

SHORT COMMUNICATION

Conformation of Poly[γ -(*o*-chlorobenzyl) L-glutamate] and Poly[γ -(*m*-chlorobenzyl) L-glutamate] in the Solid State

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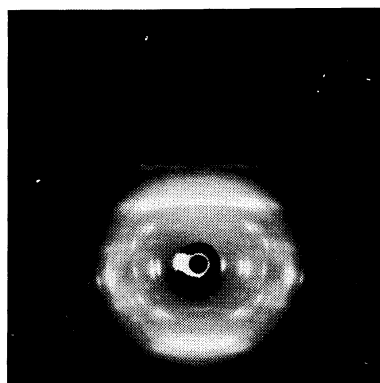
Recently, we reported that poly[γ -(*p*-chlorobenzyl) D-glutamate] (poly[D-Glu(OBzl-*p*-Cl)]) in the solid state takes on a 7-residue 2-turn (7/2) helix conformation.¹ Since the conformation of poly-(γ -benzyl L-glutamate) (poly(L-Glu-OBzl)) is believed to be an 18-residue 5-turn (18/5) helix or approximately so, the substitution of a chlorine atom at the *para* position of the benzene ring changes the conformation slightly. It is of interest to study the effect of the substitution of a chlorine atom at other positions on the conformation. Thus, we proceeded to carry out X-ray diffraction studies on poly[γ -(*o*-chlorobenzyl) L-glutamate] (poly[L-Glu(OBzl-*o*-Cl)]) and poly[γ -(*m*-chlorobenzyl) L-glutamate] (poly[L-Glu(OBzl-*m*-Cl)]) fibers. Here, we report the conformation of poly[L-Glu(OBzl-*o*-Cl)] and poly[L-Glu(OBzl-*m*-Cl)] in the fibers.

Samples of poly[L-Glu(OBzl-*o*-Cl)] and poly[L-Glu(OBzl-*m*-Cl)] were prepared by the method of ester exchange reaction.² Thin oriented fibers were obtained by dipping closed forceps into concentrated chloroform solutions of poly[L-Glu(OBzl-*o*-Cl)] and poly[L-Glu(OBzl-*m*-Cl)], taking them out of the solution, and opening them slowly. A number of birefringent fibers selected under a polarizing microscope were bundled together and annealed at 130°C for 2 h *in vacuo* to remove residual solvent and also to increase crystallinity. X-Ray photographs were taken with a cylindrical or flat-film camera. Cu- $K\alpha$ radiation was monochromatized by a LiF single-crystal monochromator. Calibration of the camera distance was achieved using Si powder which coated the specimen.

Normal and tilted X-ray diffraction photographs



(a)



(b)

Figure 1. X-Ray diffraction photographs of poly[γ -(*o*-chlorobenzyl) L-glutamate] fibers with the axis (a) normal to the beam and (b) tilted at an angle 31° from the normal to the beam. A cylindrical 35 mm radius camera was used.

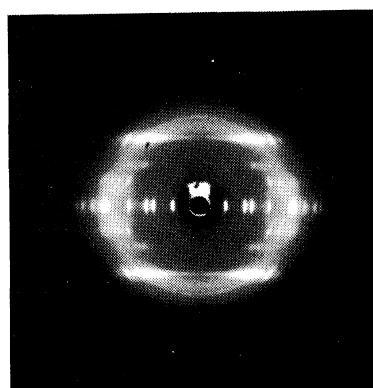
Table I. Relative intensities of layer lines for poly[γ -(*o*-chlorobenzyl) L-glutamate] and poly[γ -(*m*-chlorobenzyl) L-glutamate] and Bessel function order for the 18/5 helix

Layer line number	Bessel function order	Relative intensity ^a	
		Poly[L-Glu (OBzl- <i>o</i> -Cl)]	Poly[L-Glu (OBzl- <i>m</i> -Cl)]
0	0	vvs	vvs
1	7	vvw	vvw
2	4	m	m
3	3	m	m
4	8	vvw	—
5	1	s	s
6	6	vw	—
7	5	vw	—
8	2	w	w
9	9	—	—
10	2	vw	vw
11	5	vvw	—
12	6	—	—
13	1	vvw	—
14	8	—	—
15	3	—	—
16	4	vvw	—
17	7	—	—
18	0	w	w

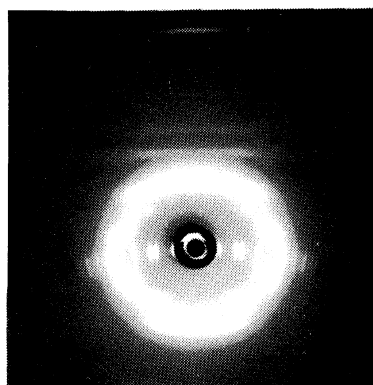
^a Abbreviation used: vvs, very very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak.

of poly[L-Glu(OBzl-*o*-Cl)] fibers are shown in Figure 1. At least 106 Bragg reflections can be observed on the equator and other layer lines, suggesting good crystallinity. A meridional reflection is observed on the 18th layer line and a few remarkably strong reflections are observed on the 5th layer line. This suggests that poly[L-Glu(OBzl-*o*-Cl)] takes on the 18/5 α -helix conformation.³ Table I shows the observed relative intensities for layer lines of poly[L-Glu(OBzl-*o*-Cl)] and the order of the Bessel function expected for the 18/5 helix on the basis of the theory of Cochran *et al.*⁴ The observed intensities are in qualitative agreement with those predicted by the theory. Fourteen equatorial reflections can be indexed on a hexagonal net of $a=15.30 \text{ \AA}$. The repeat distance along the fiber axis (*c*-axis) was determined as $c=27.02 \text{ \AA}$ from the layer line spacings and the (0, 0, 18) reflection.

Normal and tilted X-ray diffraction photographs of poly[L-Glu(OBzl-*m*-Cl)] fibers are shown in Fig-



(a)



(b)

Figure 2. X-Ray diffraction photographs of poly[γ -(*m*-chlorobenzyl) L-glutamate] fibers with the axis (a) normal to the beam and (b) tilted at an angle 31° from the normal to the beam. A cylindrical 35 mm radius camera was used.

ure 2. A number of rather sharp Bragg reflections can be observed on the equator, but most of other layer lines consist of diffuse reflections and a few Bragg reflections. The pattern of the layer lines in Figure 2 indicates that the conformation of poly[L-Glu(OBzl-*m*-Cl)] is the same 18/5 α -helix as poly[L-Glu(OBzl-*o*-Cl)]. Table I also shows the observed relative intensities for the layer lines of poly[L-Glu(OBzl-*m*-Cl)]. The observed intensities are in qualitative agreement with the predicted ones. 58 reflections were observed. Fifteen equatorial reflections can be indexed on a hexagonal net of $a=15.50 \text{ \AA}$. The repeat distance along the fiber axis (*c*-axis) was determined to be $c=27.10 \text{ \AA}$ from the layer line spacings and the (0, 0, 18) meridional

reflection.

The results obtained here suggest that the substitution of a chlorine atom at the *o*- or *m*-position of the benzene ring of poly(L-Glu-OBzl) does not appreciably change the conformation. Takeda *et al.*⁵ suggested that regular arrangement of *p*-chlorobenzyl groups of poly[β -(*p*-chlorobenzyl) L-aspartate] is generated by an inter-helix interaction rather than an intra-helix interaction. Thus, we consider that the conformational variation observed for poly[D-Glu(OBzl-*p*-Cl)] is caused by the inter-helix interaction. It is likely that the chlorine atom of poly[D-Glu(OBzl-*p*-Cl)] points outward from the helix, and the steric effect and/or the dipole-dipole interaction between different helices becomes significant. A detailed structure analysis is now in underway.

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