

SHORT COMMUNICATION

## Existence of the 11-Residue 3-Turn $\alpha$ -Helical Conformation of Polypeptides in the Solid State

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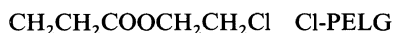
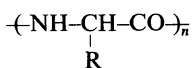
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KEY WORDS 11-Residue 3-Turn  $\alpha$ -Helix / Poly( $\gamma$ -ethyl L-glutamate) /  
Poly( $\gamma$ -2-chloroethyl L-glutamate) / X-Ray Diffraction /

It is well known that a number of synthetic polypeptides take on the  $\alpha$ -helical conformation both in the liquid and solid states. Thirty years ago, Pauling *et al.*<sup>1</sup> proposed four models for the  $\alpha$ -helix, the 48-residue 13-turn (48/13)  $\alpha$ -helix, 18-residue 5-turn (18/5)  $\alpha$ -helix, 15-residue 4-turn (15/4)  $\alpha$ -helix, and 11-residue 3-turn (11/3)  $\alpha$ -helix. At present, the 18/5  $\alpha$ -helix is considered most typical, but the existence of the other three models of the  $\alpha$ -helix can not be ruled out for synthetic polypeptides. On the other hand, most proteins have some portions consisting of  $\alpha$ -helices containing 3.3 to 3.9 residues per turn.

Several studies<sup>2,3</sup> have been reported on the molecular conformation of polypeptides in which chlorine atoms are substituted at the end of the side chain. These chlorine atoms are expected to serve as the heavy atoms in X-ray structural analysis.

In this work, poly( $\gamma$ -ethyl L-glutamate) (PELG) and poly( $\gamma$ -2-chloroethyl L-glutamate) (Cl-PELG) were investigated by X-ray measurements.



Here, the molecular conformations of PELG and Cl-PELG in their fibers are reported.

The PELG sample was prepared by an ester exchange reaction, and that of Cl-PELG was pre-

pared by polymerizing an NCA using triethylamine as an initiator. Elementary analysis showed C, 42.18%; H, 5.04%; N, 7.04%; Cl, 17.51%, which is comparable to the following calculated values: C, 43.88%; H, 5.26%; N, 7.31%; Cl, 19.50%. Oriented fibers were obtained by dipping closed forceps into concentrated chloroform solutions, taking them out of the solutions, opening the forceps slowly, and drying the fiber spun between two tips of the forceps. A number of birefringent fibers selected under a polarizing microscope were bundled together and annealed at 120°C for several hours *in vacuo* to remove any residual solvent and promote crystallization. X-Ray photographs were taken with a cylindrical camera. Cu-K $\alpha$  radiation was monochromatized by a LiF single crystal monochromator or a Ni-filter. The camera radius was calibrated using Si powder which completely coated the specimens.

Normal and tilted X-ray photographs of Cl-PELG fibers are shown in Figure 1. Eight layer lines with  $l=0, 1, 2, 3, 5, 6, 8,$  and  $11$  can be observed and most of them consist of diffuse streaks. A meridional reflection can be seen on the 11th layer line ( $\zeta^{-1}=1.506 \text{ \AA}$ ), and there are a few strong reflections on the third layer line ( $\zeta^{-1}=5.53 \text{ \AA}$ ). These features indicate that the main-chain conformation of Cl-PELG is the 11-residue 3-turn  $\alpha$ -helix.

The X-ray photographs of PELG fibers were very similar to those of Cl-PELG, though not as good as those of Cl-PELG. The main-chain conformation of

**Table I.** Relative intensities of observed layer lines for poly( $\gamma$ -ethyl L-glutamate) and poly( $\gamma$ -2-ethyl L-glutamate) and the order of the Bessel function for the 11/3 helix<sup>a</sup>

Layer line number	Bessel function order	Relative intensity	
		PELG	Cl-PELG
0	0	vvs	vvs
1	4	m	m
2	-3	w	vw
3	1	vs	vs
4	5	vw	—
5	-2	w	w
6	2	vw	vw
7	-5	—	—
8	-1	vvw	vvw
9	3	—	—
10	-4	—	—
11	0	s	s

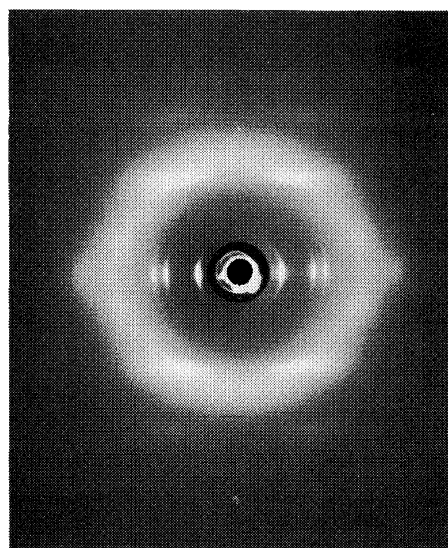
<sup>a</sup> Abbreviations used: vvs, very very strong; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak.

**Table II.** Identity periods along the fiber axis, helical pitches, and axial translations per residue of poly( $\gamma$ -ethyl L-glutamate) and poly( $\gamma$ -2-chloroethyl L-glutamate)

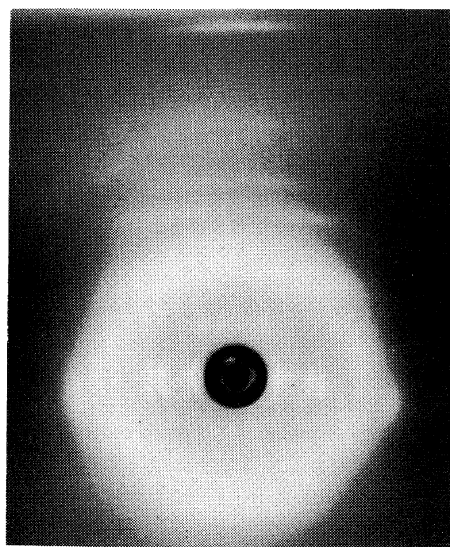
	Identical period	Helical pitch	Axial translation
	Å	Å	Å
PELG	16.4	5.47	1.48
Cl-PELG	16.56	5.53	1.506

PELG in the fiber is also considered to be the 11-residue 3-turn  $\alpha$ -helix.

Table I shows the relative intensities for the layer lines of PELG and Cl-PELG, and the order of the Bessel function expected for the 11/3 helical conformation on the basis of the theory of Cochran *et al.*<sup>4</sup> These intensities are in qualitative agreement with those predicted by the theory. Table II shows the identity periods along the fiber axis, the helical pitches, and the axial translations for each residue of PELG and Cl-PELG. The identity period was determined to be 16.4 Å for PELG and 16.56 Å for Cl-PELG from the layer line spacings and the 0011



(a)



(b)

**Figure 1.** X-Ray diffraction photographs of poly( $\gamma$ -2-chloroethyl L-glutamate) fibers with the axis (a) normal to the beam and (b) tilted at angle 31° from the normal to the beam.

meridional reflections. The axial translations of PELG and Cl-PELG were 1.48 Å and 1.506 Å, respectively. These values indicate that the 11/3  $\alpha$ -helical conformation of Cl-PELG has a somewhat

longer period than that of PELG, suggesting that substitution of a chlorine atom at the end of the side chain has effect on the detailed molecular conformation of a polypeptide.

A study was also made of unannealed samples of PELG and Cl-PELG fibers, and the same results as those for annealed samples were obtained. Thus, it is thought that the 11/3  $\alpha$ -helical conformation is one of the stable conformations of polypeptides.

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