Optical Rotatory Dispersion of Poly-L-tryptophan in the Far Ultraviolet Region

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FAR ultraviolet optical rotatory dispersion (o.r.d.) properties of poly-L-tryptophan in solution have not yet been described.[1-3] By the technique of Gratzer and Doty,[4] we prepared a block copolymer formed approximately by a 160-residue sequence of γ-ethyl-DL-glutamate and by a 30-

residue sequence of L-tryptophan. The copolymer has two advantages, (i) it is completely soluble in trifluoroethanol, a solvent transparent in the far u.v. region, (ii) the solubilizing portion does not interfere in the o.r.d. measurements.

The u.v. spectrum of the block copolymer shows typical indole absorptions at 280 mμ and 218 mμ. Absorption of the peptide bond appears at 195 mμ.

The o.r.d. spectrum of the block co-polymer is shown in the Figure. A positive Cotton effect is present in the 280 mμ region. Sharp peaks appear at 233 mμ and 200 mμ and a deep trough is present at 218 mμ.

Our findings are completely different from those reported by Fasman and co-workers.[1] According to these authors, the o.r.d. curve of a film of poly-L-tryptophan in the range 330—200 mμ revealed a large *negative* Cotton effect at 233 mμ. Moreover in dimethylformamide they found a linear relationship between b_0 values of copolymers of various ratios of L-tryptophan and γ-benzyl-L-glutamate and the copolymers' compositions. On the basis of these results Fasman *et al.* concluded that poly-L-tryptophan has a right-handed helical conformation in dimethylformamide. We found a *positive* Cotton effect at 233 mμ. However the strong overlapping of Cotton effects of peptide main-chain chromophores and indole side-chain chromophores does not allow any safe conclusion on the conformation of the poly-L-tryptophan.

We also measured the o.r.d. properties of the model compound, $PhCH_2 \cdot O \cdot CO \cdot (L\text{-}Trp)_2 \cdot OMe$ in trifluoroethanol. In the dipeptide, the side-chain chromophores exhibit very weak optical activity (Figure). On the contrary, here, these chromophores show strong optical activity in the polymer. We can therefore conclude that the indole side-chain groups in the polymer are in a dissymmetric environment, and the polymer probably exists in helical conformation in solution. More complete results including circular dichroism (c.d.) measurements in the far u.v. region on the block copolymer and o.r.d. and c.d. measurements on random co-polymers of various ratios of L-tryptophan and γ-ethyl-L-glutamate, will be reported elsewhere.

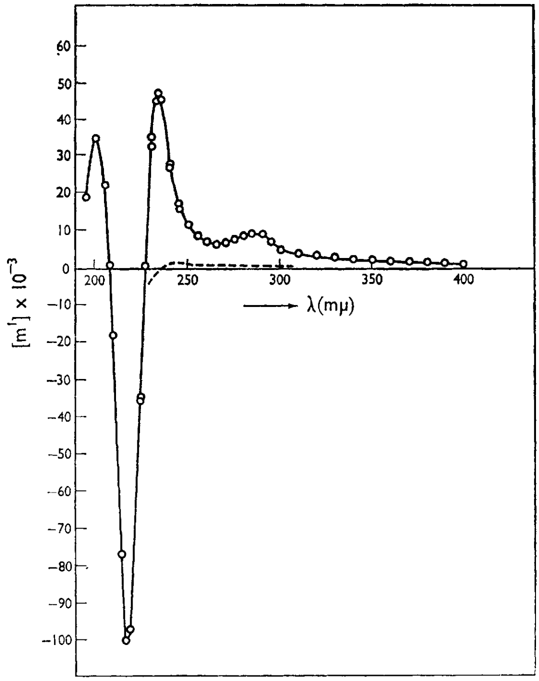

FIGURE. *Optical rotatory dispersion in trifluoroethanol of* $[\gamma\text{-ethyl-DL Glu}]_{160}$ $[L\text{-Trp}]_{30}$ (○) *and of the model compound* $PhCH_2 \cdot O \cdot CO \cdot (L\text{-}Trp)_2 \cdot OMe$ (- - -). [m'] is mean residue rotation.

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