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Solid State Conformation of Poly-N^5-(3-hydroxypropyl)-L-glutamine by X Rays

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The helix–coil transition of poly-N^5-(3-hydroxypropyl)-L-glutamine, (PHPG), in water–methanol mixtures has been studied by nuclear magnetic resonance and circular dichroism spectroscopy but the actual conformation of the polymer was not clearly defined.[1] This work deals with the conformational properties of PHPG in the solid state obtained by an x-ray investigation.

Methods and Materials

Poly-N^5-(3-hydroxypropyl)-L-glutamine samples, with molecular weight about 200 000, were synthesized as described before.[1] PHPG films were prepared by stroking out a drying film until it was solid. Fibers were also drawn by means of a claw from a viscous solution of the sample. The solvents used were water and water–methanol mixtures. Both the films and the fibers were then heated to over 100 °C in vacuo for several hours to remove the solvent and to promote crystallinity. Their density was determined by flotation using benzene–carbon tetrachloride mixture allowing the sample to reach the equilibrium position. After 1 day the measured density was 1.23 g cm^{-3}. The films and the fibers were examined in a flat camera with the sample-to-photographic film distance, d, variable from 4 to 10 cm, with Ni filtered Cu Kα radiation from a fine and normal focus x-ray tube and a 0.6 mm pinhole. Tilted specimens and equiinclination techniques were also used.

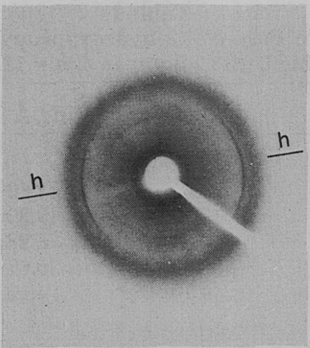

Figure 1. Normal beam x-ray diffraction pattern of PHPG oriented film; flat camera $d = 6$ cm, Cu Kα radiation; PHPG film and stroking direction horizontal (h line).

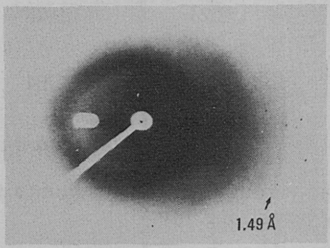

Figure 2. Equiinclination x-ray diffraction pattern of PHPG oriented film; flat camera $d = 4$ cm, Cu Kα radiation; PHPG film and stroking direction horizontal; x-ray beam at 31° to normal of the stroking direction (fiber axis) to record 1.49 Å reflection.

Results and Discussion

The diffraction pictures showed that, besides amorphous regions, some crystallinity is present in the examined samples, which also proved to be sufficiently oriented for analysis (Figure 1). Two main features of x-ray diffraction pattern are prominent: a sharp meridional reflection at 1.49 Å (Figure 2) and a layer line at 5.4 Å with a strong near meridional reflection. These data are typical of the Fourier transform of an α-helix, the helices being oriented parallel to the stroking direction.[2–5]

A detailed inspection of x-ray pictures, taken under different diffraction geometry, shows several reflections whose observed spacings, d_0, and estimated intensities, I_0, are reported in Table I. With the above data, we tried to define the unit cell dimensions. The ratio between the helical pitch (5.4 Å) and the axial translation per residue (1.49 Å) gives the number of units per turn of helix, namely 3.62 which closely corresponds to a 29/8 α-helix.[5] In addition, the relative intensities of the observed layer lines agree, well enough with the diffraction pattern of this type of helix[2] although the absence of recorded intensities for the 13th and, particularly, the 21st layer lines may appear instances of disagreement.[6] Nevertheless this behavior can be explained by remembering that the treatment of Cochran, Crick, and Vand[2] is valid in detail only when the conformational equivalence of the monomeric units (backbone and side-chain atoms) along the helix is strictly fulfilled. As the side-chain length is large the structure becomes less ordered and the previous theory may sometimes break down.

We constructed a molecular model according to the 29/8 α-helical conformation by means of a mathematical method, developed in our laboratory.[7] The results do not indicate any steric interference between the side chain and the polypeptide backbone. We may therefore assume for the true helix repeat

Table I
X-Ray Data for Poly-N^5-(3-hydroxypropyl)-L-glutamine (Orthorhombic Unit Cell a = 14.6; b = 12.3; c = 43.2 Å)

hkl	d_0, Å	d_c, Å	I_0[a]
	Equator		
100	14.6	14.60	vvs
010	12.30	12.30	s
210	6.30	6.28	m
120	5.65	5.67	mw
030	4.15	4.10	s
	8th Layer Line		
118	4.75	4.68	vs
208	4.32	4.34	m
028	4.03	4.06	m
	16th Layer Line		
0,2,16	2.43	2.47	w
0,3,16	2.24	2.25	w
	24th Layer Line		
1,3,24	1.63	1.64	w
	29th Layer Line		
0,0,29	1.49	14.9	s

[a] Abbreviations used: w, weak; m, medium; s, strong; vs, very strong; vvs, very very strong.

the value of 29 × 1.49 = 43.2 Å which represents the c parameter of the unit cell.

Among the equatorial reflections the two at 14.6 and 12.30 Å may be directly related to the distance between the helices. This is also supported by the increase of these spacings in swollen low-crystalline samples. In conclusion we found that all observed reflections can be indexed according to an orthorhombic unit cell with a = 14.6, b = 12.3, and c = 43.2 Å. Miller's indices are reported in Table I together with the calculated spacing d_c. The calculated density is $D_c = n1.15$ g cm^{-3} where n is the number of helices crossing the orthorhombic cell. Comparison with the observed density indicates that such a cell is crossed by one α-helix only. The difference of about 7% between the measured density and the calculated crystal density might not be remarkable were it not for the fact that the measured density is higher despite a substantial amorphous content of the samples as evidenced by halos in the diffraction patterns. This is, of course, an unsatisfactory situation and would normally be taken to imply that the structure under consideration is incorrect. Since there are strong indications that the chains in the polymer have the α-helical configuration it is desirable to examine possible alternative explanations of the density anomaly. One such explanation would be that the polymer contained a certain percentage of water, because stringent drying conditions have not been used; this appears particularly reasonable in view of the findings of Astbury et al.[8] that certain synthetic polypeptides crystallize with a half molecule of water per residue. A second possibility is that the amorphous regions of the polymer may contain some interchain hydrogen bonds. It may be considered that this interchain bonding would tend to pull the chains closer together and hence lead to the higher density in the amorphous regions. In addition the higher value of the measured density might come from absorption and/or adsorption of the heavier mixture component by the semicrystalline sample,[9] or, alternatively, this would be an instance of a real anomaly as has been proposed for poly(γ-methyl L-glutamate).[10] Nevertheless, it is our feeling that this discrepancy appears to be outside the limits of experimental errors.

The reflections of the lower order layer lines appear to be broad. This suggests a disordered crystalline structure in which α-helical chains are packed parallel to each other and in an orthorhombic array, but randomly arranged along and about their lengths. Such disorder would lead to the appearance of sharp spectra for truly equatorial spacings and continuous intensity distribution on the other layer lines.[11]

Taking into account the possibility of correlating the polypeptide conformation in the solid state and in solution, the present results strongly indicate that PHPG in solution assumes the α-helical conformation.

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Glass Transition Temperatures of Regularly Alternating Acrylonitrile–Vinyl Acetate Copolymers

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It has been suggested recently[1-5] that the conformational entropy may be used, as a parameter characterizing the intramolecular polymer chain flexibility, to understand the sequence distribution–glass transition effects observed[6] in copolymers. Conformational entropies calculated for copolymers and their constituent homopolymer chains have been utilized[1-5] to predict deviations away from bulk additive sequence distribution–glass transition behavior described by relations such as the Fox equation.[7]

If the conformational entropy calculated for a given copolymer chain is greater (less) than the weighted sum of entropies calculated for the constituent homopolymer chains, then the glass transition temperature, T_g, is expected to be lower (higher) than the value predicted by the Fox equation or any other bulk additive relation. This approach has been applied[1-5] to a large number of copolymer systems and has been successful in predicting negative, positive, and no deviations from bulk additive T_g–sequence distribution behavior when they occur.

Chen[8] has recently described the synthesis of 1:1 regularly alternating copolymers of acrylonitrile (AN) and vinyl acetate (VA). Although few details were given, a T_g = 85 °C was reported for this regularly alternating copolymer system. This is ca. 20 °C above the T_g predicted by the Fox equation based on the T_g's of the AN (T_g = 105 °C) and VA (T_g = 30 °C) homopolymer chains.[9]

Since both AN and VA monomers had been treated in previous copolymer conformational entropy calculations[1-5] performed on the AN-styrene, AN-α-methylstyrene, and VA–vinyl chloride systems, some of the results of these previous calculations were supplemented by the present calculations performed on AN–VA dyads to obtain the conformational entropies of the regularly alternating copolymers. Chen