Distinct Complex Precipitating from Racemic Solution of Poly(*β*-benzyl L-aspartate) and Poly(*β*-benzyl D-aspartate)

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In the polyaspartates, the energy differences between several conformations are relatively small so that the conformation is easily affected by the temperature. A typical example is poly(*β*-benzyl L-aspartate) (PBLA),[1−3] which can form the α-helix,[1] *ω*-helix,[2] and *β*-form[3] in order of increasing temperature. Recent studies[4−6] show that the sense of helical conformation is also altered with the temperature. The right-handed α-helix is converted to the left-handed α-helix in the solutions of poly(*β*-phenylethyl L-aspartate). The same homologues with longer side chains such as poly(*β*-phenylpropyl L-aspartate) show the reversible transition between the right-handed α-helix and left-handed *ω*-helix even in the solid state.[7−10] Thus, the polyaspartates are very delicate polymers which take up several conformations by the cooperative interaction along the chain.

In this communication, we report a new conformation found in the fibrous precipitation that takes place when the PBLA and poly(*β*-benzyl D-aspartate) (PBDA) solutions in chloroform are mixed together. The precipitation is composed of an equal amount of L- and D-enantiomers, showing the specific complex between the two.

PBLA and PBDA were prepared by the conventional NCA method. The molecular weights of PBLA and PBDA are 58 000 and 63 000, respectively, as estimated from the viscosity measurement.[11]

Each enantiomer was dissolved separately in chloroform to a concentration of 1.0 g dL^{-1}, and the solutions were then mixed together. Since the polyaspartate assumes an α-helical conformation in chloroform, homogeneous solution can be obtained instantaneously on mixing. However, fine fibers precipitate during 2 or 3 days. If the solutions of L- and D-enantiomers are mixed in different fractions, the weight of precipitation was twice that of the lesser component. Thus, the precipitation is composed of an equimolar complex of L- and D-enantiomers.

For the X-ray and IR analyses of the complex, oriented samples were prepared as following. At first, liquid crystalline solutions of the two enantiomers were prepared separately and then mixed together. The resulting nematic solution was placed between two concentric cylinders whose radii are 24 and 25 mm. The shear flow was applied by rotating the outer cylinder with the inner cylinder kept fixed. One of the oriented films, film A, was prepared by quick evaporation of solvent within 10 min. The other film B was prepared by slow evaporation during 2 or 3 days.

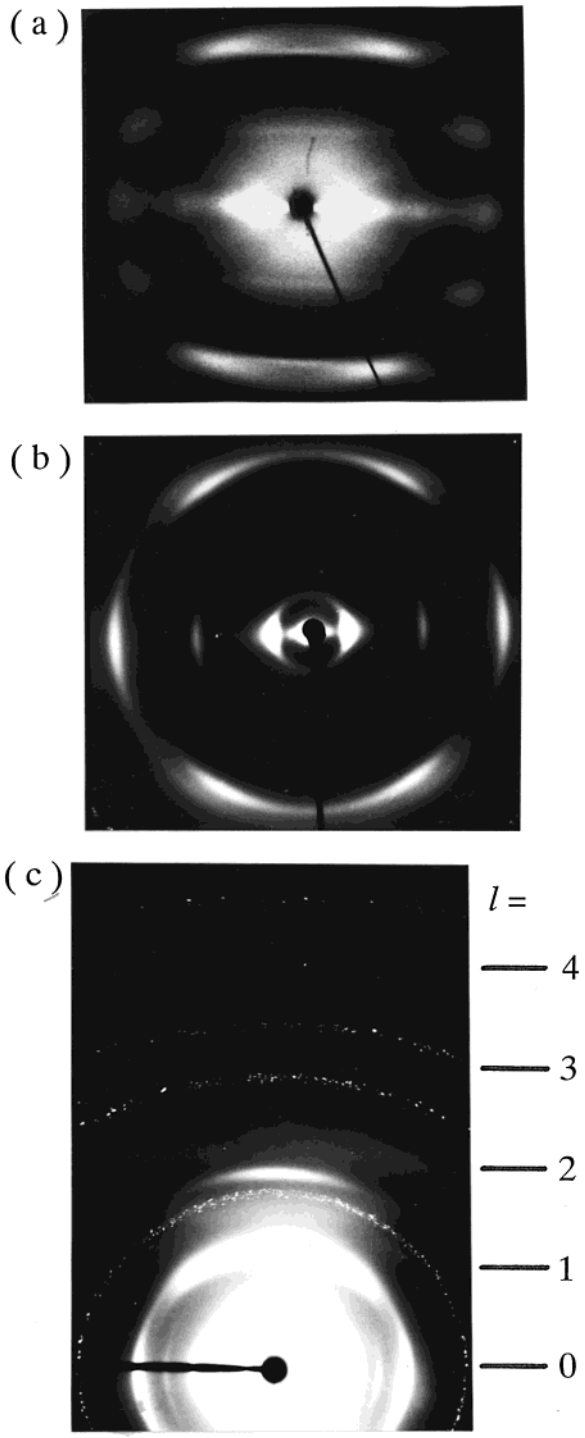

Figure 1. X-ray diffraction photographs of the oriented films prepared from racemic solution of poly(*β*-benzyl L-aspartate) and poly(*β*-benzyl D-aspartate) in chloroform. (a) Film A and (b) film B: 5 cm flat camera; X-rays normal to the orientation axis and parallel to the film surface. (c) Film B: 8 cm cylindrical camera; orientation axis tilted by 15° to X-rays and camera axis normal to plane containing oriented axis of film and X-ray beam.

In parts a and b of Figure 1 are shown the X-ray patterns of the oriented films A and B, respectively. The X-ray pattern of Figure 1c was taken for film B by a cylindrical camera. The spacings of reflections observed in film B are listed in Table 1. They coincide with those

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Table 1. X-ray Data for Film B

l (layer line)	d_{obs}/Å	d_{calcd}[a]/Å	*hkl*[a]	I_{obs}
0	20.8	21.4	100	vs
	10.8	10.7	200	vw
	7.13	7.13	300	m
	5.35	5.35	400	w
	4.28	4.28	500, 010	s
	2.14	2.14	10 00, 020	vw
	1.96	1.95	11 00	vw
1	4.64	4.64	301	s
	4.30	4.25	301	w
	3.27	3.28	501	vw
	2.46	2.50	801	vw
2	2.84	2.83	002	s
	2.32	2.32	602	vw
3	1.82	1.83	403, 203	vw
4	1.42	1.42	004	w

[a] Based on the monoclinic lattice of $a = 21.4$ Å, $b = 4.28$ Å, c (chain axis) $= 5.68$ Å, and $\beta = 84.9°$.

collected from the powder pattern of fibrous precipitation, showing that the complex is well formed even in the oriented film B.

Difference in the X-ray patterns is obvious between the two films. In film A, the main chain assumes an α-helical conformation with 7-residue 2-turn (7/2-helix). The unit height of one residue is 1.5 Å which was elucidated from the meridional reflection of the seventh layer line. On the equatorial line, only the broad reflection of 15 Å is observed. On the other hand, the oriented film B shows the sharper new pattern. The first layer line with $l = 1$ appears at a height of 1/5.68 Å^{-1}, and a meridional reflection is observed on the second layer line ($l = 2$) at 1/2.84 Å^{-1} (see Figure 1c). The third and forth layer lines are also recorded with spacings of 1.82 and 1.42 Å, respectively. This layer line profile indicates a specific conformation of 2-residue 1-turn (2/1-helix) with the residue height of 2.84 Å. On the equatorial line, several *h*00 and *0k*0 reflections are recorded and assigned to the rectangular lattice with $a = 21.4$ Å and $b = 4.28$ Å. Such a rectangular shape suggests that the projection of chain along the chain axis may not be cylindrical, but planar. All the reflections can be assigned to the monoclinic lattice of $a = 21.4$ Å, $b = 4.28$ Å, c (chain axis) $= 5.68$ Å, and $\beta = 84.9°$, with two residues included along *c*-axis. The calculated spacings correspond to the observed ones as listed in Table 1, and also the calculated density (1.30 g cm^{-3}) agrees with the observed one (1.29 g cm^{-3}).

The structure difference between the films A and B can also be recognized from IR dichroisms of amide A of Figure 2. In film B, the parallel band is weaker than the perpendicular one, while film A shows the opposite trend that is expected for the α-helix. The similar dichroisms are also observed in amide I. The amides A and I are attributed to the N−H and C═O stretching modes, respectively, leading to the conclusion that in the chain conformation of film B the N−H and C═O bonds are directed perpendicularly to the chain axis. The interchain hydrogen bond is thus likely formed as in a β-form.[12] In fact, the film B (or the precipitation) is not soluble at all in helicogenic solvents, but in random coil solvents such as dichloroacetic acid which can break the intra- or intermolecular hydrogen bond. IR band positions, 3304 cm^{-1} for amide A, 1740 cm^{-1} for ester C═O, 1656 cm^{-1} for amide I, and 1550 cm^{-1} for amide II, however, are not consistent with those of β-form.[12]

According to these basic data, the chain conformation and packing structure in the complex are proposed as following.

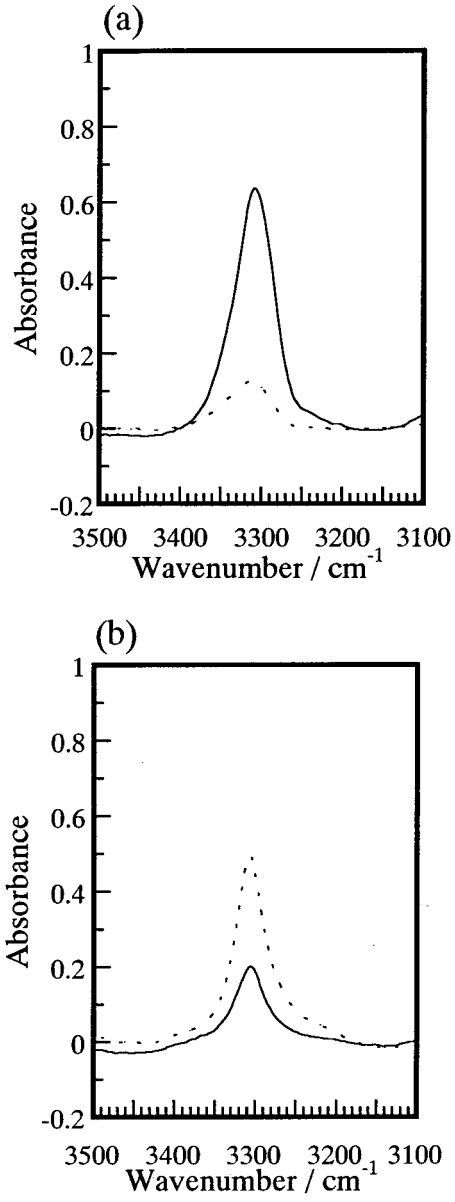

Figure 2. Polarized infrared spectra of amide A observed for (a) the oriented film A and (b) film B. Solid and dotted curves were obtained with the electric vector of the polarized infrared radiation parallel and perpendicular to the orientation axis, respectively.

If the two residues contained in axial period of 5.68 Å are equivalent, the internal rotation angles, Φ around C′−C$_\alpha$ and Ψ around N−C$_\alpha$ bonds, can be calculated from Miyazawa's equation.[13] Φ and Ψ = 0° for the trans configuration and positive angle results for right-handed rotation.[14] The calculated angles of Φ and Ψ are −102.8° and 96.6° for L-enantiomer (102.8° and −96.6° for D-enantiomer), respectively. The other conformation with Φ = 102.8° and Ψ = −96.6° for L-enantiomer (Φ = −102.8° and Ψ = 96.6° for D-enantiomer) was simultaneously obtained, but it was excluded because of the packing difficulty of side chains as mentioned below. The conformation is illustrated in Figure 3. This conformation is found to be one of the lowest energy from the contour map reported[14,15] and has been initially proposed as one of the possible conformations.[16−18] However, it has not been experimentally observed as far as we know.

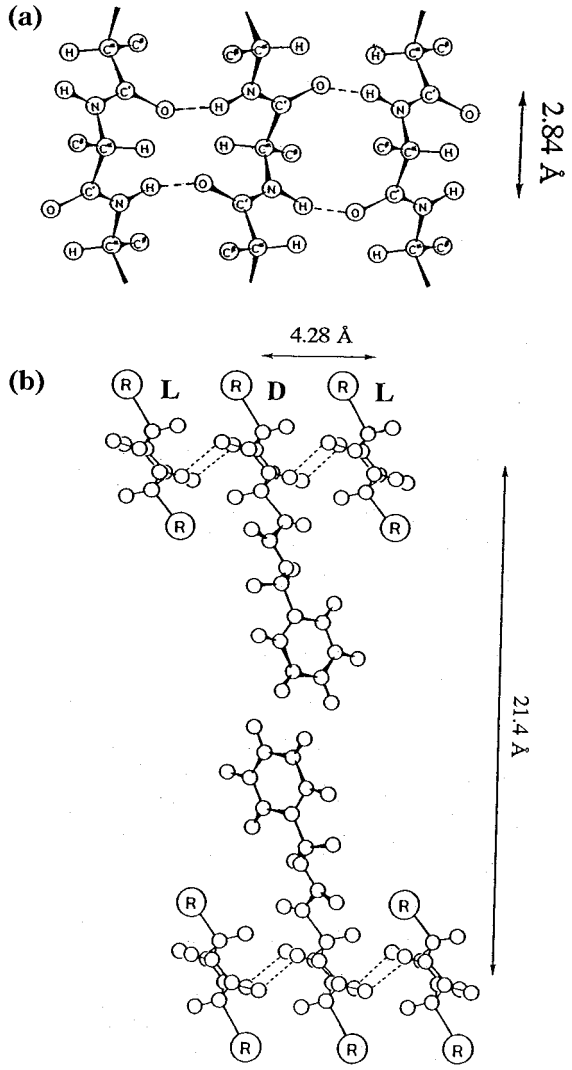

Figure 3. Tentative illustration representing the molecular packing structure of the complex: (a) projected perpendicular to the chain axis and (b) projected along the chain axis. Each molecule has the new conformation with 2-residue 1-turn, which can be produced by the rotation angles of the two bonds, $\Phi = -102.8°$ and $\Psi = 96.6°$ for L-enantiomer (or $\Phi = 102.8°$ and $\Psi = -96.6°$ for D-enantiomer). The L- and D-enantiomers are arranged in alternate and antiparallel fashions and tightly linked by the hydrogen bonds to form the main-chain layer. The side chains are spaced between the layers.

In this new conformation the interchain hydrogen bonds can be well formed between the L- and D-molecules. In other words, the L- and D-molecules can be linked in an alternate fashion to form a layer like β-sheet. Then, the unit cell elucidated from X-ray pattern is understood such that the main-chain layer constructed by a network of hydrogen bonds lies on the $b-c$ plane and that the side chains stick out in the direction of the a-axis. Since the equatorial reflections can be assigned to the unit cell in which only one chain runs, the L- and D-molecules in neighbor within each layer should give the similar projection of electron densities on a plane perpendicular to the chain axis (refer to Figure 3b). Such a situation is satisfied by only the antiparallel arrangement of L- and D-molecules. The frequency of amide A is comparable to those observed in the α-helical conformation, suggesting that the hydrogen bond length (N- - -O) may be around 2.9 Å.[19] Under these conditions, we illustrate one plausible packing structure in Figure 3.

In this packing structure, the side chains are sticking perpendicularly to the main-chain layer and so effectively accommodated between the layers. It should be noticed that such a packing structure cannot be achieved in the other conformation elucidated from the Miyazawa's equation since side chains interrupt the interchain hydrogen bond. This can be easily understood from Figure 3 if the hydrogen and side-chain C_β atoms on the C_α carbon are interchanged.

As a conclusion, the equimolar complex of PBLA and PBDA is formed as the precipitation from chloroform solution. The chain conformation in the complex is somewhat planar with 2-residue 1-turn, which can be produced by the rotation angles of the two bonds, $\Phi = -102.8°$ and $\Psi = 96.6°$ for L-enantiomer (or $\Phi = 102.8°$ and $\Psi = -96.6°$ for D-enantiomer). The L- and D-enantiomers are linked in alternate and antiparallel fashions by the hydrogen bonds to form the main-chain sheet, and the side chains are spaced between the sheets like in a β-sheet structure. It should be noted here that Pauling and Corey[20] have proposed the possible β-sheet structure which can be constructed by the racemic mixture of L- and D-enantiomers. It is called "antiparallel-chain rippled sheet" and has been found experimentally in the achiral polyglycine.[21] The structure in the present study is indeed similar to this type of rippled sheet structure, but the chain conformation is completely different. The identity length of chain in the former is 5.68 Å while the latter conformation is extended with the identity length of 7.00 Å.[20] Thus, we have to give an answer on why the poly(β-benzyl aspartate) preferred the specific conformation found in this study to the usually observed β-conformation.

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