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## Infrared Spectra and Molecular Conformations of Poly- $\gamma$ -methyl-DL-glutamate

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Polyamino acids are known to take various conformations, namely the  $\alpha$  helix,  $\beta$ -form or disordered form. For conformation diagnoses, the amide I and II bands in the infrared spectra<sup>1)</sup> are extensively used. In our previous study, the amide V bands arising from the N-H out-of-plane bending mode were also found useful for conformation studies.<sup>2)</sup> With the observed amide bands, the conformations of racemic polyamino acids were analysed in the present study.

Poly- $\gamma$ -methyl-DL-glutamate (PMDLG) were synthesized by the Leuchs method. Racemic  $\gamma$ -methyl-DL-glutamate (mp 185°C) was converted to *N*-carboxyamino acid anhydride [A] (mp 72°C), which was polymerized in dioxane, with the initiator [I]

of sodium methoxide or *n*-hexylamine. The polymer was precipitated by pouring the reaction mixture into diethyl ether, filtered, washed, and dried. The molecular weight of the polymers were estimated by viscosity measurements in dichloroacetic acid.<sup>3)</sup> Infrared absorption spectra were observed with solid films cast from chloroform solution or with potassium bromide discs. Hitachi 225 or EPI-L spectrophotometers were used for the infrared measurements.

Fig. 1A shows the infrared spectrum of PMDLG ( $A/I=100$ ). The amide I bands at 1685 and 1625  $\text{cm}^{-1}$  indicate the existence of the  $\beta$ -form. However, the strong amide I band at 1655  $\text{cm}^{-1}$ , amide II band at 1540  $\text{cm}^{-1}$ , and the strong amide V band at 635  $\text{cm}^{-1}$  indicate that the predominant conformation of this polymer is the  $\alpha$  helix. This observation is similar to the case of copoly- $\gamma$ -

1) T. Miyazawa and E. R. Blout, *J. Am. Chem. Soc.*, **83**, 712 (1961) and references cited therein.

2) T. Miyazawa, Y. Masuda and K. Fukushima, *J. Polymer Sci.*, **62**, S62 (1962); Y. Masuda and T. Miyazawa, *Makromol. Chem.*, **103**, 261 (1967).

3) P. Doty, J. H. Bradbury and A. M. Holtzer, *J. Am. Chem. Soc.*, **78**, 947 (1956).

methyl-D,L-glutamate ( $D:L=1:1$ ,  $A/I=200$ ) which exhibits a strong amide V band at  $630\text{ cm}^{-1}$ . In the far infrared region, the characteristic band<sup>4)</sup> of  $\alpha$ -helical polyglutamate esters is also observed at  $410\text{ cm}^{-1}$  for PMDLG.

For the low-molecular-weight PMDLG with  $A/I=20$  or  $8$ , the amide I bands were observed at  $1690$  and  $1630\text{ cm}^{-1}$ , amide II bands at  $1525\text{ cm}^{-1}$ , and the amide V band at  $700\text{ cm}^{-1}$ . Accordingly, these molecules are predominantly in the  $\beta$ -form. On the other hand, Fig. 1B shows the infrared spectrum of PMDLG with  $A/I=4$ . The amide I bands at  $1695$ ,  $1660$ , and  $1633\text{ cm}^{-1}$ , the amide II bands at  $1545$  and  $1530\text{ cm}^{-1}$ , and the amide V bands at about  $700$  and  $670\text{ cm}^{-1}$  indicate that there are some fractions of the disordered form together with the  $\beta$ -form. This conformation of PMDLG ( $A/I=4$ ) makes contrast with the case of PMLG ( $A/I=4$ ) which is predominantly in the  $\beta$ -form. Thus infrared observations are useful especially for conformation diagnoses of DL-poly-peptides which do not exhibit optical rotatory dispersion.

4) T. Miyazawa, K. Fukushima, S. Sugano, and Y. Masuda, in "Conformation of Biopolymers," ed. by G. N. Ramachandran, Academic Press, London (1967), p. 557.

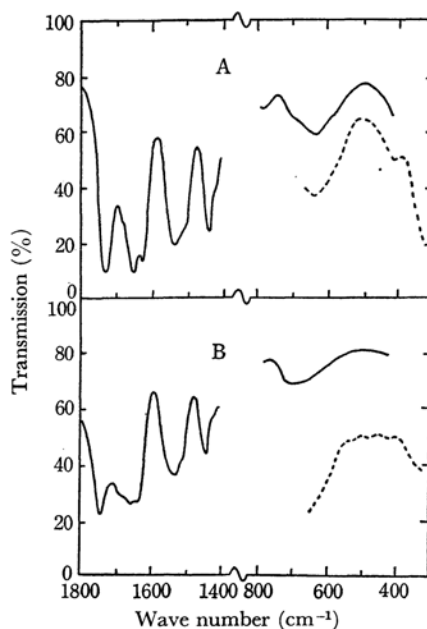


Fig. 1. Infrared Spectra of Poly- $\gamma$ -methyl-DL-glutamate,  $A/I=100$  (A) and  $A/I=4$  (B); measured with Hitachi 225 (solid line) or EPI-L (broken line).

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