_f$ where, with increasing undercooling, the onset of lamellae with f chain folds per molecule without conspicuous initial ciliation occurs. Once-folding ($f = 1$) obtains at the lowest undercooling $\Delta T^*{}_1$; this is then followed at the larger undercooling $\Delta T^*{}_2$

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