the importance of column preparation in IGC.[37]

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π-Helical Conformation of Poly(β-phenethyl L-aspartate)

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ABSTRACT: The left-handed π-helical conformation is found in a solid-state modification of poly(β-phenethyl L-aspartate). The helix contains approximately 4.25 residues per turn with a unit height along the helix axis of 1.17 Å. Atomic coordinates are presented for the model constructed with the standard dimensions of bond lengths and bond angles and torsion angles of $\phi(\mathrm{N-C}^{\alpha}) = 50.7°$, $\psi(\mathrm{C}^{\alpha}-\mathrm{C}') = 73.6°$, and $\omega(\mathrm{N-C}') = 177°$. The hydrogen bond formed between the C═O group of the *n*th residue and the NH group of the $(n + 5)$th residue is inferred to be weak from the infrared spectra. Poly(β-phenethyl L-aspartate) exists also as as right-handed α-helix and a β-pleated-sheet structure. Structures and transitions between modifications are discussed.

Pauling and Corey[1,2] proposed two helical conformations (the α and γ helices) for polypeptide chains by considering some structural restrictions. By the notation of Bragg, Kendrew, and Perutz,[3] these helices are denoted as 3.6_{13} and 5.1_{17}, respectively.[4] Several other helices were also proposed, for instance, 2.2_{7},[5] 3_{10} (the δ helix),[6] 4.4_{16} (the π helix),[7,8] and so on. Donohue estimated the strain energy for these models and suggested the possibility of the δ and π helices.[6] The 3_{10} helix was once suspected for poly(α-aminoisobutyric acid),[9] but its existence has not yet been firmly established.[10]

The π helix has a 16-atom ring of hydrogen bonds formed between the C═O group of the *n*th residue and the NH group of the $(n + 5)$th residue. The 4.4_{16}-helix model proposed by Low et al.[7,8] has an axial translation per residue, *h*, of 1.15 Å, and a small distortion (about 4°) in the bond angle $\tau(\mathrm{N,C}^{\alpha},\mathrm{C}')$. A conformation similar to the π helix is presented for alternating poly(γ-benzyl D,L-glutamate), in which the D and L residues assume different orientations with two kinds of hydrogen bonds (14 and 16 atoms in the rings).[11] The π helix as proposed by Low et al. has not been found so far.

The conformational versatility of poly(aspartate esters) has been extensively investigated. Poly(β-benzyl L-aspartate) (PBLA) exists as a left-handed α helix (α_{L}) in chloroform solution, the helix sense being opposite to the normal sense of L polypeptides.[12,13] The PBLA film obtained from chloroform solution exhibits an X-ray dif-

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fraction pattern of the α-helix type. The α form transforms irreversibly into the so-called ω form around 160 °C and then into the β form around 190 °C.[14-16] The ω form is highly crystalline and has a tetragonal unit cell of side a = 13.85 Å containing a left-handed 4_{13} helix (ω_L) of h = 1.325 Å.[14] The right-handed α helix (α_R) of PBLA has been observed in special cases such as in the monolayer prepared at the air-water interface[17] or in the solution of a mixed solvent of chloroform and trimethyl phosphate.[18,19] Poly(β-methyl L-aspartate) (PMLA)[20] and the *o*- or *m*-chlorobenzyl polymers assume the α_L helix in solution. However, the polymers obtained by substituting the methyl of PMLA by an ethyl, *n*-propyl, or *n*-butyl group or by substituting a nitro, chloro, methyl, or cyano group in the para position of the benzyl of PBLA causes a reversal of the helix sense from α_L to α_R.[20-24] Bradbury et al.[22] reported that the introduction of methyl L-aspartate residues into PBLA prevents the formation of the ω_L helix. The helix stability of these polymers has been discussed in terms of potential energy calculations.[25-27]

The side-chain group thus has an important role for the main-chain conformation of poly(aspartate esters). A similar polymorphism may be expected for poly(β-phenethyl L-aspartate) (PPELA) (phenethyl = $CH_2CH_2C_6H_5$), which has the same chemical composition as poly(γ-benzyl L-glutamate) (PBLG). According to Bradbury et al.[22] and Hashimoto and Arakawa,[23] the PPELA molecule exists as the α_R helix in chloroform solution, and the cast film of the α_R form possibly transforms into the ω_R form on heating. As reported in our previous paper,[28] the α_R helix of PPELA changes into a left-handed helix in chloroform solution when a small amount of dichloroacetic acid is added. In the present work, it has been found that the α_R form of PPELA in the solid film transforms irreversibly into the left-handed π-helix form (π_L) by annealing.

Experimental Section

Three samples of PPELA were synthesized by the *N*-carboxyanhydride method using triethylamine as the initiator in chloroform.[22] The values of the intrinsic viscosity in dichloroacetic acid at 25 °C were 0.91, 0.5, and 0.3 dL/g, respectively. Solids films were obtained by casting the solution in chloroform on a glass plate at room temperature, followed by drying in vacuo. Oriented specimens were prepared by stroking the concentrated onto a glass plate.

X-ray measurements with Ni-filtered Cu Kα radiation were carried out by using a flat-plate camera and a cylindrical camera. The cameras could be equipped with a heating system, by which the temperatures of the sample holder and its atmosphere were regulated within ±1 °C by the respective heaters. Reflection spacings were calibrated with silicon.

Optical rotatory dispersion (ORD) and circular dichroism (CD) spectra were recorded with a Jasco J-20 spectropolarimeter. The Moffitt-Yang parameter b_0 (λ_0 = 212 nm)[29] was determined from the ORD spectra measured for the chloroform solution. The right-handed helix sense of PPELA in chloroform solution was confirmed from the negative value of b_0 of about -520. The CD spectra were measured for thin films prepared on a quartz plate. The incident light was at right angles to the plate. Since the CD spectra were not changed by the rotation of the plate in its plane, the effect of the birefringence due to the molecular orientation[30] might be insignificant.

Infrared (IR) spectra were recorded with a Jasco DS-701G infrared spectrophotometer for films prepared on a KRS-5 plate.

Differential scanning calorimetric (DSC) measurements were carried out with a Perkin-Elmer DSC Model II at a scanning rate of 10 °C/min.

Results and Discussion

Modifications. The DSC thermogram of the PPELA film is shown in Figure 1. There are three endothermic transitions around 140, 200, and 235 °C (at the peaks), which can be detected by X-ray diffraction. The modifications are conveniently termed as A, B, and C, as indicated in Figure 1. Film D, obtained by annealing above 235 °C, is actually the decomposed state because of the decreased sample weight. Irregular conformations in film D are suggested from the considerably poor X-ray pattern showing broad intensity maxima at 16 and 5 Å. Characteristic amide bands are missing in the IR spectrum of film D. The β form is obtained occasionally from the C state, as will be mentioned later. The A → B, C → β, and C → D transitions are thermally irreversible, while the B $\rightleftarrows$ C transition is reversible. The enthalpy of the B $\rightleftarrows$ C transition is relatively small for the high-molecular-weight sample.

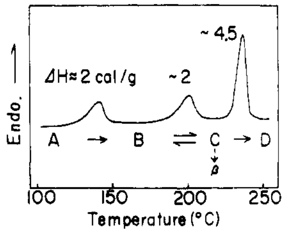

Figure 1. DSC thermogram of the poly(β-phenethyl L-aspartate) film prepared from chloroform solution.

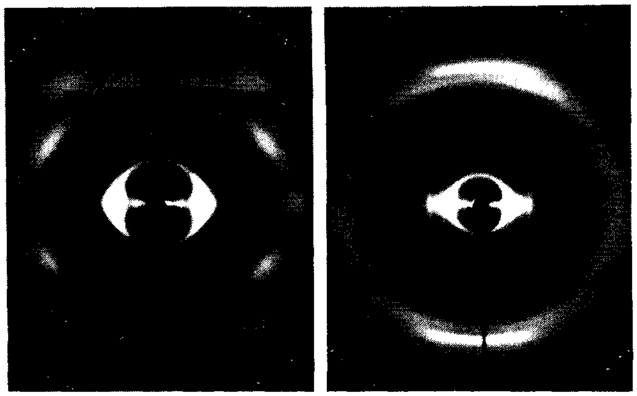
(a) (b)

Figure 2. X-ray flat-plate photographs of oriented films of (a) form A and (b) form B of poly(β-phenethyl L-aspartate).

Form A (α_R). The oriented film shows an X-ray pattern which is typical for the α-helical form (Figure 2a). The turn layer line has a spacing of 5.4 Å as expected. The 1.50-Å meridional spot is observed by tilting the oriented specimen by 30° from the normal to the beam. Broad equatorial reflections of 13.3 and 6.6 Å indicate that the two-dimensional arrangement of the α helices is not regular. The density is calculated to be 1.20 g/cm^3 for an assumed hexagonal unit cell of a = 15.3 Å (the 100 spacing = 13.3 Å) and 1.39 g/cm^3 for a tetragonal cell of a = 13.2 Å. The observed density of 1.33 g/cm^3 is indicative of tetragonal-like disordered packing.

The α-helical conformation in form A is supported by the IR absorptions (Figure 3). The wavenumbers of characteristic amide bands are compared in Table I with those of the α_R forms of poly(L-aspartate esters).

The film of form A shows a negative CD band at 226 nm (Figure 4), reflecting the right-handed helix sense. The 226-nm band is assigned to the n-π^* transition.

β Structure. Before we discuss forms B and C, the β form is described here, which is prepared by annealing the low-molecularweight sample at a temperature between 200 and 235 °C. The features of the IR spectrum (Figure 3) show that the β formation is accompanied by thermal degradation. Characteristic amide frequencies are essen-

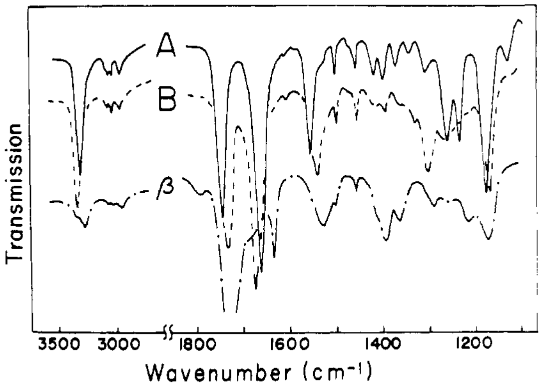

Figure 3. Infrared spectra of forms A, B, and β of poly(β-phenethyl L-aspartate).

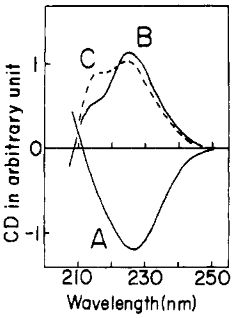

Figure 4. CD spectra of films of forms A, B, and C of poly(β-phenethyl L-aspartate).

Table I
Infrared Band Positions for Films of Poly(β-phenethyl L-aspartate) and Poly(L-aspartate esters)

	band position, cm^{-1}				
	amide A	ester C=O	amide I	amide II	amide V region
			PPELA		
A (α_R)	3298	1742	1658	1553	657, 602
B (π_L)	3332	1731	1674	1536	653, 604
β	3276	1726	1634	1525	633
			Esters		
α_R [a]	3296	1741	1659	1553	658, 602
α_L [a]	3302	1735	1666	1557	662, 614
ω_L [a]	3296	1731	1675	1536	666, 622
β [b]	3275	1726	1636	1529	

[a] Reference 22. [b] Reference 15.

tially the same as those of the β form of PBLA (Table I). X-ray data at 25 and 210 °C are listed in Table II. The interchain distance in the β sheet (the 010 spacing) is 4.65 Å at 25 °C as usual. A thermal expansion coefficient of 4.6×10^{-4} Å/°C is observed for the 100 spacing, that is, the distance between the neighboring pleated sheets.

Structure Analysis of Forms B and C (π_L). A structure involving the interchain hydrogen bonding may be excluded, since form B dissolve in chloroform, a helix-forming solvent. The CD spectra (Figure 4) show that the α_R helix of form A transforms into a left-handed helix in forms B and C. The intensity of the 215-nm band tends to increase at higher temperatures.

1. **X-ray Data.** The X-ray pattern of oriented form B is shown in Figure 2b, the data being given in Table III. The equatorial reflections, including a spot of the unexpectedly large spacing of 20 Å, are indexed with a rectangular unit cell of a = 20.3 Å and b = 11.7 Å. From simple considerations, it is concluded that one chain passes through the unit cell. The observed density of 1.30 g/cm^3 suggests that the unit height, h, should be nearly equal to 1.18 Å.

Table II
X-ray Data of the β Form of Poly(β-phenethyl L-aspartate)

	d_{obsd}, Å	
hkl	at 25 °C	at 210 °C
100	17.6 vs	~19 vs
200		9.5 w
300	5.84 w	6.34 w
010	4.65 m	4.70 m

Table III
X-ray Data of Form B of Poly(β-phenethyl L-aspartate)

d_{obsd}, Å	d_{calcd}, Å	hkl
~20 vs	20.3	100
11.7 m	11.7	010
10.1 w	10.1	200, 110
7.6 w	7.67	210
6.8 w	6.77	300
5.7 w	5.85 5.62	020, 310 120
4.95 m	on turn layer line	
4.57 s	near-meridional	
2.4 m	near-meridional	
2.2 m	near-meridional	
1.63 m	near-meridional	
1.53 m	near-meridional	
1.17 w	meridional	
1.09 w	near-meridional	

Form B undergoes a reversible transition aroung 200 °C into form C, which shows three equatorial reflections of 14.8, 8.55, and 7.40 Å. Allowed is the hexagonal molecular packing of a = 17.1 Å. From inspection of the IR spectra (discussed in the next section), the molecular conformation of form B is essentially unchanged even in form C. Therefore we conclude that the B $\rightleftarrows$ C transition is due to rearrangement of the helices caused by thermal molecular motion. The interchain distance of a = 17.1 Å in form C also implies a large-diameter helix.

2. **IR Analysis.** As shown in Table I and Figure 3, the frequencies of the stretching vibration of the side-chain C=O group, the amide I band, and the amide II band may support the ω_L conformation. The amide V frequencies, however, suggest that the main-chain conformation is different from ω_L.

It is noteworthy that the amide A frequency of 3332 cm^{-1} is extraordinarily high, indicating that hydrogen bonding is very weak. The frequency shift of the NH stretching vibration has been correlated with the length of the hydrogen bond.[31,32] The true frequency of the NH stretching vibration, ν_{NH}, is related to the frequencies of the amide A, B, and II vibrations by the expression[33]

$$\nu_{\text{NH}} = \nu_A + \nu_B - 2\nu_{\text{II}} \tag{1}$$

Correction for the interaction coefficient is inherently necessary, but the error incurred in neglecting the correction has been supposed to be small.[32] The relationship between the hydrogen bond length b(N,O) and ν_{NH} has been given by

$$b(\text{N,O}) = 0.001825\nu_{\text{NH}} - 3.1 \tag{2}$$

The amide B band of form B may be assumed to be at 3065 cm^{-1}, being overlapped with the CH stretching vibrations of the phenyl group. The frequencies of ν_A = 3332, ν_B = 3065, and ν_{II} = 1536 cm^{-1} result in ν_{NH} = 3325 cm^{-1}, and therefore b(N,O) = 2.97 Å, which is large in comparison with those of other helices.[2,32]

The IR spectrum of form C was measured at 210 °C. The features were almost the same as those for form B,

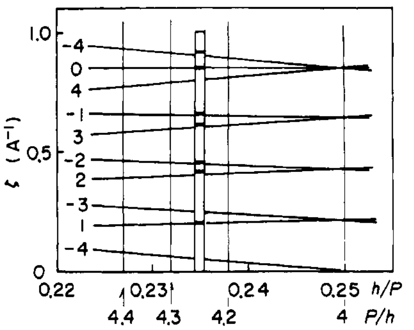

Figure 5. The ζ–h/P diagram. The value of j is indicated for each straight line. On the vertical strip at $P/h = 4.25$, the positions of the observed near-meridional reflections are marked (see text).

except the amide A frequency of 3310 cm^{-1} in form C. Therefore, the molecular conformation was considered to be kept without serious changes. The amide A frequency of 3310 cm^{-1} is still high, but the shift to the lower frequency means that hydrogen bonding becomes stronger at higher temperature. The intermolecular side-chain interaction may give rise to the deformation of the helix at lower temperatures.

3. Determination of the Helical Conformation. At the first stage, near-meridional reflections of spacings listed in Table III are found to be almost consistent with the π helix.

In the case of a helix with pitch P and unit height h, the reciprocal-space coordinate of the lth layer line, ζ, is given by the relation[34]

$$\zeta = \frac{l}{c} = \frac{j}{P} + \frac{m}{h} \tag{3}$$

where c is the axial repeat of the helix and j and m are integers. The integer j is the order of the Bessel function in the intensity formula of the helix. The smaller j is, the stronger the average intensity of that layer line.

The meridional reflection of 1.17 Å will be assigned to the unit height, h, being slightly larger than 1.15 Å of the 4.4_{16} helix of Low et al.[7,8] The ζ–h/P diagram with h = 1.17 Å is shown in Figure 5 in the case of small j values. The strong near-meridional reflection of 4.57 Å disappears above 200 °C (in form C). Therefore, this reflection may be attributable to a regular arrangement of side-chain groups such as the stacking of the benzene rings as in the case of some PBLG modifications.[35–37] The 4.95-Å reflection remains even at 200 °C, being probably on the true turn layer line. By the technique of Mitsui et al.,[37] a strip is prepared on which reciprocal values of observed spacings of higher layer line reflections are marked and slided along the h/P axis in Figure 5. A satisfactory agreement is obtained at $P/h = 4.25$, leading to a 17-residue 4-turn helix with c = 19.89 Å. Table IV shows the comparison between the observed spacings and the $1/\zeta$ values calculated for this helix. Since the reflections are not exactly on the meridian, it is reasonable that d_{obsd} values are smaller than $1/\zeta$ values.

4. Molecular Model. As described above, the 4.25_{16} helix with h = 1.17 Å and b(N,O) = 2.97 Å is the most probable conformation. However, distortion from a uniform helix is expected from the features of the X-ray pattern. In the two-dimensional molecular packing, there are two kinds of interchain distances, a = 20.3 Å and b = 11.7 Å, suggesting a special type of the side-chain orientation. The 4.57-Å near-meridional reflection may be interpreted to be due to the stacking of the benzene rings. Main-chain distortion is suggested from the frequency shift of the amide A band in the B ⇄ C transition.

Table IV
Comparison between Layer-Line Spacings $1/\zeta$ Calculated for the 4.25_{16} Helix with h = 1.17 Å and Observed Spacings of Near-Meridional Reflections of Form B of Poly(β-phenethyl L-aspartate)

j[a]	m[a]	$1/\zeta$,[b] Å	d_{obsd}, Å
−4	1	19.9	
1	0	4.97	4.95
−3	1	3.98	
2	0	2.49	2.4
−2	1	2.21	2.2
3	0	1.66	1.63
−1	1	1.53	1.53
0	1	1.17	1.17
−4	2	1.10	1.09

[a] The integers given in eq 3. [b] Calculated by eq 3.

Table V
Atomic Coordinates of an L Residue in a Left-Handed 4.25_{16} Helix

atom	x, Å	y, Å	z, Å	r, Å	θ, deg
N	1.833	−0.926	0.762	2.054	−26.8
H	1.964	−0.878	1.752	2.152	−24.1
C$^{\alpha}$	2.683	0.0	0.0	2.683	0.0
H$^{\alpha}$	3.190	0.686	0.694	3.263	12.1
C$^{\beta}$	3.734	−0.796	−0.776	3.818	−12.0
C′	1.830	0.807	−0.981	2.000	23.8
O	1.862	0.572	−2.197	1.947	17.1

Apart from such a complicated situation, a model of a uniform helix has been sought with the standard dimensions of bond lengths and bond angles.[2,38] The unit height, h, of 1.17 Å and the unit twist, t, of 275.3° in the case of the left-handed 4.25_{16} helix are related to torsion angles[39] of ϕ(N–C$^{\alpha}$), ψ(C$^{\alpha}$–C′), and ω(C′–N) by the expressions[40]

$$\cos(t/2) = -0.739 = 0.604\cos\{(\phi+\psi+\omega)/2\} - 0.274\cos\{(\phi-\psi+\omega)/2\} - 0.312\cos\{(\phi+\psi-\omega)/2\} - 0.230\cos\{(-\phi+\psi+\omega)/2\} \tag{4}$$

and

$$h\sin(t/2) = 0.788 = 2.609\sin\{(\phi+\psi+\omega)/2\} - 0.346\sin\{(\phi-\psi+\omega)/2\} - 0.358\sin\{(\phi+\psi-\omega)/2\} - 0.317\sin\{(-\phi+\psi+\omega)/2\} \tag{5}$$

Under the assumption of ω = 180° (trans), the values of ϕ = 38° and ψ = 86° give a solution to the above equations. The ϕ value, however, is too small to be acceptable. Therefore, a reasonable model has been searched by allowing out-of-plane deformation of the amide group. For a small distortion of ω, the bond length b(C′,N) with double bond character may be fixed at the assumed dimension. As a result, a model with ϕ = 50.7°, ψ = 73.6°, and ω = 177° has been found to give the hydrogen bond length b(N,O) = 2.97 Å. The angle $\tau(\mathrm{H_1,N_1,O_6})$ in the hydrogen bonding is 21°. The orthogonal and cylindrical coordinates of the main-chain atoms are listed in Table V.

In order to build up a molecular model with standard dimensions of bond lengths and bond angles, three geometrical conditions are necessary to determine the torsion angles ϕ, ψ and ω. In the present case, they are given by the unit height, the unit twist (derived from the X-ray analysis), and the hydrogen bond length (from the IR study).

The π-helix model of Low et al. has a 4° distortion in the bond angle τ(N,C$^{\alpha}$,C′).[8] According to a potential form for the bond angle[41–43]

$$U = 80(\Delta\tau)^2 \text{ kcal/mol}$$

the 4° distortion increases the strain energy by 0.4 kcal/mol. Our model has standard bond lengths and bond angles but allows out-of-plane deformation of the amide group. The energy for the small distortion in the torstion angle ω(N–C′) is expressed as

$$U = K_\omega(\Delta\omega)^2 \text{ kcal/mol}$$

The value of K_ω = 20 kcal/mol has been used in the energy calculation.[27,43-45] From the IR analysis of *N*-methylacetamide, a value of K_ω = 27 kcal/mol is derived.[46] Thus, the 3° distortion (ω = 177°) contributes only 0.05–0.07 kcal/mol to the energy increase. From this point of view, the present model may be more preferable. The π_L structure of PPELA will be subject to a more detailed examination, in particular, with respect to the stabilizing energy and the side-chain structure.

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