

# Physicochemical Properties of Amino Acid Polymer Polyglycine II

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## Introduction

Polyglycine was synthesized from glycine monomer with the improved method. However, polyglycine is classified to two molecular structural forms, zigzag form-polyglycine I and helical form-polyglycine II. Now, the physicochemical properties of polyglycine I that was obtained at the first synthesis reaction step were published on the previous paper<sup>1)</sup>. At the second reaction step, polyglycine II was converted from polyglycine I with metal halogen compound, lithium bromide. It was recognized that lithium bromide was more effective than other some salts in the reactivity of the conversion of molecular structure.

Then, the physicochemical properties, the vibrations of molecular chain, of polyglycine II were determined mainly with infrared and farinfrared spectrophotometers in the spectral range of  $4000\text{ cm}^{-1}$  to  $50\text{ cm}^{-1}$ . And the assignments to the absorption bands were carried out for molecular vibration modes.

Thus, new information on physicochemical properties of polyglycine II were gotten, those experimental results were published on the present paper.

## Experiment and results

First polymer ;

Polymerization<sup>1)</sup> : The polymer, polyglycine, was synthesized from N-carboxyanhydride<sup>2)</sup> of purified

ground monomer, glycine. The synthesized polymer was treated with purified dichloroacetic acid which was redistilled under dry state carefully. Thus, the first polymer was obtained as polyglycine I.

There is a notice property that the contained water in dichloroacetic acid decomposes the polymer, polyglycine, partially. And this purified dichloroacetic acid was not so suitable to prepare the film of polymer under opened system. However, it was suitable for that procedure under closed system, special absorption cell. And it did not damage the window material of the cell.

Trifluoroacetic acid which was another nice solvent had to be purified carefully like dichloroacetic acid. There is unexpected factor that the impure agent decomposes the polymer. But it is a very important property that the pure agent does not damage this molecular structure.

Second polymer ;

Conversion of structural form : The conversion of molecular structure from polyglycine I to polyglycine II was examined with some metal salt solutions. And the process of conversion was detected with an infrared spectrophotometer. As the conversion agents, lithium bromide, calcium chloride and other metal salt solutions were examined under the various conditions to detect the effects on precipitation, separation by centrifugation, and washing with solvent. Moreover, whether the dependency of the effect existed in the concentration, solubility, and temperature or not was investigated at

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the same time as a fundamental point. Above all, the results of lithium bromide were only shown on this paper. The results obtained from other salt solutions may be reported on the other papers.

The representative concentrations of lithium bromide were 0.2%, 1.0%, 2.0%, and saturation. The temperatures were 10°C, 25°C, 40°C, and 60°C. At last the suitable and convenient condition was saturated aqueous solution at room temperature, 25°C.

Calculation: All process of this calculation<sup>1,3,4,5,6,7,8,9,10,11,12</sup> was so long and complicate that only main part was shown partially on this paper.

The normal vibrations of infinite helical polymeric chains were specified with the phase difference  $\delta$  between the vibrational displacements of the icorresponding atoms which were adjacent units. The number of the

$$\begin{array}{cccccccc}
 R_{m-s}^\dagger & \cdots & R_{m-2}^\dagger & R_{m-1}^\dagger & R_m^\dagger & R_{m+1}^\dagger & R_{m+2}^\dagger & \cdots & R_{m+s}^\dagger & \cdots \\
 R_{m-1} & \cdots & G^{s-1} & \cdots & G^1 & G^0 & G^1 & G^2 & G^3 & \cdots & G^{s+1} & \cdots \\
 R_m & \cdots & G^s & \cdots & G^2 & G^1 & G^0 & G^1 & G^2 & \cdots & G^s & \cdots \\
 R_{m+1} & \cdots & G^{s+1} & \cdots & G^3 & G^2 & G^1 & G^0 & G^1 & \cdots & G^{s-1} & \cdots
 \end{array}$$

The infinite  $G$  or  $F$  matrix was factored into the set of matrices  $G^+(\delta)$  or  $F^+(\delta)$  corresponding to the phase difference of  $\delta$ . The internal symmetry coordinate vectors for the phase difference  $\delta$  were expressed by (1) and (2):

$$S^+(\delta) = N^{-\frac{1}{2}} \sum R_m \exp(im\delta) \quad (1)$$

$$G^+(\delta) = G^0 + \sum \{G^s \exp(is\delta) + G^{s\dagger} \exp(-is\delta)\} = G^0 + \frac{1}{2} \sum (G^s + G^{s\dagger}) \cos s\delta + \frac{1}{2} i \sum (G^s - G^{s\dagger}) \sin s\delta \quad (3)$$

$$G^-(\delta) = G^0 + \sum \{G^s \exp(is\delta) + G^{s\dagger} \exp(-is\delta)\} = G^0 + \frac{1}{2} \sum (G^s + G^{s\dagger}) \cos s\delta - \frac{1}{2} i \sum (G^s - G^{s\dagger}) \sin s\delta \quad (4)$$

where the vector  $S^+(\delta)$ : the complex conjugate of the vector  $S^-(\delta)$ , the matrix  $G^-(\delta)$ : the complex conjugate of the matrix  $G^+(\delta)$ . The order of the  $G^+(\delta)$  or the  $G^-(\delta)$  matrix was equal to the number ( $n$ ) of the internal coordinates per repeating unit. For the  $A$  vibrations with the phase difference of  $\delta=0$ , the  $G(0)$  matrix was expressed by (5),

$$G(0) = G^0 + \sum_{s=1}^{\infty} (G^s + G^{s\dagger}) \quad (5)$$

The potential energy matrices,  $F^+(\delta)$  and  $F^-(\delta)$ , for the phase difference  $\delta$  were expressed in the same forms as the  $G^+(\delta)$  and  $G^-(\delta)$  matrices.

The elements of the  $G^+$  or  $G^-$  matrices as showed by (3) and (4) were complex numbers. It was, however, more practical to deal with real  $G$  and  $F$  matrices.

normal vibrations for any given phase difference was expressed in terms of the number ( $p$ ) of the atoms per repeating units. There are  $3p-2 A$  vibrations, with the phase difference of  $\delta=0$ ;  $6p-2E(\delta)$  vibrations ( $3p-1$  degenerate pairs) for the phase difference of  $\delta=\theta$ ; and  $6pE(\delta)$  vibrations ( $3p$  pairs) for the phase differences  $\delta \neq \theta$ , where the angle  $\theta$  is the angle of rotation about the helix axis on passing from an atom to the corresponding atom of the adjacent unit.

The normal vibrations of infinite helical polymers by the  $GF$  matrix method was considered first by Higgs. The infinite  $G$  matrix (the potential energy matrix) was expressed, in terms of the vectors,  $R_m$ , for the internal coordinates or the local internal symmetry coordinates associated with the  $m$ th unit.

$$S^-(\delta) = N^{-\frac{1}{2}} \sum R_m \exp(-im\delta) \quad (2)$$

where  $N^{-\frac{1}{2}}$ : the normalization factor. The  $G$  matrix for the phase difference  $\delta$  was now factored into the  $G^+(\delta)$  matrix and the  $G^-(\delta)$  matrix, each associated with the symmetry coordinate vectors,  $S^+(\delta)$  and  $S^-(\delta)$ , respectively.

The  $GF$  matrix was transformed into symmetrical form, and diagonalized to yield the characteristic values and characteristic vectors. The real internal symmetry coordinates,  $S^c(\delta)$  and  $S^s(\delta)$ , for the phase difference of  $\delta$  were obtained from the complex symmetry coordinates,  $S^+(\delta)$  and  $S^-(\delta)$ .

$$S^c(\delta) = 2^{-\frac{1}{2}} \{S^+(\delta) + S^-(\delta)\} = (2/N)^{\frac{1}{2}} \sum_m R_m \cos m\delta \quad (6)$$

$$S^s(\delta) = -2^{-\frac{1}{2}} i \{S^+(\delta) - S^-(\delta)\} = (2/N)^{\frac{1}{2}} \sum_m R_m \sin m\delta \quad (7)$$

The  $G(\delta)$  matrix for the phase difference  $\delta$  was expressed by

$$G(\delta) = \begin{bmatrix} G^{cc}(\delta) & G^{cs}(\delta) \\ G^{sc}(\delta) & G^{ss}(\delta) \end{bmatrix} \quad (8)$$

The submatrices,  $G^{cc}(\delta)$  and  $G^{ss}(\delta)$ , were associated

with the vectors,  $S^c(\delta)$  and  $S^s(\delta)$ , respectively, and were expressed by

$$G^{cc}(\delta) = G^0 + \sum_{s=1}^{\infty} (G^s + G^{s\dagger}) \cos s\delta \equiv G_1(\delta) \quad (9)$$

$$G^{ss}(\delta) = G_1(\delta) \quad (10)$$

The submatrix,  $G^{sc}(\delta)$  associated with  $S^s(\delta)$  and  $S^c(\delta)^\dagger$ , was expressed by

$$G^{sc}(\delta) = \sum_{s=1}^{\infty} (G^s - G^{s\dagger}) \sin s\delta \equiv G_2(\delta) \quad (11)$$

and the submatrix,  $G^{cs}(\delta)$ , associated with  $S^c(\delta)$  and  $S^s(\delta)^\dagger$  was expressed by

$$G^{cs}(\delta) = -G_2(\delta) \quad (12)$$

The submatrix  $G_1(\delta)$  was symmetric, whereas the submatrix  $G_2(\delta)$  was skew-symmetric. The  $G(\delta)$  matrix was real and symmetric. Making use of (9)-(12), the  $G(\delta)$  matrix for the phase difference  $\delta$  was expressed by

$$G(\delta) = \begin{bmatrix} G_1(\delta) & -G_2(\delta) \\ G_2(\delta) & G_1(\delta) \end{bmatrix} \quad (13)$$

The order of the  $G(\delta)$  matrix as expressed by (13) was twice the number ( $n$ ) of the coordinates per repeating unit, but, the number of the independent elements was equal to  $n^2$ , since the number of independent elements of the  $G_1(\delta)$  and  $G_2(\delta)$  submatrices was equal to  $\frac{1}{2}n(n+1)$  and  $\frac{1}{2}n(n-1)$ , respectively.

The characteristic values and characteristic vectors of real symmetric matrices were calculated by the modified Jacobi method. The largest off-diagonal element  $G_{ji}$  was selected and the transformation

$$R' = TR \quad (14)$$

was carried out, where the diagonal elements of the  $T$  matrix were

$$t_{ii} = t_{jj} = \cos \alpha \quad (15)$$

$$\text{and } t_{kk} = 1 \text{ (for } i \neq k \neq j) \quad (16)$$

and the off-diagonal elements were equal to zero except for

$$t_{ij} = -t_{ji} = \sin \alpha \quad (17)$$

After the transformation, the element  $G_{ji}'$  was expressed by

$$G_{ji}' = G_{ji}' = \frac{1}{2}(G_{ii} - G_{jj}) \sin 2\alpha + G_{ji} \cos 2\alpha \quad (18)$$

The element  $G_{ji}'$  was reduced to zero if the value of the angle  $\alpha$  was taken

$$\text{as } \alpha = \frac{1}{2} \tan^{-1}(4u) \quad (19)$$

$$\text{where } u = G_{ji}/2(G_{ii} - G_{jj}) \quad (20)$$

The diagonalization of the  $G$  matrix

$$GL_G = L_G \Lambda_G \quad (21)$$

was performed by repeating the transformations (14) until all the off-diagonal elements were negligibly small. Then the matrix  $L_G$  was expressed by

$$L_G = \prod_k T^{(k)} \quad (22)$$

The modified Jacobi method was used for diagonalization of the  $G$  or  $F$  matrix associated with the degenerate vibrations of infinite helical polymeric chains. Supposed the off-diagonal element  $G_{ji}$  was located in the  $G^{cc}(\delta)$  matrix [ $\equiv G_1(\delta)$ ]. The transformation matrix  $T_1'$  was calculated by (15)-(18). For the  $G(\delta)$  matrix, the off-diagonal element  $G_{j+n, i+n}$  was equal to  $G_{ji}$  and, accordingly, the transformation  $T_1'$  was followed by the transformation  $T_1''$  specified by

$$(t_1'')_{i+n, i+n} = (t_1'')_{j+n, j+n} = \cos \alpha \quad (23)$$

$$(t_1'')_{i+n, j+n} = -(t_1'')_{j+n, i+n} = \sin \alpha \quad (24)$$

These two transformations were carried out in one step and denoted as  $T_1$

$$(t_1)_{i,i} = (t_1)_{i+n, i+n} = (t_1)_{j,j} = (t_1)_{j+n, j+n} = \cos \alpha \quad (25)$$

$$(t_1)_{i,j} = (t_1)_{i+n, j+n} = -(t_1)_{j,i} = -(t_1)_{j+n, i+n} = \sin \alpha \quad (26)$$

Then, if the off-diagonal element  $G_{j+n, i}$  to be reduced was located in the  $G^{sc}(\delta)$  submatrix [ $\equiv G_2(\delta)$ ], the elements of the first transformation matrix  $T_2'$  were expressed by

$$(t_2')_{i,i} = (t_2')_{j+n, j+n} = \cos \alpha \quad (27)$$

$$-(t_2')_{j+n, i} = (t_2')_{i, j+n} = \sin \alpha \quad (28)$$

For the  $G(\delta)$  matrix, the off-diagonal element  $G_{i+n, j}$  was equal to  $-G_{j+n, i}$  and the transformation  $T_2'$  was followed by the second transformation  $T_2''$  which was specified as

$$(t_2'')_{j,j} = (t_2'')_{i+n, i+n} = \cos \alpha \quad (29)$$

$$-(t_2'')_{i+n, j} = (t_2'')_{j, i+n} = \sin \alpha \quad (30)$$

These two transformations,  $T_2'$  and  $T_2''$ , were carried out in one step, and were denoted as  $T_2$ , with elements obtained by dropping the prime's in (27) and (28), and the double prime's in (29) and (30). For the special case of  $n=2$ , the  $T_1$  and  $T_2$  matrices were

expressed below :

$$T_1 = \begin{bmatrix} \cos \alpha & \sin \alpha & 0 & 0 \\ -\sin \alpha & \cos \alpha & 0 & 0 \\ 0 & 0 & \cos \alpha & \sin \alpha \\ 0 & 0 & -\sin \alpha & \cos \alpha \end{bmatrix} \quad (31)$$

$$T_2 = \begin{bmatrix} \cos \alpha & 0 & 0 & \sin \alpha \\ 0 & \cos \alpha & \sin \alpha & 0 \\ 0 & -\sin \alpha & \cos \alpha & 0 \\ -\sin \alpha & 0 & 0 & \cos \alpha \end{bmatrix} \quad (32)$$

$$T^{(k)} T^{(k+1)} = \begin{bmatrix} T_\alpha^{(k)} & -T_\beta^{(k)} \\ T_\beta^{(k)} & T_\alpha^{(k)} \end{bmatrix} \begin{bmatrix} T_\alpha^{(k+1)} & -T_\beta^{(k+1)} \\ T_\beta^{(k+1)} & T_\alpha^{(k+1)} \end{bmatrix} = \begin{bmatrix} T_\alpha^{(k)} T_\alpha^{(k+1)} - T_\beta^{(k)} T_\beta^{(k+1)} & -T_\beta^{(k)} T_\alpha^{(k+1)} - T_\alpha^{(k)} T_\beta^{(k+1)} \\ T_\beta^{(k)} T_\alpha^{(k+1)} + T_\alpha^{(k)} T_\beta^{(k+1)} & T_\alpha^{(k)} T_\alpha^{(k+1)} - T_\beta^{(k)} T_\beta^{(k+1)} \end{bmatrix} \quad (34)$$

It follows, that the  $L_G$  matrix [=  $II T^{(k)}$ ] was expressed in the form expressed in (33). Only the elements of the  $T_\alpha$  and  $T_\beta$  submatrices were taken as the independent elements of the  $T$  matrix. Also, it

$$T^\dagger G T = \begin{bmatrix} T_\alpha^\dagger & T_\beta^\dagger \\ -T_\beta^\dagger & T_\alpha^\dagger \end{bmatrix} \begin{bmatrix} G_1 & -G_2 \\ G_2 & G_1 \end{bmatrix} \begin{bmatrix} T_\alpha & -T_\beta \\ T_\beta & T_\alpha \end{bmatrix} = \begin{bmatrix} G_1' & -G_2' \\ G_2' & G_1' \end{bmatrix} \quad (35)$$

were the  $G_1'$  submatrix was symmetric and was expressed by

$$G_1' = T_\alpha^\dagger G_1 T_\alpha + T_\beta^\dagger G_2 T_\beta - T_\alpha^\dagger G_2 T_\beta + T_\beta^\dagger G_1 T_\alpha \quad (36)$$

and the  $G_2'$  submatrix was symmetric and was expressed by

$$G_2' = -T_\beta^\dagger G_1 T_\alpha + T_\alpha^\dagger G_2 T_\alpha + T_\beta^\dagger G_2 T_\beta + T_\alpha^\dagger G_1 T_\beta \quad (37)$$

In diagonalization, only  $n^2$  drum locations were necessary for the independent elements of the  $G_1(\delta)$  and  $G_2(\delta)$  submatrices, until all the off-diagonal elements were reduced negligibly small. The resultant diagonal matrix  $A_G$  was expressed by

$$A_G = \begin{bmatrix} A_{G_a} & 0 \\ 0 & A_{G_b} \end{bmatrix} \quad (38)$$

$$A_{G_a} = A_{G_b} \quad (39)$$

The  $GF$  matrix was transformed into the symmetrical

$$F_C(\delta) = (L_G A_G \frac{1}{2})^\dagger \begin{bmatrix} F_1(\delta) & -F_2(\delta) \\ F_2(\delta) & F_1(\delta) \end{bmatrix} (L_G A_G \frac{1}{2}) = \begin{bmatrix} F_{C1}(\delta) & -F_{C2}(\delta) \\ F_{C2}(\delta) & F_{C1}(\delta) \end{bmatrix} \quad (44)$$

$$\text{where } F_{C1} = A_{G_a} \frac{1}{2} (L_{G_a}^\dagger F_1 L_{G_a} + L_{G_b}^\dagger F_2 L_{G_a} - L_{G_a}^\dagger F_2 L_{G_b} + L_{G_b}^\dagger F_1 L_{G_b}) A_{G_a} \frac{1}{2} \quad (45)$$

$$\text{and } F_{C2} = A_{G_a} \frac{1}{2} (L_{G_a}^\dagger F_2 L_{G_a} - L_{G_b}^\dagger F_1 L_{G_a} + L_{G_a}^\dagger F_1 L_{G_b} + L_{G_b}^\dagger F_2 L_{G_b}) A_{G_a} \frac{1}{2} \quad (46)$$

Thus, the  $F_C$  matrix was expressed in the form expressed by (13), and was diagonalized just as for the case of  $G(\delta)$  matrix. On substituting (43) and the  $L_G$  matrix

$$L_G = \begin{bmatrix} L_{C_\alpha} & -L_{C_\beta} \\ L_{C_\beta} & L_{C_\alpha} \end{bmatrix} \quad (47)$$

in (42), the  $L$  matrix for the degenerate vibrations was found to be

Reviewing the two kinds of transformations,  $T_1$  and  $T_2$ , it was remarked that either one was expressed in the form

$$T = \begin{bmatrix} T_\alpha & -T_\beta \\ T_\beta & T_\alpha \end{bmatrix} \quad (33)$$

If the two transformations,  $T^{(k)}$  and  $T^{(k+1)}$ , were carried out the resultant transformation was expressed in the form as expressed by (33)

was shown that, even after the transformation  $T$  [(33)], the  $G(\delta)$  matrix retained the original form as expressed by (13).

form

$$F_C = (L_G A_G \frac{1}{2})^\dagger F (L_G A_G \frac{1}{2}) \quad (40)$$

and the characteristic values of the normal vibrations were calculated by diagonalizing the  $F_C$  matrix,

$$F_C L_C = L_C A \quad (41)$$

The  $L$  matrix was expressed by

$$L = L_G A_G \frac{1}{2} L_C \quad (42)$$

In the case of the degenerate vibrations of infinite helical polymers, the  $L_G A_G \frac{1}{2}$  matrix was derived to be

$$L_G A_G \frac{1}{2} = \begin{bmatrix} L_{G_a} A_{G_a} \frac{1}{2} & -L_{G_b} A_{G_a} \frac{1}{2} \\ L_{G_b} A_{G_a} \frac{1}{2} & L_{G_a} A_{G_a} \frac{1}{2} \end{bmatrix} \quad (43)$$

The  $F_C$  matrix for the degenerate vibrations was expressed by

$$L = \begin{bmatrix} L_\alpha & -L_\beta \\ L_\beta & L_\alpha \end{bmatrix} \quad (48)$$

$$\text{where } L_\alpha = L_{G_a} A_{G_a} \frac{1}{2} L_{C_\alpha} - L_{G_b} A_{G_a} \frac{1}{2} L_{C_\beta} \quad (49)$$

$$\text{and } L_\beta = L_{G_b} A_{G_a} \frac{1}{2} L_{C_\alpha} + L_{G_a} A_{G_a} \frac{1}{2} L_{C_\beta} \quad (50)$$

Spectral absorption bands: The absorption bands of the film of Polyglycine II which was prepared with purified trifluoroacetic acid were determined under dried

Polyglycine II

and wetted conditions by the special cell. The cell was invented by the author was very convenient to other various objects. The dried state was kept by concentrated sulphuric acid. The wetted state was kept with saturated sodium perchloride solution of water or heavy water.

The absorption bands of the KBr pellet and its self pellet of glycine or polyglycine II in the spectral region of  $4000\text{ cm}^{-1}$  to  $50\text{ cm}^{-1}$  are listed in Table I or Table II respectively. Also, the calculated frequencies and energy distribution for molecular vibration modes

are listed in Table II.

Many absorption bands were determined with the spectrophotometers, Perkin-Elmer 121 (NaCl, KBr prisms), Perkin-Elmer 521 (grating), Hitachi EG-1 (grating) for infrared range, Perkin-Elmer 201 C ( $450\text{ cm}^{-1}$  to  $290\text{ cm}^{-1}$ ,  $280\text{ cm}^{-1}$  to  $185\text{ cm}^{-1}$ ,  $190\text{ cm}^{-1}$  to  $120\text{ cm}^{-1}$ ,  $140\text{ cm}^{-1}$  to  $110\text{ cm}^{-1}$ ,  $120\text{ cm}^{-1}$  to  $95\text{ cm}^{-1}$ ,  $100\text{ cm}^{-1}$  to  $65\text{ cm}^{-1}$ ) and Hitachi FIS-1 for farinfrared range.

For various calculations, the large electronic computers placed at Osaka University, The University of Tokyo, and Tohoku University were operated.

Table I. Vibrational frequencies of glycine in the spectral region of  $4000\text{ cm}^{-1}$  to  $50\text{ cm}^{-1}$ . ( $\text{cm}^{-1}$ )

KBr pellet (NaCl prism range in infrared range)	KBr pellet (KBr prism range in infrared range)	Its-self pellet (Farinfrared range)
3170 s		
2890 s		
2618 s		
2381 sh		
2128 m		
1595 s		
1520 s		
1451 s		
1420 s		
1340 s		
1115 m		
1033 m		
	912 s	
896 s	984 s	
	836 s	
	694 s	
	666 sh	
	604 s	
	503 3	
		361
		283
		245 sh
		192 ww
		139
		110 ww
		84
		73

Table II. Vibrational frequencies and assignments of polyglycine II  
in the spectral region of 4000 cm<sup>-1</sup> to 50 cm<sup>-1</sup>. (cm<sup>-1</sup>)

KBr pellet (NaCl prism range in in- frared)	Its-self film (grating, in infrared range)			$\nu$ calc.	Assignment, energy distribution
	H <sub>2</sub> SO <sub>4</sub> (dried)	H <sub>2</sub> O (wetted)	D <sub>2</sub> O (wetted)		
			3440 sh		
				3335 A	$\Delta NH$
3293 s	3270 s	3270 s	3270 s		
3110 s	3085 m	3090 m	3085 m		
2950 s	2930 m	2930 m	2930 m		
2857 sh					
			*2480 s		
1658 s				1660 E	$\Delta CO(77)$
				1659 A	$\Delta CO(78)$
1555 s	1550 s	1550 s	1555 s		
				1519 A	$\phi NH(73)$ , $\Delta NC(34)$
				1515 E	$\phi NH(74)$ , $\Delta NC(33)$
			*1465 s		
1427 s	1415 s	1415 s	1415 s		
1386 m	1375 m	1375 m	1380 m		
1351 sh					
1287 s	1283 s	1285 s	1285 m	1285 E	$\Delta NC(33)$ , $\phi NH(23)$ , $\Delta CM(24)$
	1280 s	1280 m	1280 s		
				1266 A	$\Delta NC(38)$ , $\phi NH(24)$ , $\Delta CM(20)$
1250 s	1250 s	1250 s	1250 s		
	1203 m	1205 m			
	1180 sh	1185 sh	1185 sh		
	1135 s	1140 s	1138 s		
1121 sh					
				1084 A	$\Delta MN(69)$ , $\Delta CM(23)$
1032 s	1030 s	1030 s	1030 s		
				1010 E	$\Delta MN(40)$ , $\Delta CM(17)$
			* 960 sh	959 A	$\Delta CM(22)$ , $\angle MNC(16)$ , $\Delta CO(13)$
				947 E	$\Delta MN(37)$ , $\Delta CM(24)$
903 s	900 s	900 s	900 s		
	835 m	837 m	835 m		
	800 w	803 w	803 w		
				768 A	$\pi NH(57)$ , $\pi CO(30)$
	750 sh	750 sh	750 sh		
735 sh					

Polyglycine II

698 bro			
668 sh			
(KBr prism			
range in in-			
frared)			
978 s			
899 s			
745 sh			
729 sh		724 E	$\pi NH(77), \phi CO(14), \pi CO(14)$
694 sh		664 E	$\pi CO(64)$
		606 A	$\pi NH(76), tNC(29), \phi CO(11)$
		601 E	$\pi NH(54), tNC(28), \phi CO(20)$
		601 A	$\pi CO(54), \phi CO(27)$
It self pellet	It self pellet		
(Farinfrared	(Farinfrared		
range)	range)		
	494 ww		
		376 A	$\angle MNC(37), \phi CO(15), tNC(11)$
363	368		
		342 E	$\angle MNC(29), tNC(21)$
	286		
265		265 A	$\angle CMN(25), tNC(24), tNM(16), \phi CO(15)$
		236 E	$\angle MNC(28), \angle CMN(25), tNC(19)$
	214 ww		
		187 A	$\angle MCN(65), \angle AMN(12), \angle MNC(10)$
	147 ww		
115			
	104 ww		
	(87)	94 E	$tNM(36), \angle CMN(20)$
84	(81)		
	(74)		
		72 A	$tNC(52), tCM(30), \angle CMN(15)$
	(68)		
		59 E	$tCM(49), tNC(38)$

Intensity : s=strong, m=medium, w=weak, ww=very weak, sh=shoulder, bro=broad  
 $\nu$  calc. : calculated frequency ( $cm^{-1}$ )

**Discussion**

Polyglycine is a fundamental polymer which is polymerized from a fundamental amino acid, glycine. How-

ever, the number of investigation into polyglycine is very small in comparison with other polymers of amino acid. As one of the reason, polyglycine selects only a few solvents, namely the solubility in many

ordinary solvents is very small value. Also, the investigator had to consider the decomposition and the conversion of molecule at the same time and the degree of polymerization. Then, the experiment on polyglycine is complicate unexpectedly.

Now, the infrared and farinfrared absorption spectra of polyglycine I which is antiparallel  $\beta$  form structure is different from these absorption spectra of polyglycine II. So, there is a very large difference in molecular structure between polyglycine I and polyglycine II which is three screw fold helix-form structure. Especially in the range of infrared, the absorption spectra of polyglycine I was completely different from those spectra of polyglycine II.

The determination of dichroism is one effective method to analyse the molecular structure of polymer and to recognize the assignments of absorption bands observed in infrared spectra. Therefore, the determinations of dichroism of polyglycines have been carried on partially. However, the used instrument has been not latest that the experiment has been very hard. Moreover, it has spent very much time. Then, the rest part of the determination for them may be tried with a latest instrument.

The X-ray diffraction method is more effective to analyze the crystallinity of polymer. Also, that the determination of the monomer is carried on with the polymer at the same time is very important like the case of infrared spectrometry. On the basis of such a consideration, one part of those experiments has been carried out for polymers, polyglycine I and polyglycine II, and for monomer, glycine.

On the other hand, to make such a comparison between polymer and monomer is an effective method which checks up the purity of sample, the operating condition of instrument, and the precision and accuracy of data.

Some results obtained from the experiments of dichroism and crystallinity were effective to decide the molecular vibrations partially. Then, new experimental results in a progressive procedure and the unpublished results may be reported on the other paper.

At last, on the physicochemical properties the comparison of polyglycine II with polyglycine I which was reported on the previous paper<sup>1)</sup> might be better on the same paper. However, it had to be separated two papers owing to reason of compilation. And the multiple description about contents of two sections, experiment and results, and discussion, of this paper was eliminated as pertinent as possible. Because this paper became too long already.

### Summary

One of two molecular structures in polyglycine is  $\alpha$ -helical structure which is called polyglycine II. The polyglycine II was converted from polyglycine I which was treated with dichloroacetic acid. In this conversion, that aqueous saturated lithium bromide solution was better than some other salt solutions was recognized after the effects of concentration, temperature, and solubility for it were examined as fundamental experiments.

The physical properties of polyglycine II was determined with infrared and farinfrared spectrophotometers in the range of  $4000\text{ cm}^{-1}\sim 50\text{ cm}^{-1}$ .

Then, some new appeared absorption bands were attempted to assign against the corresponding molecular modes. Also, their potential energy distributions were calculated for them as detailed as possible.

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アミノ酸重合物の物理化学的性質

ポリグリシン II

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ポリグリシンにおける 2 つの分子構造の 1 つはポリグリシン II といわれる  $\alpha$ -ラセン構造である。ポリグリシン II はジクロロ酢酸で処理されたポリグリシン I から変換された。この変換において、それに対する濃度、温度、溶解度の効果が基礎的実験として実験された後に、臭化リチウムの飽和水溶液がいくつかの他の塩溶液より良いということが確認された。ポリグリシン II の物性は  $4000\text{ cm}^{-1}$  から  $50\text{ cm}^{-1}$  の領域において、赤外および遠赤外分光器により測定された。

さらに現われた新しいいくつかの吸収帯についてそれらの相当する振動様式に対する帰属を試みた。なお、ポテンシャルエネルギーの分布も可能な限り計算した。