

## 報 文

## ポリグリシンの低温構造とC - H...O = C水素結合\* (英文)

KIYOSHI . KUROIWA \*\* S . KRIMM \*\*\*

ポリグリシン 構造(型)と 構造(helix型)の常温スペクトルから - 170 までの赤外スペクトルを測定し, 温度による構造変化, C - H...O = C水素結合, N - H...O = C水素結合の変化を比較検討した。ポリグリシン 型はどんな温度にてもC - H...O = C水素結合はないが, 型は常温, 低温にても存在しCH<sub>2</sub>伸縮振動が4本認められた。鎖間距りは低温になるにしたがって短くなり, N - H...O = C結合は強くなるのに反してC - H...O = C結合は鎖の回転によってその結合距りが遠くなり, 吸収波数がだんだんと 型のCH<sub>2</sub>stの吸収位置に近づいてくる。

### Low Temperature Infrared Spectra of Polyglycines and C - H...O = C Hydrogen Bonding in Polyglycine

#### INTRODUCTION

A modified structure of polyglycine has recently been proposed<sup>1</sup> in which it was suggested that C - H...O = C hydrogen bonds could be formed in addition to the usual N - H...O = C hydrogen bonds. In order to test this proposal, a study was undertaken of the infrared spectra of polyglycines and in the C - H stretching region.<sup>2</sup> Coupled with the evidence for antiparallel chains in the crystal structure of polyglycine,<sup>3</sup> this analysis showed that C - H...O = C bonds could indeed be present in the structure of the form. Although these spectroscopic arguments are compelling, other explanations of the data may be possible. It is therefore important that new experimental results be obtained which would provide further tests of the suggested spectral interpretations. To this end we have studied the low-temperature infrared spectra of polyglycines and . It was hoped that in this way we might be able to modify the N - H...O = C interaction (since the structure would contract at low temperatures), and thereby influence

the C - H...O = C interaction in an interpretable manner.

#### EXPERIMENTAL AND RESULTS

The polyglycine used in this study (and obtained from New England Nuclear Corp.) was of high but unknown molecular weight. Polyglycine I was prepared by casting a film from dichloroacetic acid solution. Polyglycine was obtained by precipitation with water from a 1% solution of the polymer in saturated aqueous lithium bromide.

Specimens were deposited on AgCl plates, and the spectra were obtained with a Perkin-Elmer 421 double-beam grating spectrophotometer. An evacuated Dewar-type cold cell was used to cool the specimen from a reservoir of liquid nitrogen, and a thermocouple in contact with the sample was used for measuring its temperature.

The infrared spectra of polyglycine I at room temperature and at about - 170 . are shown in Figures 1a and 1b, respectively, and the comparable spectra for polyglycine are given in Figures 2a and 2b. Expanded spectra of the CH<sub>2</sub> stretching region of polyglycine are shown in Figures 3a and 3b. The spectral changes with temperature are completely reversible. In Table I we compare

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\*\* Central Customs Laboratory, 531, IWASE, MATSUDO, CHIBA.

\*\*\* University of Michigan, Ann, Arbor, Michigan. U.S.A.

the frequencies of some of the bands of polyglycines and at the two temperatures.

## DISCUSSION

In the earlier spectroscopic study<sup>2</sup> it was pointed out that the two additional bands in the  $\text{CH}_2$  stretching region of polyglycine, observed at 2977 and 2805  $\text{cm}^{-1}$  in the present work, could be

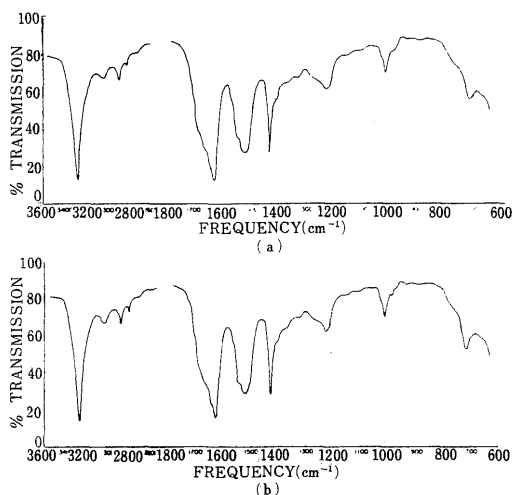


Fig.1. Infrared spectra of polyglycine films : (a) at room temperature ; (b) at about - 170 °C .

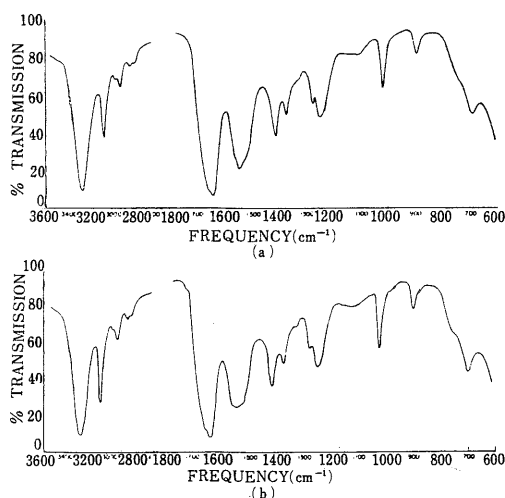


Fig.2. Infrared spectra of polyglycine films : (a) at room temperature ; (b) at about - 170 °C .

assigned to stretching modes of  $\text{CH}_2$  groups which participate in hydrogen bonding. The two bands at 2935 and 2850  $\text{cm}^{-1}$  correspond to modes of unbonded  $\text{CH}_2$  groups, this being indicated by the closeness of these frequencies to those of polyglycine I (where no  $\text{C} - \text{H} \cdots \text{O} = \text{C}$  hydrogen bonding can occur). The presence of both types of  $\text{CH}_2$  groups is consistent with an antiparallel chain structure for polyglycine,<sup>3</sup> since in such a structure not all  $\text{CH}_2$  groups can form  $\text{C} - \text{H} \cdots \text{O} = \text{C}$  hydrogen bonds.<sup>4</sup> The existence of an upshifted  $\text{CH}_2$  stretching frequency (2977  $\text{cm}^{-1}$ ) as well as a downshifted Frequency (2805  $\text{cm}^{-1}$ ) was shown<sup>2</sup> to imply that one  $\text{C} - \text{H}$  stretching force constant was increased over the normal value at the same time that the other constant (associated with the bonded  $\text{C} - \text{H}$ ) was lowered. It is in the light of these arguments that we wish to see if the effects of temperature on the spectra can be interpreted.

## Spectrum of Polyglycine

As can be seen from Figure 1 and Table , the spectrum of polyglycine is altered very little by cooling to - 170 °C . There is a small decrease in



Fig.3. Expanded infrared spectra of polyglycine films in the  $\text{CH}_2$  stretching region : (a) (top curve) at room temperature, (b) (bottom curve) at about - 170 °C .

the N - H stretching frequency ( amide A band ), which could be indicative of a slightly stronger N - H...O = C hydrogen bond. This is not unexpected, since the structure should contract with lowering of the temperature. There is no perceptible change in the amide and amide frequencies, but the amide V frequency ( the N - H out-of-plane deformation modo<sup>5)</sup> does increase at the lower temperature, also consistent with a stronger N - H...O = C hydrogen bond. The CH<sub>2</sub> stretching frequencies decrease slightly at lower temperature, probably as a result of the environmental change resulting from closer contacts between CH<sub>2</sub> groups which face each other between the hydrogen-bonded sheets of this extended polypeptide chain structure.<sup>6</sup> The small changes in the spectrum of polyglycine I can thus be understood on the basis of slightly closer approaches between chains resulting from contraction of the structure at lower temperatures.

### Spectrum of Polyglycine

The spectrum of polyglycine is altered more substantially than that of polyglycine I by decrease of temperature. There are evident effects both on the N - H...O = C hydrogen bonds and on the CH<sub>2</sub> stretching frequencies, and we shall consider these in turn.

TABLE

Frequencies of Some Bands of Polyglycines and

	Frequency, cm <sup>-1</sup> ,	
	Room temperature	-170 °C.
Polyglycine I		
Amide A	3295	3290
Amide B	3075	3078
CH <sub>2</sub> stretch	2920	2917
	2850	2848
Amide I	1624	1624
Amide II	1520	1520
CH <sub>2</sub> bend	1432	1432
Amide V	708	720
Polyglycine II		
Amide A	3290	3275
Amide B	3090	3097
CH <sub>2</sub> stretch	2977	2947
	2935	2937
	2850	2850
	2805	2815
Amide I	1640	1635
Amide II	1550	1562
		1545
CH <sub>2</sub> bend	1414	1420
Amide V	750	760

The spectral changes in bands associated with the peptide group indicate that the N - H...O = C hydrogen bond is significantly stronger in the low temperature structure. This is evident from the decreases in the N - H stretching (amide A) and C = O stretching (amide ) frequencies, and from the increase in the N - H out-of-plane deformation (amide V) frequency. The amide band (N - H in-plane deformation plus C - N stretch) shows a multiple structure, with a component at 1562 cm.<sup>-1</sup> being intensified in the low temperature spectrum. If this corresponds to the 1550 cm.<sup>-1</sup> band in the room temperature spectrum, then this shift would also be consistent with an increase in the N - H...O = C hydrogen bond strength in the low-temperature structure. ( The multiple structure of the amide

band has a counterpart in that of the amide band: in Figure 2b there is a definite shoulder at 1655 cm.<sup>-1</sup> in addition to the main peak at 1635 cm.<sup>-1</sup> This is not unexpected, since it can be shown<sup>4</sup> that in an antiparallel chain structure of polyglycine not all N - H...O = C hydrogen bonds are equivalent. Those between similarly directed chains have a different length than those between oppositely directed chains in the structure. This would account for the multiple structures of the amide and amide bands, as well as for the greater breadth of the amide A band in polyglycine as compared to polyglycine . ) A better indication of the change in N - H...O = C hydrogen bond strength is obtained by calculating the unperturbed N - H stretching frequencies, since the amide A and amide B bands are believed to originate from a Fermi resonance between the N - H stretching frequency and the overtone of the amide mode.<sup>7</sup> According to this calculation, the unperturbed frequency in the room temperature spectrum is 3280 cm.<sup>-1</sup> while that in the low - temperature spectrum is 3248 cm.<sup>-1</sup> The observed intensity ratios (B)/ (A) (based on integrated band intensities) are in reasonable agreement with the predicted ratios:<sup>7</sup> 0.095 compared to 0.093 for the room-temperature spectrum, and 0.145 compared to 0.179 for the lowtemperature spectrum. There may still be some difficulties with this analysis,<sup>8</sup> but both it and the spectral data strongly indicate a significant increase in N - H...O = C hydrogen bond strength in the low-temperature

structure.

On the other hand, the changes in CH<sub>2</sub> frequencies indicate that the C - H...O = C bond weakens with decreasing temperature. As can be seen from Figure 3 and Table , while lowering the temperature has essentially no effect on the unperturbed CH<sub>2</sub> stretching modes at 2850 and 2935 cm.<sup>-1</sup> the perturbed modes at 2805 and 2977 cm.<sup>-1</sup> undergo large shifts, to 2815 and 2947 cm.<sup>-1</sup> respectively. The CH<sub>2</sub> bending mode also shifts in the direction of its unperturbed value ( taken to be the frequency in polyglycine ). This would be consistent with a weakening of the C - H...O = C bond. The large change in the upshifted frequency, from 2977 to 2947 cm.<sup>-1</sup> is not unreasonable : we anticipate that as the influence of the hydrogen bond on one C - H force constant diminishes, the secondary effect to raising the force constant of the other C - H bond<sup>2</sup> should also lessen. These two effects need not be linearly proportional to each other ; in fact, it may well be that the secondary effect is a very sensitive function of the primary perturbation of one C - H bond. It should be noted that these results lend further support to the assignment<sup>2</sup> of the 2805 and 2977 cm.<sup>-1</sup> bands to stretching modes of a different set of CH<sub>2</sub> groups than the ones which give rise to the 2850 and 2935 cm.<sup>-1</sup> bands.

### Attractive versus Repulsive C - H...O = C Interaction

In this and the previous<sup>2</sup> discussions we have been assuming that the spectroscopic data are to be interpreted in terms of an attractive C - H...O = C interaction, that is in terms of what could be called a bond. It might be argued, however, that while the 2805 and 2977 cm.<sup>-1</sup> bands of polyglycine represent perturbed CH<sub>2</sub> stretching modes, the perturbation could as well be repulsive instead of attractive. The present results from low temperature spectra indicate that the latter possibility is unlikely.

In the first place, if the interaction were repulsive we would expect the perturbation of the CH<sub>2</sub> stretching frequencies to increase at low temperature. This would follow from the fact that the structure contracts at low temperature (as eviden-

ced, for example, by the stronger N - H...O = C bond), with a consequent enhancement expected of any repulsion effects already present in the room temperature structure. Also the stronger N - H...O = C bond could accommodate a higher C - H...O = C repulsion energy. In fact, we see that the opposite effect is observed, namely that the displaced CH<sub>2</sub> stretching frequencies are less perturbed at low temperature : the 2805 and 2977 cm.<sup>-1</sup> bands move to 2815 and 2947 cm.<sup>-1</sup> respectively, closer to the unperturbed frequencies. This behavior is not consistent with a repulsive C - H...O = C interaction. On the other hand, the change to a structure with stronger N - H...O = C and weaker C - H...O = C hydrogen bonds is a feasible one, since it is known that polyglycine can form a structure in which only N - H...O = C hydrogen bonds occur<sup>9</sup>. It is only necessary to reverse the small rotation of each chain about its axis which was invoked to get from the above structure to one in which C - H...O = C bonds could be made.<sup>1</sup> Such a change is probably associated with the stronger N - H...O = C bond which can form in the contracted structure, resulting in a relatively greater decrease in energy even though the C - H...O = C bond becomes weaker.

Secondly, in the low-temperature spectrum of polyglycine the upshifted CH<sub>2</sub> stretching frequency ( now at 2947 cm.<sup>-1</sup> ) has moved much closer to the unperturbed mode than has the downshifted frequency (now at 2815 cm.<sup>-1</sup>). This implies that the more significant perturbation in this case is associated with a lowering of a CH<sub>2</sub> stretching frequency. ( This was not evident from the room temperature spectrum since both shifts were about the same. ) Since this corresponds to the usual behavior of a stretching mode when hydrogen bonding occurs, we can conclude that the interaction leading to the perturbation of the CH<sub>2</sub> frequency is an attractive one.

The changes in the spectra of polyglycines and at low temperature can therefore be interpreted in terms of the presence of a C - H...O = C hydrogen bond in the structure of the latter, and further provide strong direct evidence that this interaction is an attractive one.

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