

Low Temperature Infrared Spectra of Polyglycines and C—H···O=C Hydrogen Bonding in Polyglycine II

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Synopsis

Infrared spectra of polyglycines I and II obtained at -170°C . have been compared with those obtained at room temperature. The changes in frequency of some of the C—H stretching bands are consistent with the earlier suggestion that C—H···O=C hydrogen bonds are present in the structure of polyglycine II.

INTRODUCTION

A modified structure of polyglycine II has recently been proposed¹ 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 I and II in the C—H stretching region.² Coupled with the evidence for antiparallel chains in the crystal structure of polyglycine II,³ this analysis showed that C—H···O=C bonds could indeed be present in the structure of the II 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 I and II. 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 II was obtained by precipitation with water from a 1% solution of the polymer in saturated aqueous lithium bromide. Specimens were

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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°C . are shown in Figures 1*a* and 1*b*, respectively, and the comparable spectra for polyglycine II are given in Figures 2*a* and 2*b*. Expanded spectra of the CH_2 stretching region of polyglycine II are shown in Figures 3*a* and 3*b*. The spectral changes with temperature are completely reversible. In Table I we compare the frequencies of some of the bands of polyglycines I and II at the two temperatures.

DISCUSSION

In the earlier spectroscopic study² it was pointed out that the two additional bands in the CH_2 stretching region of polyglycine II, observed at 2977 and 2805 cm^{-1} in the present work, could be assigned to stretching

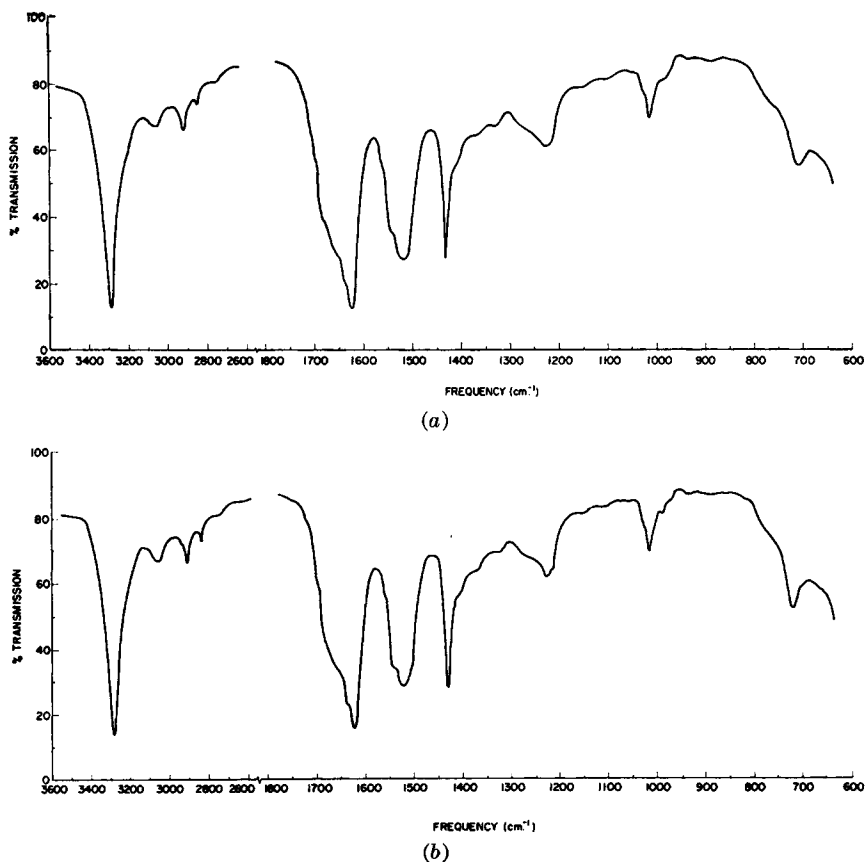


Fig. 1. Infrared spectra of polyglycine I films: (a) at room temperature; (b) at about -170°C .

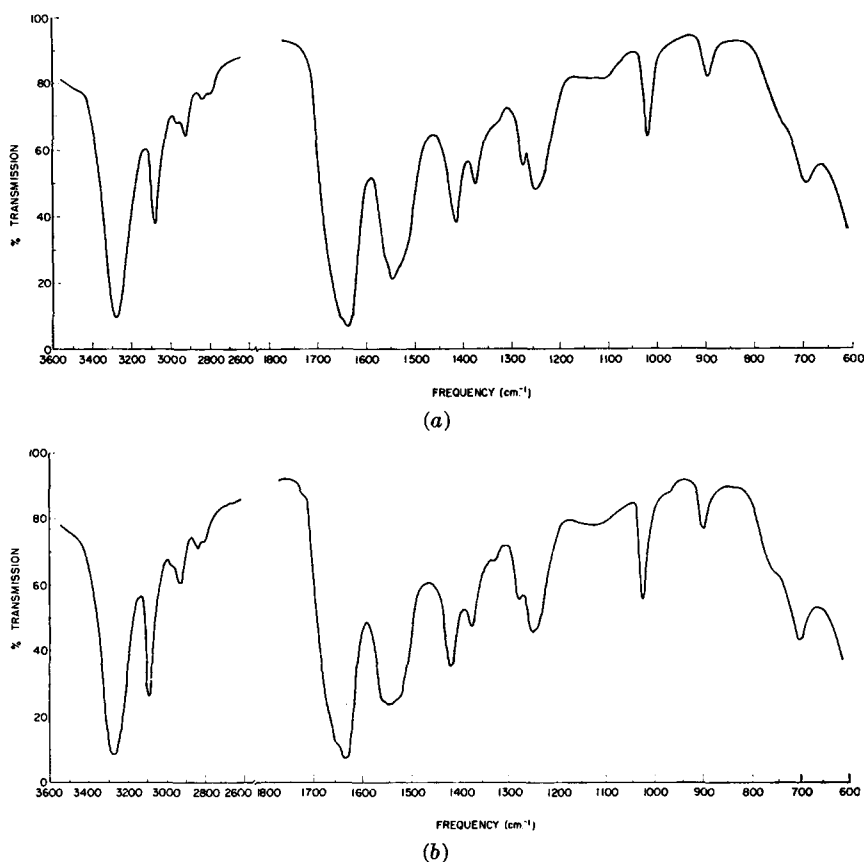


Fig. 2. Infrared spectra of polyglycine II films: (a) at room temperature; (b) at about -170°C .

modes of CH_2 groups which participate in hydrogen bonding. The two bands at 2935 and 2850 cm^{-1} correspond to modes of unbonded 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 CH_2 groups is consistent with an anti-parallel chain structure for polyglycine II,³ since in such a structure not all CH_2 groups can form $\text{C}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds.⁴ The existence of an upshifted CH_2 -stretching frequency (2977 cm^{-1}) as well as a downshifted frequency (2805 cm^{-1}) was shown² 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 I

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

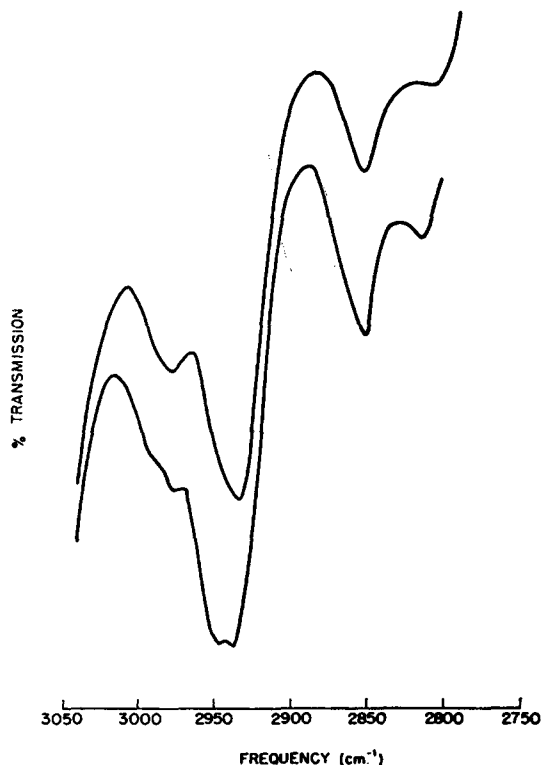


Fig. 3. Expanded infrared spectra of polyglycine II films in the CH_2 stretching region: (a) (top curve) at room temperature, (b) (bottom curve) at about -170°C .

the N—H stretching frequency (amide A band), which could be indicative of a slightly stronger $\text{N—H}\cdots\text{O}=\text{C}$ hydrogen bond. This is not unexpected, since the structure should contract with lowering of the temperature. There is no perceptible change in the amide I and amide II frequencies, but the amide V frequency (the N—H out-of-plane deformation mode⁵) does increase at the lower temperature, also consistent with a stronger $\text{N—H}\cdots\text{O}=\text{C}$ hydrogen bond. The CH_2 stretching frequencies decrease slightly at lower temperature, probably as a result of the environmental change resulting from closer contacts between CH_2 groups which face each other between the hydrogen-bonded sheets of this extended polypeptide chain structure.⁶ 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 II

The spectrum of polyglycine II is altered more substantially than that of polyglycine I by decrease of temperature. There are evident effects both on the $\text{N—H}\cdots\text{O}=\text{C}$ hydrogen bonds and on the CH_2 stretching frequencies, and we shall consider these in turn.

TABLE I
Frequencies of Some Bands of Polyglycines I and II

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

The spectral changes in bands associated with the peptide group indicate that the $\text{N—H}\cdots\text{O}=\text{C}$ hydrogen bond is significantly stronger in the low temperature structure. This is evident from the decreases in the N—H stretching (amide A) and $\text{C}=\text{O}$ stretching (amide I) frequencies, and from the increase in the N—H out-of-plane deformation (amide V) frequency. The amide II band (N—H in-plane deformation plus C—N stretch) shows a multiple structure, with a component at 1562 cm.^{-1} being intensified in the low temperature spectrum. If this corresponds to the 1550 cm.^{-1} band in the room temperature spectrum, then this shift would also be consistent with an increase in the $\text{N—H}\cdots\text{O}=\text{C}$ hydrogen bond strength in the low-temperature structure. (The multiple structure of the amide II band has a counterpart in that of the amide I band: in Figure 2b there is a definite shoulder at 1655 cm.^{-1} in addition to the main peak at 1635 cm.^{-1} . This is not unexpected, since it can be shown⁴ that in an antiparallel chain structure of polyglycine II not all $\text{N—H}\cdots\text{O}=\text{C}$ 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 I and amide II bands, as well as for the greater breadth of the amide A band in polyglycine II as compared to polyglycine I.) A better indication of the change in $\text{N—H}\cdots\text{O}=\text{C}$ hydrogen bond strength is ob-

tained 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 II mode.⁷ According to this calculation, the unperturbed frequency in the room temperature spectrum is 3280 cm^{-1} while that in the low-temperature spectrum is 3248 cm^{-1} . The observed intensity ratios $I(B)/I(A)$ (based on integrated band intensities) are in reasonable agreement with the predicted ratios:⁷ 0.095 compared to 0.053 for the room-temperature spectrum, and 0.145 compared to 0.179 for the low-temperature spectrum. There may still be some difficulties with this analysis,⁸ but both it and the spectral data strongly indicate a significant increase in N—H \cdots O=C hydrogen bond strength in the low-temperature structure.

On the other hand, the changes in CH_2 frequencies indicate that the C—H \cdots O=C bond weakens with decreasing temperature. As can be seen from Figure 3 and Table I, while lowering the temperature has essentially no effect on the unperturbed CH_2 stretching modes at 2850 and 2935 cm^{-1} , the perturbed modes at 2805 and 2977 cm^{-1} undergo large shifts, to 2815 and 2947 cm^{-1} , respectively. The CH_2 bending mode also shifts in the direction of its unperturbed value (taken to be the frequency in polyglycine I). This would be consistent with a weakening of the C—H \cdots O=C bond. The large change in the upshifted frequency, from 2977 to 2947 cm^{-1} , is not unreasonable: we anticipate that as the influence of the hydrogen bond on one C—H force constant diminishes, the secondary effect of raising the force constant of the other C—H bond² 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 assignment² of the 2805 and 2977 cm^{-1} bands to stretching modes of a different set of CH_2 groups than the ones which give rise to the 2850 and 2935 cm^{-1} bands.

Attractive versus Repulsive C—H \cdots O—C Interaction

In this and the previous² discussions we have been assuming that the spectroscopic data are to be interpreted in terms of an attractive C—H \cdots 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^{-1} bands of polyglycine II represent perturbed CH_2 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_2 stretching frequencies to increase at low temperature. This would follow from the fact that the structure contracts at low temperature (as evidenced, for example, by the stronger N—H \cdots 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 CH₂ stretching frequencies are less perturbed at low temperature: the 2805 and 2977 cm.⁻¹ bands move to 2815 and 2947 cm.⁻¹ 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 II can form a structure in which only N—H···O=C hydrogen bonds occur.⁹ 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.¹ 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 II the upshifted CH₂ stretching frequency (now at 2947 cm.⁻¹) has moved much closer to the unperturbed mode than has the downshifted frequency (now at 2815 cm.⁻¹). This implies that the more significant perturbation in this case is associated with a lowering of a CH₂ 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 CH₂ frequency is an attractive one.

The changes in the spectra of polyglycines I and II 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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