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Dimorphism of polyglycine I: structural models for crystal modifications

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Re-examination of the known data on crystalline forms of polyglycine reveals that the crystal modification 'polyglycine I' has two different three-dimensional structures depending on the molecular weight. Structural models for both low molecular weight (LMW) and high molecular weight (HMW) polyglycine I crystals are described. In the LMW crystal model, the molecules have an unusual extended conformation generated by alternation of two mirror-symmetrical residual conformations along the chain. The molecules are parallel and each chain forms interpeptide hydrogen bonds with four adjacent chains. The structural model for the HMW crystal represents a composition of twinning crystallites. The crystallites themselves consist of antiparallel enantiomorphous chains united by hydrogen bonds to form rippled sheets. Calculations of the diffraction patterns and packing energy show that these polyglycine I structures have a higher level of conformity with the experimental data than previously suggested models. New insight into the structure of the polyglycine associates opens up the possibility of designing improved silk-like and nylon materials.

1. Introduction

Special interest in polyglycine crystal structures is caused by their relevance to the biologically important structures of collagen, silk fibroin and aperiodic glycine-rich proteins (Gomes *et al.*, 1988; Keller *et al.*, 1988; Cretin & Puigdomenech, 1990; Lei & Wu, 1991), as well as widespread artificial nylon materials (Tormo *et al.*, 1992). Polyglycine, composed almost entirely of the main-chain atoms of the polypeptide, is the unique molecule for the evaluation of the conformational, thermodynamic and spectral features of the polypeptide backbone (Krimm & Abe, 1972; Fanconi & Finegold, 1975; Finegold & Kumar, 1980; Gresh & Giessner-Prettre, 1990). Since 1934, when two different X-ray powder patterns of polyglycine were observed (Meyer & Go, 1934), the presence of two crystalline forms (I and II) has been presumed. A three-dimensional structure of polyglycine II was postulated by Crick & Rich (1955) on the basis of one of these powder X-ray diagrams. Over the years, the amount of experimental evidence significantly increased; however, none of it cast any doubt upon the correctness of the postulated structure of polyglycine form II. The structural arrangement of the so-called polyglycine I has been revised several times. Its X-ray powder diagram was first interpreted by Astbury (1949) as arising from a β-structure. The β-structural model was further detailed by Pauling & Corey (1953*a*) who proposed an antiparallel β-pleated sheet structure for polyglycine I. The appearance of single-crystal electron-diffraction data for a low molecular-weight (LMW) polyglycine consisting of about ten

residue molecules (Lotz, 1974) caused a revision of this β-structural model. Examination of the possible sheet structures for conformity with these electron-diffraction data and packing-energy calculations (Collonna-Cesari *et al.*, 1974) have suggested that polyglycine I does not have the antiparallel β-pleated sheet structure, but rather a modification of the antiparallel rippled sheet structure first described by Pauling & Corey (1953*b*). However, in order to explain the X-ray and electron-diffraction data, Lotz (1974) modified the original rippled-sheet structure in such a manner that its interpeptide hydrogen bonds became non-linear. Subsequent experimental reinvestigation of polyglycine crystals, using high molecular weight (HMW) molecules (~90 residues), has resulted in growing of long lath-like crystals. These crystals have an electron-diffraction pattern showing reflections on the two rings (1/4.36 and 1/3.44 Å^{-1}) characteristic of the powder pattern of polyglycine I (Munoz-Guerra *et al.*, 1983). However, the locations of the reflections on these rings were different from those of the LMW polyglycine I crystal (Lotz, 1974). This difference has been explained by longitudinal dislocations of independent crystallites having the same modified rippled structure as was suggested for the LMW crystals (Lotz, 1974). The latest theoretical analysis has shown that, in addition to the sheet structures, the polyglycine molecules can associate in a packing scheme with a spatial network of hydrogen bonds, and that this packing may be related to form I (Kajava, 1985).

In this paper, reinterpretation of the known experimental data is described. It reveals that the LMW and HMW polyglycine crystals known under the same name (that is, 'form I') have two different three-dimensional structures. Structural models for both HMW and LMW polyglycine I crystals are described.

2. Materials and methods

2.1. Derivation of the three-dimensional structures and calculation of packing energy

The unit cells and atomic coordinates for the rippled-sheet models with linear and non-linear hydrogen bonds, as well as the β-pleated sheet model, were taken from previous work (Collonna-Cesari *et al.*, 1974; Lotz, 1974). The unit cell and atomic coordinates for the parallel network model (Kajava, 1985) were refined in this work on the basis of energy minimization and better conformity with the diffraction data. The structure of the antiparallel network model was obtained based on the chain conformation of the parallel network model and on the suggested orthorhombic unit cell. Conformations of turns for the rippled-sheet structure of the HMW crystal were first adjusted manually by varying torsion angles and then refined by 200 steps of conjugate-gradient minimization. Energy minimization and molecular-dynamics simulations were carried out using the *X-PLOR* program (Brünger, 1992). The calculations were carried out using the CHARMM PARAM19 parameter set (Brooks *et al.*, 1991), with a value for the dielectric constant of $\varepsilon = 3.0$ which may be assigned for the interior of the proteins (Rogers, 1990).

2.2. Calculation of the diffraction patterns

Intensities of the theoretical diffraction patterns were calculated as $F^2 P d_{hkl} f_T$, where F is the structural factor, P is the multiplicity factor, f_T is the temperature factor and d_{hkl} is the distance between the reflecting planes. F was computed by a set of mathematical programs *FROG* (Urzhumtsev *et al.*, 1989). f_T was taken as $\exp[-(\alpha h^2/4a^2) - (\beta k^2/4b^2) - (\gamma l^2/4c^2)]$, with α, β and γ equal to 5, 10 and 15, respectively, for the sheet models (by analogy with the calculations of Lotz, 1974) and $\alpha = \beta = \gamma = 10$ for the network models, which are assumed to be less anisotropic.

3. Results and discussion

3.1. Structural model for the LMW polyglycine I

It is known that only about 10% of hydrogen bonds in polypeptide structures have an angle H—N—O greater than 28° (Baker & Hubbard, 1984), and that such a deviation from hydrogen-bond linearity is a consequence of steric tension and constraints in the covalent structure. However, in the Lotz (1974) model for polyglycine I, the only model that adequately explained the observed diffraction data, this angle is equal to 33° for all interpeptide hydrogen bonds. Moreover, our analysis shows that no steric tension in this structure can justify such a strong distortion of the hydrogen bonds. Additonally, analysis of the diffraction data shows that the Lotz rippled model cannot bring all the predicted reflections into accordance with the experimental ones. For example, the intensities of the −401 and 201 reflections predicted by the Lotz model differ by a factor of 40, while the corresponding observed intensities are almost identical. In addition, the intensities of −202 and 002 reflections differ by a factor of 10, but the observed reflections are of nearly the same intensity (Table 1 and Fig. 1). Thus, the inexplicable imperfection of all hydrogen bonds in the Lotz structure and the serious discrepancy of the X-ray data interpretation encouraged me to undertake a revision of the existent polyglycine I model.

All known canonical structures, such as the β-pleated or rippled sheet structures, cannot be assigned to the LMW polyglycine I because of apparent discrepancy with the observed electron-diffraction data. The solution was found in a packing scheme with a spatial network of hydrogen bonds. The geometry of the polypeptide chain is such that alternation of mirror-symmetrical residual conformations taken from the second and fourth quadrants of the Ramachandran plot brings a linear structure to the chain. The aggregates of polyglycine molecules with alternating sequences of the mirror-symmetrical conformations satisfy a general principle where each residue should have an equivalent surrounding in the crystal. In this structure, the glycyl residue does not contain an asymmetric Cα atom and the intra-chain contacts are identical for mirror-symmetrical conformations. On the other hand, these chains can be packed in such a manner that each residue has identical inter-chain contacts. Energy minimization of this spatial arrangement results in a structure having a regular chain conformation with torsion angles $\varphi_1 = 153.0$, $\psi_1 = 158.2$,

Table 1
Observed and calculated spacings and intensities for polyglycine I.

Predicted spacings and intensities that were not observed are in italic.

Observed†		Calculated for parallel network model			Calculated for antiparallel network model			Calculated for antiparallel rippled models with non-linear‡ and linear hydrogen bonding			
d (Å)	*I*	*d* (Å)	Index	*I*	*d* (Å)	Index	*I*	*d* (Å)	Index	*I*‡	*I*
4.35	30	4.37	020	7.0	4.36	020	6.5	4.39	200	5.5	7.6
		4.27	−111	4.3							
3.40	20	3.44	110	29.9	3.45	110	27.9	3.39	−201	8.4	4.0
		3.42	021	4.2				3.38	001	10.9	21.8
—	—				*3.11*	*111*	*6.1*	*3.06*	*−211*	*4.1*	*2.2*
								3.05	*011*	*1.1*	
2.80	∼2	2.75	002	2.7	2.70	031	0.4	2.75	220	0.7	
								2.70	310		0.7
—	—				*2.60*	*102*	*2.8*	*2.62*	*−311*	*1.85*	
2.33	6	2.36	111	2.2	2.31	013	3.4	2.44	021	1.9	2.7
		2.30	30	2.5	2.30	130	2.3	2.44	−221	0.1	0.2
		2.27	−113	4.2	2.26	032	2.6	2.30	−401	0.3	0.9
		2.26	-132	3.0				2.28	201	—	0.3
—	—							*2.27*	130	2.8	4.7
								2.25	320	1.3	2.8
2.08	∼8	2.13	−222	0.5	2.10	023	0.9	2.19	400	0.8	0.3
		2.03	041	0.8	2.09	041	0.6	2.18	−411	0.3	0.9
		2.02	−221	0.8				2.08	−410	0.9	0.9
								2.07	230	1.3	0.3
—	—	*1.96*	*−223*	*2.3*				*1.98*	*−131*		*1.3*
1.87	4	1.87	200	0.8	1.87	200	0.8	1.93	−231	0.4	0.1
		1.83	−133	1.3	1.85	033	0.7	1.93	031	0.5	—
					1.83	123	2.8	1.92	−421	0.6	0.1
								1.84	−202	1.0	—
								1.83	330		1.3
—	—							*1.81*	*−331*	*0.6*	*0.5*
								1.80	*131*	*1.1*	*1.7*
1.68	2	1.72	220	2.1	1.72	220	2.0	1.69	002	0.1	0.9
		1.71	112	0.8	1.68	221	0.9	1.69	−402	—	0.1
		1.69	023	1.4	1.67	142	0.5				
					1.66	133	0.6				
					1.66	202	0.3				
—	—							*1.66*	*321*		*1.1*
1.58	1	1.58	−241	0.3	1.58	150	0.3	1.59	−601	0.9	0.5
		1.58	150	0.3				1.58	401	0.2	—
		1.57	−152	0.3							
		1.56	−312	0.4							
		1.55	−243	0.7							
—	—	*1.42*	*240*	*0.3*	*1.48*	*143*	*0.5*	*1.52*	*022*		*0.6*
		1.42	*−333*	*0.3*	*1.42*	*240*	*0.3*	*1.51*	*340*	*0.3*	*0.5*
		1.42	*221*	*0.4*				*1.49*	*−341*	*0.4*	*0.6*
1.30	<1	1.31	024	0.1	1.32	233	0.2	1.35	620		0.5
		1.29	062	0.5	1.28	214	0.2	1.32	−631	0.2	0.1
—	—							*1.24*	*630*	*0.3*	
1.174	3	1.18	−316	0.3	1.19	016	0.3	1.18	−731	0.5	0.7
		1.17	−206	0.3	1.18	163	0.2	1.17	060	—	0.3
					1.17	171	0.2				

† Electron-diffraction powder pattern observed by Lotz (1974). ‡ Using the unit cell and atomic coordinates of the Lotz (1974) model.

$\varphi_2 = -153.0$ and $\psi_2 = -158.2^\circ$ (Fig. 2). In this model, each chain forms interpeptide hydrogen bonds with four adjacent chains. Hence, unlike the previous models of polyglycine I that are hydrogen bonded within the sheets, this structure has a spatial network of hydrogen bonds. The stereochemical analysis shows that both parallel and antiparallel orientations of chains having similar conformation are possible. In the parallel packing, the adjacent chains forming linear inter-chain hydrogen bonds (H—N—O angle 2.9°, N···O distance 2.95 Å) are shifted relative to each other along the chain axis by 1.58 Å. The proposed structure has space group *Cc* and a monoclinic unit cell with parameters $a = 4.90$, $b = 8.73$, $c = 7.18$ Å (chain axis) and $\beta = 130.1^\circ$. The antiparallel model has an orthorhombic unit cell with parameters $a = 3.75$, $b = 8.73$, $c = 7.20$ Å (chain axis) and space group $P2_1cn$. These network structures are compatible with the observed diffraction pattern of the LMW polyglycine I (Table 1 and Fig. 1). The parallel network structure appears to be more probable than the antiparallel one because of its conformity with the observed near-meridianal reflections. In addition, the *R* factor of the parallel network model, calculated as $[\sum(kI_c^{1/2} - I_o^{1/2})^2]^{1/2}/(\sum I_o)^{1/2}$ (where k is a coefficient), is equal to 0.4267 compared with 0.5496 for the antiparallel network model. Fig. 1 (left) shows the calculated diffraction pattern of the parallel network model when the electron beam is normal to the ($h0k$) plane. This projection has symmetry axes, while the observed one (Fig. 1, centre) is slightly asymmetrical. This discrepancy disappears when the ($h0k$) plane of the calculated pattern is gently (∼10°) tilted about the [120] axis relative to the screen projection (the tilted pattern is not shown). This suggests that the orientation of the electron beam yielding the observed diffraction (Fig. 1, centre) is not perfectly parallel to the polypeptide chain axis. Remarkably, neither tilting nor other operations on the calculated pattern of the Lotz model can resolve the contradiction with the experimental pattern.

Table 2
Atomic fractional coordinates of the glycyl repeat unit.

LMW polyglycine I (space group *Cc*)

Atom	*x*/*a*	*y*/*a*	*z*/*c*
N	−0.031	−0.018	−0.189
H	−0.121	−0.123	−0.222
Cα	0.000	0.070	0.000
Hα	−0.241	0.134	−0.083
Hα	0.224	0.147	0.089
C′	0.057	−0.042	0.188
O	0.176	−0.170	0.213

HMW polyglycine I (space group $P2_1/c$)
Orientation of the axes was taken to be as in Lotz (1974).

Atom	*x*/*a*	*y*/*a*	*z*/*c*
N	0.232	−0.160	0.539
H	0.122	−0.154	0.507
Cα	0.317	0.018	0.679
Hα	0.406	0.030	0.565
Hα	0.371	0.018	0.992
C′	0.206	0.186	0.537
O	0.072	0.173	0.500

Energy calculations and molecular-dynamics simulations also argue that the parallel arrangement is a more satisfactory model for the LMW polygycine I than the antiparallel one. The antiparallel network structure is easily transformed to the antiparallel β-structure by a short session (500 steps) of energy minimization. This structure also loses its specific arrangement after molecular-dynamics simulation (1000 steps at 300 K with a time step of 0.001 ps). All these indicate that the antiparallel network structure is probably not at an energy minimum and hence cannot be fixed in this state. At the same time, the parallel structure keeps its specific chain conformation and network of hydrogen bonds either after the same energy-minimization procedure or after molecular-dynamics simulations. Thus, re-examination of the experimental data and

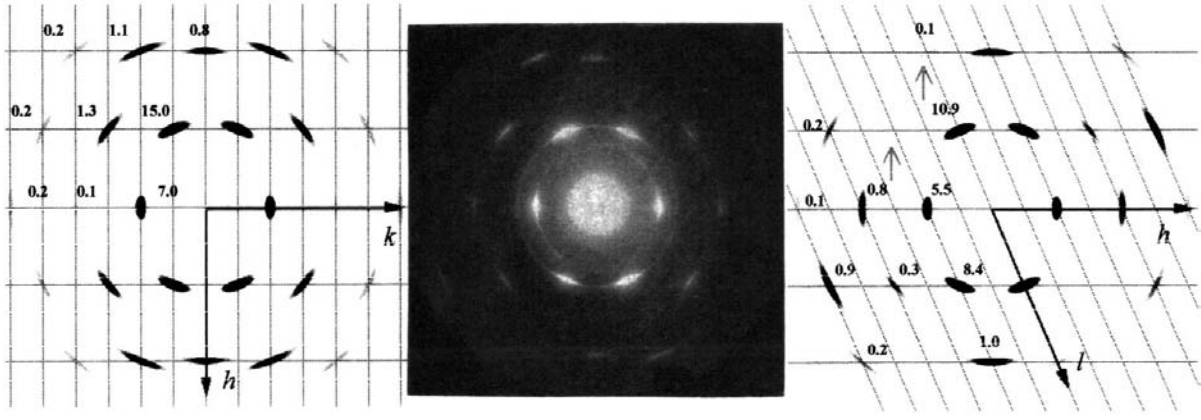

Figure 1
Electron-diffraction patterns of the LMW polyglycine I. The observed pattern is in the centre (reproduced from Lotz, 1974, with permission of the *Journal of Molecular Biology*). The photowritten diffraction pattern calculated from the Lotz model is on the right. Numbers indicate the intensity values in arbitrary units. Arrows show some intensities which do not correspond to the observed ones. The photowritten diffraction pattern calculated from the parallel network model is on the left. When compared with the intensities in Table 1, the values of the off-axis intensities are less by half, owing to the fact that the formula for calculation of the projection intensities does not have the multiplicity factor *P*.

structural models leads to the conclusion that the LMW polyglycine I most probably has the parallel network structure (Table 2).

It is worth mentioning that a search of the literature data resulted in evidence that supports this conclusion. In the X-ray crystal structure of L-alanyl-glycyl-glycine, the tripeptides are united into a network structure similar to that suggested here for the LMW polyglycine I (Subramanian & Latitha, 1983). Supporting evidence also follows from the similarity of polyglycine to nylons. The structure of nylon 2/3 showing a spatial network of hydrogen bonds similar to that of the LMW polyglycine I has been determined by X-ray study (Tormo *et al.*, 1992).

3.2. Structural model for the HMW polyglycine I

It has been suggested that HMW polyglycine I has the same rippled structure with non-linear hydrogen bonds as predicted for LMW polyglycine I (Lotz, 1974; Munoz-Guerra *et al.*, 1983). The difference between LMW and HMW polyglycine I was explained by the double orientation of independent crystallites composing the HMW crystals. Therefore, doubts about the existence of the Lotz structure with the unusual geometry of the hydrogen bonds also bear on the HMW crystals of polyglycine. This initiated the re-examination of the structural model for the HMW polyglycine I.

Our analysis shows that, assuming that the HMW polyglycine forms a single crystal, it is impossible to explain the observed diffraction pattern by any of the known arrangements of polyglycine molecules. It shows that the HMW crystal probably consists of double-oriented crystallites, as has previously been suggested (Munoz-Guerra *et al.*, 1983).

The HMW polyglycine crystals have a significantly different shape to the LMW ones. The electron-diffraction pattern from the HMW crystals (Munoz-Guerra *et al.*, 1983) looks similar to, but is not identical to, the one generated by twinning of the experimental LMW diffraction pattern (Lotz, 1974). For example, the superimposed double-oriented diffraction patterns of the LMW crystals have more sharp and split intensities of the innermost 1/4.36 $Å^{-1}$ reflections than are observed in the HMW diffraction pattern. All these suggest that the atomic structure of the HMW crystallites differs from that of the LMW crystal.

Subsequent analysis shows that the rippled structure with linear hydrogen bonds (Pauling & Corey, 1953*b*) has a higher level of conformity with the observed diffraction pattern (Fig. 3) than the Lotz modification of the rippled structure or the network structures. The rippled hydrogen-bonded layer consists of two enantiomorphous chains with torsion angles for one chain of $\varphi = 149.9$ and $\psi = 146.5^\circ$ and for the other of $\varphi = -149.9$ and $\psi = -146.5^\circ$, which alternate along the hydrogen-bond direction. The proposed structure has space group $P2_1/c$ and a monoclinic unit cell with unit-cell parameters $a = 9.54$, $b = 7.044$ (chain axis), $c = 3.76$ Å and $\beta = 114.0^\circ$ (Table 2). It is also shown that the β-pleated sheet structure is in agreement with the known diffraction data. Thus, the models with double oriented crystallites of either the β-pleated sheet (Pauling & Corey, 1953*a*) or the rippled structure (Pauling & Corey, 1953*b*) can give a satisfactory explanation of the observed diffraction pattern. The crystallographic data were insufficient to distinguish clearly between these two possible models. Therefore, a further analysis of the intersheet packing has been undertaken.

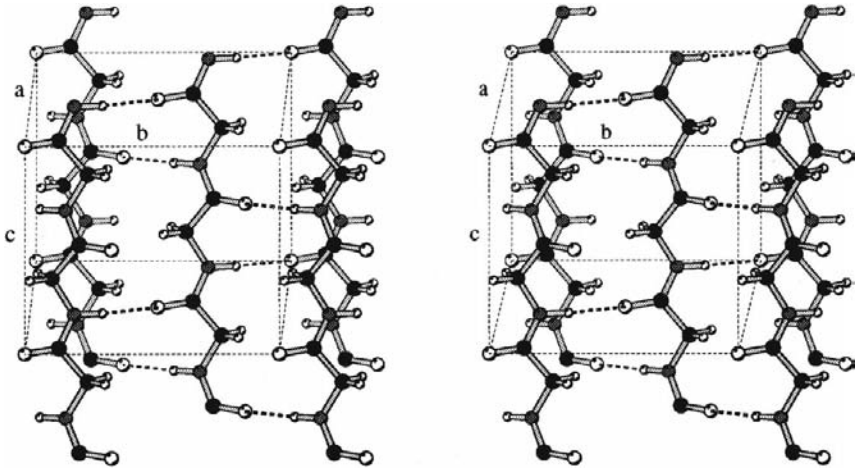

Figure 2
Stereoview of the three-dimensional structure of the parallel network model for the LMW polyglycine I. Hydrogen bonds are shown by broken lines and the unit cell of the crystal by thin dotted lines. Small open circles correspond to H atoms, large open circles to O atoms, filled circles to C atoms and grey circles to N atoms. This figure was generated with the program *MOLSCRIPT* (Kraulis, 1991).

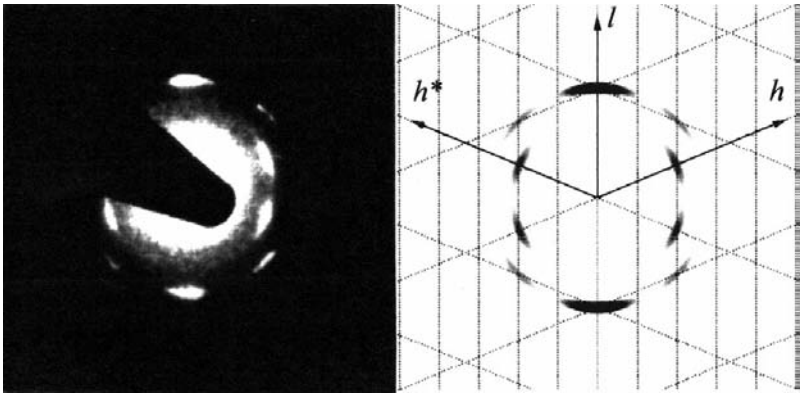

Figure 3
Electron-diffraction patterns of the HMW polyglycine I. The observed pattern is on the left (reproduced from Munoz-Guerra *et al.*, 1983, with permission of the *Journal of Molecular Biology*). The photowritten diffraction pattern calculated from the canonical rippled model is on the right.

3.3. Analysis of the intersheet packing of models for the HMW polyglycine I

To estimate optimal packing, the considered sheet consisting of three 12-residue chains was shifted along the hydrogen bonds relative to the sheet consisting of six chains. The 12-residue chain length followed from the dimension of the HMW crystal. The intersheet distance was fixed at 3.44 Å, in accordance with the diffraction data. The energy calculation reveals that the packing-energy minimum for the β-pleated sheet arrangement does not coincide with the arrangement resulting from the diffraction data (Fig. 4). This suggests that the HMW crystals do not have the β-pleated sheet structure. At the same time, it is shown that the lowest energy of the syncline packing of the rippled sheets coincides with the arrangement predicted for the observed unit cell (Fig. 4). Thus, analysis of the intersheet packing suggests that the HMW crystals have the rippled sheet structure with syncline packing within the crystallites.

Syncline packing of the rippled sheets is assigned for the crystallites, while anticline packing is assumed to exist only in the interface of the twinning crystallites. Therefore, syncline packing should be more favourable than anticline. However, the energy calculation does not explain the preference of the syncline arrangement over the anticline, as they have almost equal packing energy (Fig. 4). A more comprehensive analysis reveals that the preference for syncline packing can be explained by taking into account intersheet interactions of polyglycine turns. The crystal thickness in the chain direction is 50 Å (Munoz-Guerra *et al.*, 1983). Therefore, one ~90-residue chain of the HMW polyglycine should have up to six turns in the crystal. Our analysis shows that, in principle, four different turn conformations are possible for the rippled structure: types I, I′, II and II′ (nomenclature taken from Venkachatalam, 1968). The energy-minimization calculation shows that the best syncline and anticline packing arrangements are present when the rippled sheets have type II and II′ turns alternating along the chain. At the same time, owing to the introduction of these turns, the anticline packing becomes less favourable than the syncline (with some variation of the energy values, depending on the calculation procedure). In the syncline arrangement, the intersheet hydrogen bonds formed between the turns have a more optimal geometry (d_{NO} = 2.83 Å; H—N—O angle = 16°) than in the anticline (d_{NO} = 2.85 Å; H—N—O angle = 68°) (Fig. 5) and this may explain this difference in the packing energy.

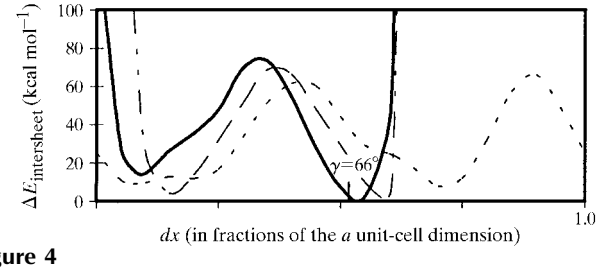

Figure 4
Profiles of the inter-sheet packing energy. The solid line corresponds to the syncline rippled-sheet packing, the broken line to the anticline packing of the rippled sheets and the dotted line to the β-pleated sheet packing. The value dx corresponding to the unit-cell arrangement (γ = 66°) is specially denoted.

4. Conclusions

The re-examination of the experimental data and structural models reveals that the crystalline form of polyglycine known by the name 'polyglycine I' has two different three-dimensional structures depending on the weight of the constituent molecules. Moreover, the other name of this crystal modification, 'β-structural', does not precisely reflect the real structural arrangement, since neither the LMW nor the HMW polyglycine I have the familiar β-structure. The polyglycine chains of the LMW crystals form a spatial network of hydrogen bonds and have an unusual extended conformation, with the mirror-symmetrical residual conformations alternating along the chain. The HMW crystal has the rippled sheet structure. Remarkably, the rippled sheet model was described many years ago (Pauling & Corey, 1953*b*); however, until now this arrangement has not been assigned to an existing structure. It is worth mentioning that in the model of the HMW polyglycine I the orientation of the chains is antiparallel, while it is parallel in the LMW model. This predicts that one crystal modification cannot be transformed into the other by mechanical or other treatments.

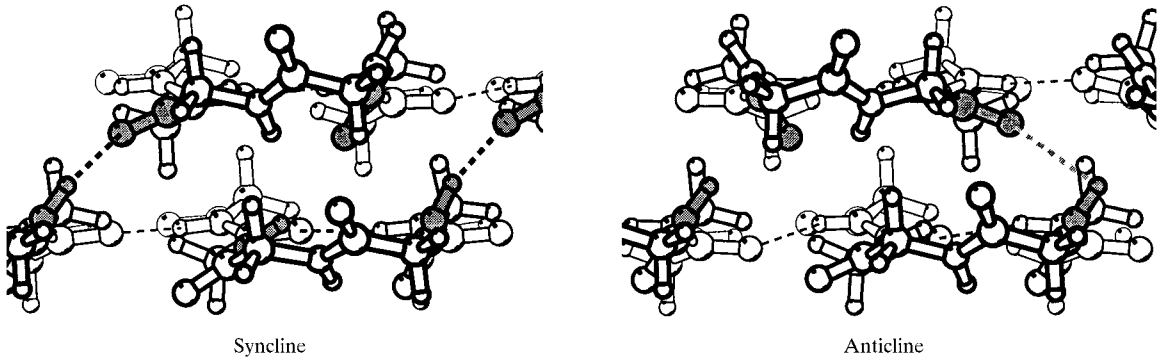

Figure 5
Ball-and-stick representation of the intersheet syncline and anticline packing of the rippled structure in the place of type II and II′ turns. Thicker lines highlight the turns. The CO and NH groups of the turns forming the intersheet hydrogen bonds are shown in grey. The intersheet hydrogen bonds are shown by broken lines. This figure was generated with *MOLSCRIPT* (Kraulis, 1991).

Finally, it should be noted that owing to the fact that data from polyglycine I associates are used for the determination of the vibrational states and other spectral parameters of the β-structural conformation, the suggestion of the new models for polyglycine crystals may cause a revision of these basic parameters.

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