

Vibrational Dynamics of Poly(L-glutamic acid) (β_2 Form)

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ABSTRACT: The dispersion curves for β_2 sheet form of poly(L-glutamic acid) (PLG) are reported alongwith full normal coordinate analysis. Several earlier assignments have been revised. Characteristic features of the dispersion curves, such as repulsion, exchange of character etc., are discussed. Separate contributions to the heat capacity due to purely skeletal, pure side chain, and mix-modes have also been calculated *via* density-of-states. It is found that the maximum contribution comes from the mixed modes and minimum from the pure backbone modes.

KEY WORDS Dispersion Curves / Poly(L-glutamic acid) / Density-of States / Heat Capacity /

In an earlier communication in this journal the authors have reported a study of the normal modes and their dispersion in right handed α -helix of poly(L-glutamic acid) (PLG).¹ In continuation of this work we report for completeness, similar study on the β sheet form of the same polymer. It has been reported by Itoh, *et al.*² that a temperature induced α -helix to β -sheet transition (β_1 and β_2) can be obtained. Temperature between 40°C to 85°C produces a β form with a spacing between pleated sheets d_{001} of 9.03 Å termed as β_1 and is similar to the ordinary antiparallel pleated sheet structure. On heating further above 85°C, β_1 form undergoes another conformational transition reducing the d_{001} from 9.03 to 7.83 Å termed β_2 , without any significant change in the polypeptide backbone conformation and in the distance between adjacent hydrogen bonded polypeptide backbones. The change from β_1 to β_2 is also accompanied by the exclusion of water molecules from the cavities between the hydrogen bonded sheets of the β_1 form. As a result of this transition the β_2 structure gets more compact and there is an interpenetration of carboxylic group. They have also reported that in β_1 form the planes of the carboxyl groups of the side chains lie parallel to the chain axis and hydrogen bonds are formed between pairs of carboxyl groups of neighbouring sheets. On the contrary in β_2 form the carboxyl group lie in the plane normal to the chain axis and the hydrogen bonds are formed within the same sheet. The degree of order or crystallinity of the β_2 structure is higher than β_1 structure.

Sengupta and Krimm³ have earlier reported the Raman and infrared spectroscopic studies and the normal mode analysis for the β form of calcium (Ca)-poly(L-glutamate) by using valance force field. However to the best of our knowledge dispersion of phonons have not been reported so far. In earlier publications we have reported vibrational analysis and phonon dispersion for a number of polymeric systems (α , β , ω , and 3_{10} helices),^{4–16} in the present communication, we report a similar study of poly(L-glutamic acid) in β_2 form by

using Urey Bradley-Shimanouchi force field.¹⁷ We have used the X-ray data of Ca salt of poly(L-glutamic acid) in β form reported by Keith.¹⁸ Ir and Raman spectroscopic studies on β Ca-poly(L-glutamate) reported by Sengupta and Krimm³ have proved to be of great importance in the assignment of several normal modes. The heat capacity has been calculated within the temperature range 200–500 K. The calculations show that the major contribution comes from the backbone and side chain coupled modes and minimum from the pure backbone modes. The normal modes for *N*-deuterated systems have also been studied to check the validity of assignments and the force field.

THEORY AND EXPERIMENT

Calculation of Normal Modes

The calculation of normal mode frequencies has been carried out according to Wilson's G. F. matrix method¹⁹ as modified by Higgs²⁰ for an infinite chain using Urey Bradley-Shimanouchi force field which takes into account non-bonded interactions. The Wilson GF matrix method consists of writing the inverse kinetic energy matrix *G* and the potential energy matrix *F* in internal coordinates *R*. In the case of infinite isolated helical polymer, there are an infinite number of internal coordinates which lead to *G* and *F* matrices of infinite order. Due to the screw symmetry of the polymer a transformation similar to that given by Born and Von Karman can be performed which reduces the infinite problem to finite dimensions. The transformation consists of defining a set of symmetry coordinates

$$S(\delta) = \sum_{s=-\infty}^{\infty} R^n \exp(is\delta) \quad (1)$$

where δ is the vibrational phase difference between the corresponding modes of the adjacent residue units.

The elements of the *G*(δ) and *F*(δ) matrices have the form.

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$$G_{ik}(\delta) = \sum_{s=-\infty}^{\infty} G_{ik}^s \exp(is\delta) \quad (2)$$

$$F_{ik}(\delta) = \sum_{s=-\infty}^{\infty} F_{ik}^s \exp(is\delta) \quad (3)$$

The vibrational secular equation which gives normal mode frequencies and their dispersion as a function of phase angles has the form.

$$|G(\delta)F(\delta) - \lambda(\delta)I| = 0, \quad 0 \leq \delta \leq \pi \quad (4)$$

The vibration frequencies $\nu(\delta)$ (in cm^{-1}) are related to eigen values $\lambda(\delta)$ by the following relation.

$$\lambda(\delta) = 4\pi^2 c^2 \nu^2(\delta) \quad (5)$$

Force Constant Evaluation

In the present work, Urey Bradley force field has been used which takes into account both bonded and non-bonded interactions as well as internal torsions. The potential energy can be written as:

$$\begin{aligned} V = & \sum_{m,j,k} K'_{jk} r_{jk}^{(m)} (\Delta r_{jk}^{(m)})^2 / 2 \\ & + \sum_{m,i,j,k} H'_{ijk} r_{ij}^{(m)} r_{jk}^{(m)} (\Delta \alpha_{ijk}^{(m)}) + H_{ijk} r_{ij}^{(m)} r_{jk}^{(m)} (\Delta \alpha_{ijk}^{(m)})^2 / 2 \\ & + \sum_{m,i,j,k} F'_{ik} q_{ik}^{(m)} (\Delta q_{ik}^{(m)}) + F_{ik} (\Delta q_{ik}^{(m)})^2 / 2 \\ & + \sum_j K_j^\tau (\Delta \tau_j)^2 + \sum_j K_j^\omega (\Delta \omega_j)^2 \end{aligned} \quad (9)$$

where the symbols have their usual meaning. The primed quantities are introduced as internal tensions. Non-bonded interactions involve attraction and repulsion of atoms due to the overlap of their electron shells. These effects are usually expressed by the 6-exp or 6-12 type potentials. The tension terms are assumed to be all zero.

The force constants have been obtained by the least square fitting. In order to obtain the "best fit" with the observed frequencies the following procedure is adopted. Initially approximate force constants for backbone are transferred from poly(L-alanine)²¹ (β form) and for the side chain from poly(L-glutamic acid)¹ (α -form). These force constants are somewhat different from those of Sengupta and Krimm³ because they have used only valence force constants. The calculated frequencies agreed with the observed ones within 1% except for the mixed mode appearing at 297 cm^{-1} (Table IV). Thus starting with the approximate F matrix F_0 and the observed frequencies λ_{obs} (related through a constant), one can solve the secular matrix equation

$$GF_0 L_0 = L_0 \lambda_0 \quad (6)$$

Let $\lambda_i = \lambda_{i_{\text{obs}}} - \lambda_{i_0}$ in the above equation. It can be shown that in the first order approximation

$$\Delta \lambda = J \Delta F$$

where J is computed from L_0 . We wish to compute the corrections to F_0 so that the errors $\Delta \lambda$ are minimized. We use the theory of least squares and calculate

$$J' P \Delta \lambda = (J' P J) \Delta F$$

where P is a weighting matrix and J' is the transpose of J . The solution to this equation is obtained by inverting $(J' P J)$ to give

$$\Delta F = (J' P J)^{-1} J' P \Delta \lambda$$

If the number of frequencies is greater than the number of F matrix elements, the matrix $J' P J$ should be non-singular and we obtain the corrections ΔF which will minimize the sum of the weighted squares of the residuals. If the corrections ΔF are fairly large, the linear relation between force constant and frequency term in the matrix eq 6 breaks down. In such a situation, further refinement using higher order terms in the Taylor's series expansion of $\Delta \lambda_i$ is needed. This procedure has been developed by King *et al.*²²

Calculation of Heat Capacity

One of the important uses of dispersion curves is that the microscopic behaviour of a crystal can be correlated with its macroscopic properties such as heat capacity. For a one dimensional system the density-of-states function or the frequency distribution function, which expresses the way energy is distributed among the various branches of normal modes in the crystal, is calculated from the relation

$$g(\nu) = \sum_j (\partial \nu_j / \partial \delta)^{-1} \Big|_{\nu_j(\delta) = \nu} \quad (7)$$

The sum is over all branches j . Considering a solid as an assembly of harmonic oscillators, the frequency distribution $g(\nu)$ is equivalent to a partition function. It can be used to compute thermodynamic quantities such as free energy, entropy, heat capacity and enthalpy.²³ The constant volume heat capacity is obtained using the following relation which is based on Born, Von Karman, and Debye's approach

$$C_v = \sum_j g(\nu_j) k N_A (h\nu_j / kT)^2 \frac{\exp(h\nu_j / kT)}{[\exp(h\nu_j / kT) - 1]^2} \quad (8)$$

with

$$\int g(\nu_j) d\nu_j = 1$$

The constant volume heat capacity C_v , given by eq 8 is converted into constant pressure heat capacity C_p using the Nernst-Lindemann approximation²⁴

$$C_p - C_v = 3 R A_0 (C_p^0 T / C_v T_m^0) \quad (9)$$

where A_0 is a constant often of a universal value [$3.9 \times 10^{-3} \text{ K mol J}^{-1}$] and T_m^0 is the estimated equilibrium melting temperature, which is taken to be 573 K. Equation 9 has been tested for several biopolymers with side group ranging from hydrogen in polyglycine to $-\text{CH}_2-\text{C}_6\text{H}_4-\text{OH}$ in poly(L-tyrosine).

RESULTS AND DISCUSSION

Poly(L-glutamic acid) contains 16 atoms per unit which give rise to 48 dispersion curves. The vibrational frequencies were calculated for the values of δ ranging from 0 to π in steps of 0.05π . The calculated frequencies are compared with the observed frequencies. Force con-

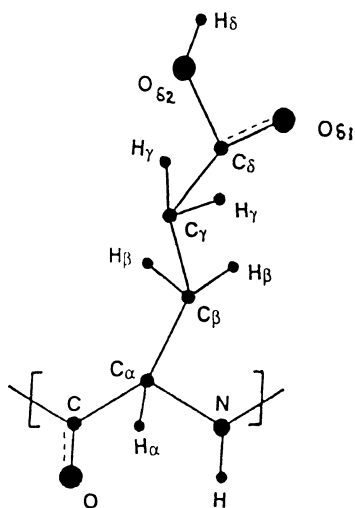


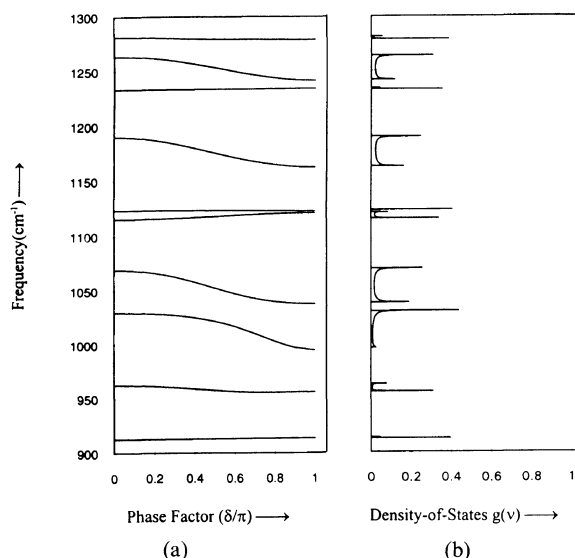
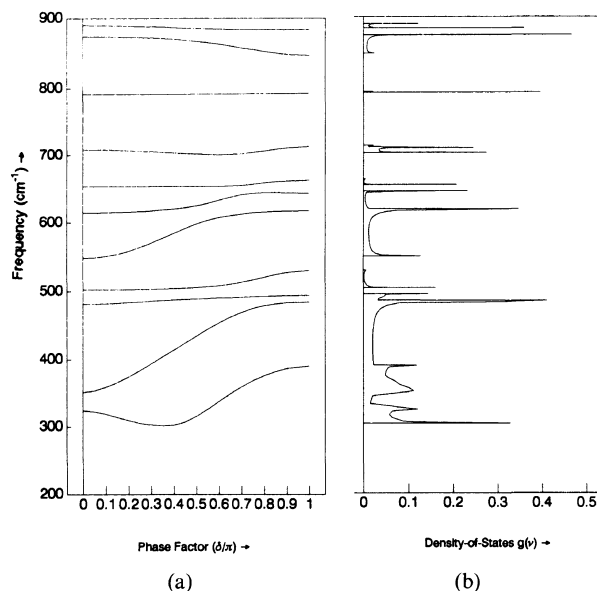
Figure 1. Chemical repeat unit of poly(L-glutamic acid).

Table I. Internal coordinates and Force constants ($\text{md } \text{\AA}^{-1}$)^a

$\nu(\text{N}-\text{C}_\alpha)$	3.300	$\phi(\text{C}_\alpha-\text{C}_\beta-\text{C}_\gamma)$	0.650 (0.22)
$\nu(\text{C}_\alpha-\text{H}_\alpha)$	4.000	$\phi(\text{H}_{\beta\beta}-\text{C}_\beta-\text{H}_{\beta\alpha})$	0.408 (0.27)
$\nu(\text{C}_\alpha-\text{C}_\beta)$	3.700	$\phi(\text{C}_\beta-\text{C}_\gamma-\text{H}_{\gamma\beta})$	0.395 (0.25)
$\nu(\text{H}_{\beta\beta}-\text{C}_\beta)$	4.360	$\phi(\text{C}_\beta-\text{C}_\gamma-\text{H}_{\gamma\alpha})$	0.395 (0.25)
$\nu(\text{H}_{\beta\alpha}-\text{C}_\beta)$	4.360	$\phi(\text{C}_\delta-\text{C}_\gamma-\text{H}_{\gamma\beta})$	0.395 (0.25)
$\nu(\text{C}_\beta-\text{C}_\gamma)$	3.300	$\phi(\text{C}_\delta-\text{C}_\gamma-\text{H}_{\gamma\alpha})$	0.395 (0.25)
$\nu(\text{C}_\gamma-\text{H}_{\gamma\alpha})$	4.420	$\phi(\text{C}_\beta-\text{C}_\gamma-\text{C}_\delta)$	0.550 (0.22)
$\nu(\text{C}_\gamma-\text{H}_{\gamma\beta})$	4.420	$\phi(\text{H}_{\gamma\beta}-\text{C}_\gamma-\text{H}_{\gamma\alpha})$	0.374 (0.27)
$\nu(\text{C}_\gamma-\text{C}_\delta)$	3.800	$\phi(\text{C}_\gamma-\text{C}_\delta-\text{O}_{\delta 2})$	0.920 (0.50)
$\nu(\text{C}_\delta-\text{O}_{\delta 2})$	5.880	$\phi(\text{C}_\gamma-\text{C}_\delta = \text{O}_{\delta 1})$	0.770 (0.60)
$\nu(\text{C}_\delta = \text{O}_{\delta 1})$	9.300	$\phi(\text{O}_{\delta 2}-\text{C}_\delta = \text{O}_{\delta 1})$	0.320 (0.42)
$\nu(\text{C}_\alpha-\text{C})$	2.200	$\phi(\text{C}_\delta-\text{O}_{\delta 2}-\text{H}_\delta)$	0.640 (0.55)
$\nu(\text{C} = \text{O})$	8.200	$\phi(\text{N} = \text{C}-\text{C}_\alpha)$	0.500 (0.60)
$\nu(\text{C} = \text{N})$	5.350	$\phi(\text{C}_\alpha-\text{C} = \text{O})$	0.180 (0.60)
$\nu(\text{N}-\text{H})$	5.240	$\phi(\text{C} = \text{N}-\text{H})$	0.365 (0.60)
$\nu(\text{O}_{\delta 2}-\text{H}_\delta)$	5.850	$\phi(\text{N} = \text{C} = \text{O})$	0.200 (0.90)
$\phi(\text{N}-\text{C}_\alpha-\text{H}_\alpha)$	0.195 (0.80)	$\phi(\text{H}-\text{N}-\text{C}_\alpha)$	0.380 (0.50)
$\phi(\text{N}-\text{C}_\alpha-\text{C})$	0.320 (0.50)	$\phi(\text{C} = \text{N}-\text{C}_\alpha)$	0.500 (0.35)
$\phi(\text{N}-\text{C}_\alpha-\text{C}_\beta)$	0.200 (0.50)	$\omega(\text{C} = \text{O})$	0.430
$\phi(\text{H}_\alpha-\text{C}_\alpha-\text{C})$	0.280 (0.22)	$\omega(\text{N}-\text{H})$	0.073
$\phi(\text{H}_\alpha-\text{C}_\alpha-\text{C}_\beta)$	0.280 (0.22)	$\omega(\text{C}_\delta = \text{O}_{\delta 1})$	0.420
$\phi(\text{C}-\text{C}_\alpha-\text{C}_\beta)$	0.520 (0.20)	$\tau(\text{C}-\text{C}_\alpha)$	0.040
$\phi(\text{C}_\alpha-\text{C}_\beta-\text{H}_{\beta\beta})$	0.390 (0.25)	$\tau(\text{C}_\alpha-\text{C}_\beta)$	0.023
$\phi(\text{C}_\alpha-\text{C}_\beta-\text{H}_{\beta\alpha})$	0.390 (0.25)	$\tau(\text{C}_\beta-\text{C}_\gamma)$	0.054
$\phi(\text{C}_\gamma-\text{C}_\beta-\text{H}_{\beta\beta})$	0.390 (0.25)	$\tau(\text{C}_\gamma-\text{C}_\delta)$	0.016
$\phi(\text{C}_\gamma-\text{C}_\beta-\text{H}_{\beta\alpha})$	0.390 (0.25)	$\tau(\text{C}_\delta-\text{O}_{\delta 2})$	0.004
		$\tau(\text{C} = \text{N})$	0.089
		$\tau(\text{N}-\text{C}_\alpha)$	0.014

^a ν , ϕ , ω , and τ denote stretch, angle bend, wag, and torsion, respectively. Non bonded force constants are given in parantheses.

stants which generate the best fit with the experimental values are given in Table I. Since all the modes above 1281 cm^{-1} are nondispersive, dispersion for modes below 1281 cm^{-1} only are shown in the Figure 2(a), 3(a), and 4(a). The four zero frequencies correspond to the acoustic modes which represent the translations parallel and perpendicular to the helix axis and rotation about the helical axis. The assignments are made on the basis of potential energy distribution in different modes, IR and Raman spectra,^{2,3} line shape, line intensity and presence absence of the modes in the molecules in similar environments. For the sake of discussions it is convenient to group the normal vibrational frequencies as backbone modes, side chain modes and mixed modes.

Figure 2. (a): Dispersion curves of poly(L-glutamic acid) ($1300\text{--}900 \text{ cm}^{-1}$). (b) Density-of-states $g(\nu)$ ($1300\text{--}900 \text{ cm}^{-1}$).Figure 3. (a): Dispersion curves of poly(L-glutamic acid) ($900\text{--}250 \text{ cm}^{-1}$). (b): Density-of-states $g(\nu)$ ($900\text{--}250 \text{ cm}^{-1}$).

BACK BONE MODES

Modes involving the motion of amide group, ($\text{N}-\text{C}_\alpha$) stretch, $\text{C}-\text{C}_\alpha$ stretch, $\text{C}-\text{C}_\alpha-\text{N}$ bending motions and their mixtures are regarded as skeletal or backbone modes. All backbone, side chain and mixed modes are listed in Tables II, III, and IV together with the observed bands and potential energy distribution. A comparison of various amide modes with other polypeptides having similar conformation has been made in Table V. These bands have been found to be sensitive to the main chain conformation as well as the side chain composition. Amide A mode, which is $\text{N}-\text{H}$ stretch is observed at 3230 cm^{-1} in the IR spectra.³ Calculated value of this mode is 3250 cm^{-1} . The lower value of amide A as compared to β -poly(L-alanine) (3293 cm^{-1})²¹ and β -poly(L-valine) (3290 cm^{-1})¹⁴ is consistent with the stronger hydrogen bond in β poly(L-glutamic acid). This also justifies a somewhat lower value of $\nu(\text{N}-\text{H})$ force constant in β

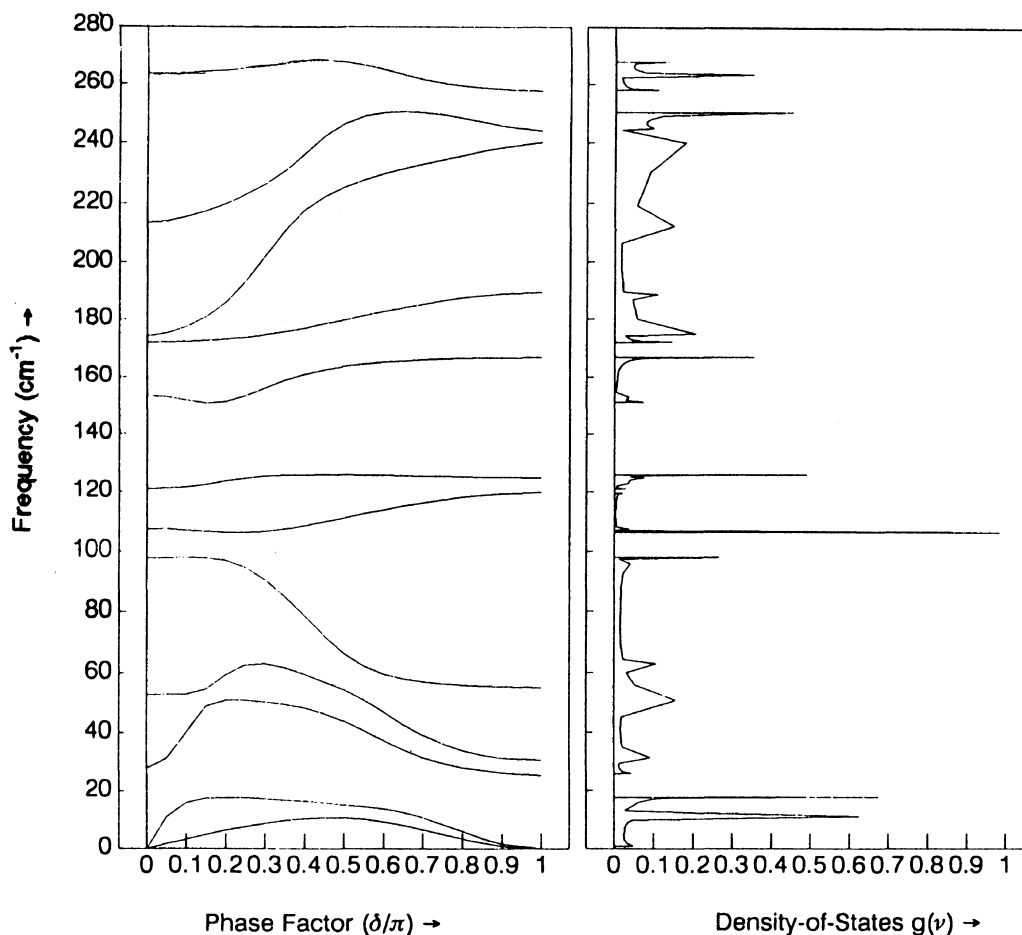


Figure 4. (a): Dispersion curves of poly(L-glutamic acid) below 300 cm^{-1} . (b): Density-of-states $g(\nu)$ below 300 cm^{-1} .

Table II. Pure back bone modes^a

Calcd	Obsd	Assignment (% P.E.D. $\delta=0.0$)	Calcd	Obsd	Assignment (% P.E.D. $\delta=1.00$) π
3250	3230	$\nu(\text{N-H})(100)$ {Amide A}	3250	3230	$\nu(\text{N-H})(100)$ {Amide A}
1625	1624	$\nu(\text{C}=\text{O})(63) + \nu(\text{C}=\text{N})(13) + \phi(\text{C}=\text{N-H})(9)$ {Amide I}	1629	1624	$\nu(\text{C}=\text{O})(60) + \phi(\text{C}=\text{N-H})(12) + \nu(\text{C}=\text{N})(10) + \phi(\text{H-N-C}_\alpha)(6)$ {Amide I}
1557	1560	$\phi(\text{H-N-C}_\alpha)(34) + \phi(\text{C}=\text{N-H})(33) + \nu(\text{C}=\text{N})(22) + \nu(\text{N-C}_\alpha)(5)$ {Amide II}	1548	1560	$\phi(\text{H-N-C}_\alpha)(31) + \phi(\text{C}=\text{N-H})(29) + \nu(\text{C}=\text{N})(24) + \nu(\text{C}=\text{O})(7) + \nu(\text{N-C}_\alpha)(6)$ {Amide II}
709	705	$\omega(\text{N}=\text{H})(31) + \omega(\text{C}=\text{O})(19) + \tau(\text{N-C}_\alpha)(17) + \tau(\text{C}=\text{N})(15)$ {Amide V}	713	705	$\omega(\text{N}=\text{H})(19) + \tau(\text{C}=\text{N})(13) + \tau(\text{N-C}_\alpha)(13) + \phi(\text{O}=\text{C}=\text{N})(8) + \phi(\text{C}=\text{N-C}_\alpha)(7) + \phi(\text{N-C}_\alpha\text{-C})(5)$ {Amide V}

^a All frequencies are in cm^{-1} .

Table III. Side chain modes^a

Calcd	Obsd	Assignment (% P.E.D. $\delta=0.0$)	Calcd	Obsd	Assignment (% P.E.D. $\delta=0.0$)
3299	—	$\nu(\text{O}_{\delta 2}\text{-H}_\delta)(100)$	1420	1414	$\phi(\text{H}_{\gamma\beta}\text{-C}_\gamma\text{-H}_{\gamma\alpha})(39) + \phi(\text{C}_\delta\text{-O}_{\delta 2}\text{-H}_\delta)(16) + \nu(\text{C}_\delta\text{-O}_{\delta 2})(10) + \nu(\text{C}_\gamma\text{-C}_\delta)(9) + \phi(\text{C}_\beta\text{-C}_\gamma\text{-H}_{\gamma\alpha})(6) + \nu(\text{C}_\beta\text{-C}_\gamma)(5)$
2983	2980	$\nu(\text{C}_\gamma\text{-H}_{\gamma\beta})(55) + \nu(\text{C}_\gamma\text{-H}_{\gamma\alpha})(39)$	1233	1225	$\nu(\text{C}_\delta\text{-O}_{\delta 2})(16) + \phi(\text{C}_\beta\text{-C}_\gamma\text{-H}_{\gamma\beta})(13) + \phi(\text{C}_\delta\text{-C}_\gamma\text{-H}_{\gamma\beta})(12) + \phi(\text{C}_\delta\text{-C}_\gamma\text{-H}_{\gamma\alpha})(10) + \phi(\text{C}_\beta\text{-C}_\gamma\text{-H}_{\gamma\alpha})(10) + \phi(\text{C}_\delta\text{-O}_{\delta 2}\text{-H}_\delta)(8) + \phi(\text{C}_\alpha\text{-C}_\beta\text{-H}_{\beta\alpha})(8) + \nu(\text{C}_\delta=\text{O}_{\delta 1})(6) + \phi(\text{C}_\gamma\text{-C}_\beta\text{-H}_{\beta\alpha})(5)$
2964	—	$\nu(\text{C}_\beta\text{-H}_{\beta\alpha})(68) + \nu(\text{C}_\beta\text{-H}_{\beta\beta})(26)$	1123	1130	$\phi(\text{C}_\beta\text{-C}_\gamma\text{-H}_{\gamma\alpha})(28) + \phi(\text{C}_\beta\text{-C}_\gamma\text{-H}_{\gamma\beta})(25) + \phi(\text{C}_\delta\text{-C}_\gamma\text{-H}_{\gamma\alpha})(23) + \phi(\text{C}_\delta\text{-C}_\gamma\text{-H}_{\gamma\beta})(14)$
2939	2943	$\nu(\text{C}_\gamma\text{-H}_{\gamma\alpha})(57) + \nu(\text{C}_\gamma\text{-H}_{\gamma\beta})(42)$	792	797	$\phi(\text{C}_\beta\text{-C}_\gamma\text{-H}_{\gamma\beta})(15) + \phi(\text{C}_\delta\text{-C}_\gamma\text{-H}_{\gamma\alpha})(15) + \phi(\text{C}_\beta\text{-C}_\gamma\text{-H}_{\gamma\alpha})(13) + \tau(\text{C}_\beta\text{-C}_\gamma)(11) + \phi(\text{C}_\gamma\text{-C}_\beta\text{-H}_{\beta\alpha})(11) + \phi(\text{C}_\gamma\text{-C}_\beta\text{-H}_{\beta\alpha})(7) + \phi(\text{C}_\delta\text{-C}_\gamma\text{-H}_{\gamma\beta})(7)$
2915	2920	$\nu(\text{C}_\beta\text{-H}_{\beta\beta})(70) + \nu(\text{C}_\beta\text{-H}_{\beta\alpha})(29)$			
2879	2875	$\nu(\text{C}_\alpha\text{-H}_\alpha)(99)$			
1732	1732	$\nu(\text{C}_\delta=\text{O}_{\delta 1})(64) + \nu(\text{C}_\delta\text{-O}_{\delta 2})(16) + \phi(\text{C}_\delta\text{-O}_{\delta 2}\text{-H}_\delta)(7) + \phi(\text{C}_\gamma\text{-C}_\delta\text{-O}_{\delta 2})(6)$			
1458	1452	$\phi(\text{H}_{\beta\beta}\text{-C}_\beta\text{-H}_{\beta\alpha})(49) + \phi(\text{H}_{\gamma\beta}\text{-C}_\gamma\text{-H}_{\gamma\alpha})(15) + \nu(\text{C}_\gamma\text{-C}_\delta)(8)$			
1450	1440	$\phi(\text{H}_{\beta\beta}\text{-C}_\beta\text{-H}_{\beta\alpha})(25) + \phi(\text{H}_{\gamma\beta}\text{-C}_\gamma\text{-H}_{\gamma\alpha})(18) + \nu(\text{C}_\gamma\text{-C}_\delta)(16) + \nu(\text{C}_\delta\text{-O}_{\delta 2})(8) + \phi(\text{C}_\delta\text{-C}_\gamma\text{-H}_{\gamma\beta})(7) + \phi(\text{C}_\delta\text{-O}_{\delta 2}\text{-H}_\delta)(6)$			

^a All frequencies are in cm^{-1} .

Table IV. Mix modes^a

Calcd	Obsd	Assignment (% P.E.D. $\delta=0.0$)	Calcd	Obsd	Assignment (% P.E.D. $\delta=\pi$)
1356	1360	$\nu(C_\alpha-C_\beta)(16) + \phi(C_\delta-O_{\delta 2}-H_\delta)(15) + \nu(C_\beta-C_\gamma)(14) + \phi(N-C_\alpha-H_\alpha)(9) + \phi(C_\gamma-C_\beta-H_{\beta\alpha})(8) + \phi(C_\gamma-C_\beta-H_{\beta\beta})(5)$	1356	1359	$\nu(C_\alpha-C_\beta)(16) + \phi(C_\delta-O_{\delta 2}-H_\delta)(16) + \nu(C_\beta-C_\gamma)(15) + \phi(C_\gamma-C_\beta-H_{\beta\alpha})(8) + \phi(N-C_\alpha-H_\alpha)(6) + \phi(C_\gamma-C_\beta-H_{\beta\beta})(5) + \phi(C_\alpha-C_\beta-H_{\beta\alpha})(5)$
1340	1323	$\phi(N-C_\alpha-H_\alpha)(49) + \phi(H_\alpha-C_\alpha-CO)(14) + \phi(C_\alpha-C_\beta-H_{\beta\alpha})(6)$	1339	1323	$\phi(N-C_\alpha-H_\alpha)(48) + \phi(H_\alpha-C_\alpha-CO)(13) + \nu(C-C_\alpha)(6)$
1281	1287	$\phi(C_\delta-O_{\delta 2}-H_\delta)(25) + \nu(C_\gamma-C_\delta)(9) + \nu(C_\alpha-C_\beta)(7) + \nu(C_\delta-O_{\delta 2})(7) + \nu(C=O)(7) + \nu(N-C_\alpha)(6)$	1279	1287	$\phi(C_\delta-O_{\delta 2}-H_\delta)(32) + \nu(C_\gamma-C_\delta)(12) + \nu(C_\delta-O_{\delta 2})(10) + \nu(C_\alpha-C_\beta)(8) + \phi(C_\alpha-C_\beta-H_{\beta\alpha})(6) + \phi(C_\gamma-C_\beta-H_{\beta\alpha})(6) + \nu(C_\delta=O_{\delta 1})(6)$
1264	1259	$\nu(C=O)(29) + \nu(N-C_\alpha)(13) + \phi(C_\delta-O_{\delta 2}-H_\delta)(8) + \nu(C=O)(8) + \nu(C-C_\alpha)(8) + \phi(H-N-C_\alpha)(5) + \nu(C_\delta-O_{\delta 2})(5)$ {Amide III}	1241	—	$\nu(C=O)(31) + \nu(N-C_\alpha)(22) + \nu(C-C_\alpha)(11) + \nu(C=O)(9)$
1190	1187	$\nu(N-C_\alpha)(24) + \phi(C_\alpha-C_\beta-H_{\beta\alpha})(11) + \nu(C-C_\alpha)(11) + \nu(C=O)(9) + \phi(C_\alpha-C_\beta-H_{\beta\beta})(9) + \nu(C_\alpha-C_\beta)(6) + \phi(C_\gamma-C_\beta-H_{\beta\beta})(5)$	1162	1176	$\phi(C_\alpha-C_\beta-H_{\beta\alpha})(19) + \nu(C=O)(13) + \nu(C_\alpha-C_\beta)(12) + \phi(C_\gamma-C_\beta-H_{\beta\alpha})(11) + \phi(C_\alpha-C_\beta-H_{\beta\beta})(9) + \nu(N-C_\alpha)(9) + \phi(C_\gamma-C_\beta-H_{\beta\beta})(6)$
1115	1130	$\phi(C_\alpha-C_\beta-H_{\beta\beta})(26) + \phi(C_\gamma-C_\beta-H_{\beta\beta})(26) + \nu(C_\alpha-C_\beta)(16) + \nu(N-C_\alpha)(10)$	1121	1130	$\phi(C_\alpha-C_\beta-H_{\beta\beta})(23) + \nu(C_\alpha-C_\beta)(20) + \phi(C_\gamma-C_\beta-H_{\beta\beta})(17) + \nu(N-C_\alpha)(8) + \phi(C_\delta-C_\gamma-H_{\gamma\alpha})(6)$
1069	1066	$\nu(C_\alpha-C_\beta)(22) + \phi(H_\alpha-C_\alpha-C_\beta)(13) + \phi(C_\gamma-C_\beta-H_{\beta\alpha})(13) + \nu(N-C_\alpha)(11) + \nu(C-C_\alpha)(10) + \phi(H_\alpha-C_\alpha-C)(9) + \phi(C_\alpha-C_\beta-H_{\beta\alpha})(6)$	1037	1040	$\nu(C_\beta-C_\gamma)(32) + \phi(H_\alpha-C_\alpha-C_\beta)(21) + \phi(C_\gamma-C_\beta-H_{\beta\alpha})(9) + \phi(C_\alpha-C_\beta-C_\gamma)(7)$
1030	1018	$\nu(C_\beta-C_\gamma)(33) + \phi(H_\alpha-C_\alpha-C_\beta)(11) + \phi(C_\alpha-C_\beta-C_\gamma)(8) + \nu(N-C_\alpha)(7) + \nu(C_\alpha-C_\beta)(6)$	995	—	$\nu(N-C_\alpha)(35) + \nu(C_\alpha-C_\beta)(13) + \phi(H_\alpha-C_\alpha-C)(8) + \nu(C=O)(8)$
963	957	$\nu(C_\beta-C_\gamma)(29) + \phi(H_\alpha-C_\alpha-C_\beta)(17) + \nu(C-C_\alpha)(10)$	956	943	$\nu(C_\beta-C_\gamma)(28) + \phi(H_\alpha-C_\alpha-C_\beta)(22) + \nu(C-C_\alpha)(10) + \nu(C_\alpha-C_\beta)(7)$
913	900	$\phi(H_\alpha-C_\alpha-C_\beta)(12) + \nu(C_\gamma-C_\delta)(12) + \phi(C_\delta-C_\gamma-H_{\gamma\beta})(11) + \phi(C_\alpha-C_\beta-H_{\beta\beta})(8) + \phi(H_\alpha-C_\alpha-C)(8) + \nu(C_\delta=O_{\delta 1})(6) + \phi(C_\alpha-C_\beta-H_{\beta\alpha})(5)$	914	900	$\nu(C_\gamma-C_\delta)(13) + \phi(C_\delta-C_\gamma-H_{\gamma\beta})(13) + \phi(H_\alpha-C_\alpha-C_\beta)(10) + \phi(C_\alpha-C_\beta-H_{\beta\beta})(8) + \phi(C_\alpha-C_\beta-H_{\beta\alpha})(7) + \nu(C_\delta=O_{\delta 1})(6) + \phi(H_\alpha-C_\alpha-C)(6)$
890	891	$\nu(C_\gamma-C_\delta)(25) + \nu(C-C_\alpha)(14) + \nu(C_\delta-O_{\delta 2})(13) + \phi(H_\alpha-C_\alpha-C)(6) + \nu(C_\delta-O_{\delta 1})(5)$	884	891	$\nu(C_\gamma-C_\delta)(28) + \nu(C_\delta-O_{\delta 2})(20) + \phi(C_\delta-C_\gamma-H_{\gamma\alpha})(8) + \phi(C_\alpha-C_\beta-H_{\beta\beta})(7)$
874	—	$\nu(C-C_\alpha)(14) + \phi(C_\delta-C_\gamma-H_{\gamma\alpha})(10) + \nu(C_\delta-O_{\delta 2})(8) + \phi(C_\gamma-C_\beta-H_{\beta\beta})(7) + \phi(C_\alpha-C_\beta-H_{\beta\alpha})(7) + \phi(C_\alpha-C_\beta-H_{\beta\beta})(7) + \phi(C_\delta-C_\gamma-H_{\gamma\beta})(7)$	847	—	$\nu(C-C_\alpha)(47) + \nu(C=O)(6)$
654	653	$\omega(C=O)(32) + \tau(C=O)(22) + \omega(C_\delta=O_{\delta 1})(13) + \tau(N-C_\alpha)(9) + \phi(C-C_\alpha-C_\beta)(5)$ {Amide VI}	662	—	$\tau(C=O)(23) + \tau(N-C_\alpha)(13) + \omega(N=H)(11) + \omega(C=O)(9) + \phi(C=O-N-C_\alpha)(8) + \phi(O=C=O)(7) + \phi(C-C_\alpha-C_\beta)(6) + \omega(C_\delta=O_{\delta 1})(6)$
615	625	$\omega(C_\delta=O_{\delta 1})(58) + \omega(C=O)(14) + \phi(C_\beta-C_\gamma-C_\delta)(7)$	643	653	$\omega(C=O)(50) + \phi(N-C_\alpha-C)(12) + \nu(N-C_\alpha)(5) + \omega(N=H)(5)$
549	—	$\phi(O=C=O)(28) + \phi(C_\alpha-C=O)(15) + \phi(C_\alpha-C_\beta-C_\gamma)(11) + \phi(C_\gamma-C_\delta-O_{\delta 2})(6) + \phi(C-C_\alpha-C_\beta)(6) + \phi(C=O-N-C_\alpha)(5)$ {Amide IV}	617	625	$\omega(C_\delta=O_{\delta 1})(59) + \omega(C=O)(9) + \phi(C_\beta-C_\gamma-C_\delta)(8)$
502	497	$\phi(C_\gamma-C_\delta-O_{\delta 1})(36) + \phi(C_\gamma-C_\delta-O_{\delta 2})(31) + \tau(C_\beta-C_\gamma)(8)$	530	—	$\phi(N=C-C_\alpha)(31) + \phi(C_\gamma-C_\delta=O_{\delta 1})(11) + \tau(C_\beta-C_\gamma)(8) + \phi(C_\alpha-C=O)(7) + \phi(N-C_\alpha-C_\beta)(7) + \phi(C_\gamma-C_\delta-O_{\delta 2})(6) + \omega(C=O)(6)$
482	484	$\phi(O_{\delta 2}-C_\delta=O_{\delta 1})(32) + \phi(C_\gamma-C_\delta-O_{\delta 2})(20) + \phi(C_\gamma-C_\delta=O_{\delta 1})(18) + \phi(O=C=O)(6) + \omega(C_\delta=O_{\delta 1})(6) + \phi(C_\alpha-C=O)(5)$	494	497	$\phi(C_\gamma-C_\delta-O_{\delta 2})(45) + \phi(O_{\delta 2}-C_\delta=O_{\delta 1})(26) + \phi(C_\alpha-C_\beta-C_\gamma)(5)$
351	—	$\phi(N-C_\alpha-C_\beta)(52) + \phi(C_\alpha-C=O)(6) + \tau(C_\beta-C_\gamma)(6)$	484	484	$\phi(C_\gamma-C_\delta=O_{\delta 1})(44) + \phi(N=C-C_\alpha)(11) + \phi(O_{\delta 2}-C_\delta=O_{\delta 1})(9) + \phi(C_\gamma-C_\delta-O_{\delta 2})(5)$
324	334	$\phi(C-C_\alpha-C_\beta)(13) + \phi(C_\alpha-C_\beta-C_\gamma)(12) + \phi(C_\alpha-C=O)(8) + \phi(C_\beta-C_\gamma-C_\delta)(8) + \phi(N-C_\alpha-C_\beta)(8) + \phi(N=C-C_\alpha)(7)$	390	—	$\phi(N-C_\alpha-C_\beta)(26) + \phi(N-C_\alpha-C)(15) + \tau(C=O)(14) + \omega(N=H)(6) + \phi(C-C_\alpha-C_\beta)(6) + \phi(C_\alpha-C_\beta-C_\gamma)(5)$
263	297	$\phi(C-C_\alpha-C_\beta)(14) + \phi(C_\alpha-C=O)(12) + \phi(C_\beta-C_\gamma-C_\delta)(12) + \phi(N=C-C_\alpha)(11) + \phi(C_\alpha-C_\beta-C_\gamma)(9) + \nu(C-C_\alpha)(7)$	258	—	$\phi(O=C=O)(21) + \phi(C_\alpha-C=O)(18) + \phi(C-C_\alpha-C_\beta)(13) + \phi(C_\beta-C_\gamma-C_\delta)(10) + \phi(C_\alpha-C_\beta-C_\gamma)(7)$
213	210	$\tau(C_\alpha-C_\beta)(15) + \phi(C=O-N-C_\alpha)(12) + \phi(N=C-C_\alpha)(11) + \phi(O=C=O)(9) + \phi(C_\alpha-C_\beta-C_\gamma)(7) + \omega(C=O)(6)$	244	—	$\phi(C_\alpha-C_\beta-C_\gamma)(38) + \phi(N-C_\alpha-C_\beta)(10) + \phi(N-C_\alpha-C)(9)$
174	—	$\phi(C=O-N-C_\alpha)(16) + \phi(N-C_\alpha-C)(16) + \tau(C_\beta-C_\gamma)(9) + \phi(O=C=O)(7) + \omega(N=H)(7) + \omega(C=O)(6)$	240	—	$\tau(C_\alpha-C_\beta)(13) + \phi(C_\alpha-C=O)(11) + \phi(N-C_\alpha-C_\beta)(11) + \phi(C-C_\alpha-C_\beta)(10) + \tau(C_\gamma-C_\delta)(10) + \tau(C_\beta-C_\gamma)(8) + \phi(O=C=O)(7)$
172	—	$\tau(C_\delta-O_{\delta 2})(86)$	190	—	$\tau(C_\delta-O_{\delta 2})(26) + \phi(C_\beta-C_\gamma-C_\delta)(19) + \tau(C-C_\alpha)(17)$
153	—	$\tau(C_\gamma-C_\delta)(27) + \tau(C_\alpha-C_\beta)(18) + \tau(C-C_\alpha)(10) + \phi(N-C_\alpha-C)(7) + \phi(N=C-C_\alpha)(7) + \tau(C=O)(6)$ {Amide VII}	167	—	$\tau(C_\delta-O_{\delta 2})(69) + \tau(C-C_\alpha)(10) + \phi(C_\beta-C_\gamma-C_\delta)(5)$
121	—	$\tau(C_\beta-C_\alpha)(16) + \tau(C_\gamma-C_\delta)(12) + \phi(C_\beta-C_\gamma-C_\delta)(10) + \tau(C=O)(5)$	125	—	$\tau(C_\gamma-C_\delta)(32) + \tau(C_\beta-C_\gamma)(24) + \tau(C_\alpha-C_\beta)(17)$
108	—	$\phi(C_\beta-C_\gamma-C_\delta)(16) + \tau(C_\beta-C_\gamma)(11) + \tau(C-C_\alpha)(10) + \phi(N=C-C_\alpha)(6) + \tau(C_\gamma-C_\delta)(5)$	120	—	$\tau(C-C_\alpha)(29) + \tau(N-C_\alpha)(16) + \phi(C_\beta-C_\gamma-C_\delta)(15) + \tau(C=O)(7) + \phi(C-C_\alpha-C_\beta)(6)$
98	—	$\phi(C_\alpha-C_\beta-C_\gamma)(24) + \tau(C-C_\alpha)(16) + \phi(C_\beta-C_\gamma-C_\delta)(11) + \phi(C-C_\alpha-C_\beta)(10) + \phi(H_\alpha-C_\alpha-C_\beta)(7)$	55	—	$\tau(C_\gamma-C_\delta)(43) + \tau(C_\alpha-C_\beta)(28) + \tau(C_\beta-C_\gamma)(13)$
53	—	$\tau(C_\gamma-C_\delta)(40) + \tau(C_\alpha-C_\beta)(34) + \tau(C_\beta-C_\gamma)(9)$	31	—	$\phi(C-C_\alpha-C_\beta)(24) + \tau(N-C_\alpha)(23) + \phi(C_\alpha-C_\beta-C_\gamma)(12) + \tau(C=O)(9)$

Table IV. (continued)

Calcd	Obsd	Assignment (% P.E.D. $\delta=0.0$)	Calcd	Obsd	Assignment (% P.E.D. $\delta=\pi$)
28	—	$\omega(N=H)(17) + \tau(C=O)(14) + \tau(C_\alpha-C_\beta)(12) + \phi(C-C_\alpha-C_\beta)(11) + \tau(C_\beta-C_\gamma)(9) + \phi(N-C_\alpha-C_\beta)(8) + \omega(C=O)(6)$	25	—	$\phi(N-C_\alpha-C_\beta)(23) + \tau(C_\alpha-C_\beta)(22) + \tau(C_\beta-C_\gamma)(11) + \tau(C-C_\alpha)(9)$

^a All frequencies are in cm^{-1} .

Table V. Comparison of Amide modes of β PLG with other Polypeptides in β form^a

	PLG		PLS		PLA		PLV	
	$\delta=0$	$\delta=\pi$	$\delta=0$	$\delta=\pi$	$\delta=0$	$\delta=\pi$	$\delta=0$	$\delta=\pi$
Amide A	3230	3230	3318	3318	3283	3283	3290	3290
I	1624	1624	1628	1628	1695	1634	1638	1638
II	1560	1560	1537	1528	1524	1524	1545	1545
III	1259	1241*	1249	1239	1224	1241	1228	1228
IV	549*	—	533	773	594	657	548	684
V	705	705	713*	685	622	705	715	715
VI	653	653	627*	647	594	657	615	628

^a All frequencies are in cm^{-1} . *marked frequencies are the calculated ones; PLG=poly(L-glutamic acid); PLA=poly(L-alanine); PLV=poly(L-valine). PLS=poly(L-serine).

poly(L-glutamic acid) than in β forms of poly(L-valine) and poly(L-alanine). On *N*-deuteration it shifts down to 2370 cm^{-1} . The 1624 cm^{-1} observed mode can be assigned to amide I. It is calculated at 1625 cm^{-1} showing a very good agreement with the observed value. The amide II and amide III modes are calculated at 1557 cm^{-1} and 1264 cm^{-1} respectively. These modes are assigned at 1560 and 1259 cm^{-1} bands. Although the backbone conformation of β_1 and β_2 forms is same but the amide II band is observed at different values in both the forms. In case of β_1 form² it is observed at 1523 cm^{-1} while in β_2 it appears at 1560 cm^{-1} .³ The difference in the frequency may be due to the change in the dielectric constant caused by the exclusion of water molecules during β_1 to β_2 transition as well as due to the strong interaction between the side chain and polypeptide backbone.² On *N*-deuteration amide II and amide III modes are shifted to 1388 cm^{-1} and 1039 cm^{-1} , respectively.

Frequency of the (N-H) out of plane vibrations *i.e.*, amide V does not depend solely on main chain and side chain conformation but hydrogen bond strength also plays an important role.²⁵ This mode appears at 709 cm^{-1} and is compared with the observed band at 705 cm^{-1} in the IR spectra. On *N*-deuteration it shows a considerable downward shift and moves to 506 cm^{-1} where it corresponds to 506 cm^{-1} band. The observed band at 240 cm^{-1} has been considered to be the backbone deformation vibration by Itoh *et al.*² They have reported that in general all the polypeptides having antiparallel pleated sheet structure have a strong band in the region $260\text{--}230 \text{ cm}^{-1}$. Therefore, from the occurrence of 240 cm^{-1} it is clear that the backbone structure of β_2 form of poly(L-glutamic acid) is similar to antiparallel pleated sheet structure. In our calculations backbone deformation modes are calculated at 244 and 240 cm^{-1} .

It is observed that below 1200 cm^{-1} the skeletal vibrations are largely influenced by side chain vibrations. The CH_2 wagging modes are calculated at 1356 and 1281 cm^{-1} and are assigned to 1359 and 1287 cm^{-1} ,

respectively. Both of these modes are mixed modes. 1356 cm^{-1} mode shows a mixing of H_α bending and CH_2 wag with side chain C-C stretches. The mode calculated at 1281 cm^{-1} is a mixed mode of CH_2 wag, C-O-H bending, C-C stretch. Both of these modes are nondispersive. H_α bending mode is calculated at 1340 cm^{-1} which corresponds to the observed band at 1323 cm^{-1} . Krimm *et al.*³ have assigned this mode to 1414 cm^{-1} which is in disagreement with our assignment. However, our assignment is supported by the observed modes at 1343 cm^{-1} in β poly(L-valine)¹⁴ and at 1341 cm^{-1} in poly(L-lysine).²⁶ Frequencies calculated at 1069 and 1030 cm^{-1} consist of mainly $(C_\alpha-C_\beta)$ and $(C_\beta-C_\gamma)$ stretches mixed with some other backbone and side chain modes. Former has a potential energy predominantly $(C_\alpha-C_\beta)$ stretch mixed with H_α bending, $(N-C_\alpha)$, $(C-C_\alpha)$ stretch, and CH_2 wag. The latter one shows a mixing of H_α bend and $(N-C_\alpha)$ stretch with $(C_\beta-C_\gamma)$ stretch. These modes are assigned to 1066 cm^{-1} and 1018 cm^{-1} bands, respectively.

The torsional vibration about the peptide $C=O$ bond which gives rise to the amide VII band is expected to be quite sensitive to the chain conformation as it spreads over the entire chain. The calculated frequency at 153 cm^{-1} at $\delta=0$ can be assigned to this mode which moves up to 390 cm^{-1} at $\delta=\pi$ showing a reverse behaviour to that of α helical form of poly(L-glutamic acid). The similar behaviour is observed in case of poly(L-alanine).²¹

SIDE CHAIN MODES

Side chain of poly(L-glutamic acid) contains two CH_2 groups at α and β positions and one COOH group attached at the γ position. All the side chain modes which are rocking, twisting, wagging of CH_2 group have been found to exhibit nondispersive behaviour. In our calculations $C_\delta=O_{\delta 1}$ stretching vibration of COOH group appears as a pure side chain mode. It is calculated at 1732 cm^{-1} and in good agreement with the observed

frequency at the same position² (1732 cm^{-1}). Potential energy distribution is $v(\text{C}_\delta=\text{O}_{\delta 1})(64) + v(\text{C}_\delta-\text{O}_{\delta 2})(16) + \phi(\text{C}_\delta-\text{O}_{\delta 2}-\text{H}_\delta)(7) + \phi(\text{C}_\gamma-\text{C}_\delta-\text{O}_{\delta 2})(6)$. Difference in the environment of the carboxylic group between two β forms can be demonstrated by the frequency of ($\text{C}_\delta=\text{O}_{\delta 1}$) stretch. In case of β_1 form the corresponding frequency is observed at 1711 cm^{-1} . Such a shift in the frequency confirms the results of X-ray diffraction studies² that substantial alterations in the side chain conformation have occurred as a result of β_1 to β_2 transition. The higher value of $v(\text{C}_\delta=\text{O}_{\delta 1})$ in β_2 form also indicates that the hydrogen bonding of the carboxylic group is weaker in case of β_2 form than in β_1 . Further it is observed that the amide I, and amide V bands are observed at lower frequencies in β_2 as compared to β_1 . This could be due to the difference in the intersheet packing strength in β_2 and β_1 as reported by X-ray diffraction studies¹⁸ wherein it has been observed that the transition from β_1 to β_2 is accompanied by an interpenetration of carboxylic groups in β_2 . It also effects the overall non-bonded interactions. C_βH_2 and $\text{C}_\gamma\text{H}_2$ scissoring modes are calculated at 1458 cm^{-1} and 1450 cm^{-1} , respectively. Observed values of these modes are 1452 cm^{-1} and 1440 cm^{-1} .³ Another mode calculated at 1420 cm^{-1} shows a mixing of ($\text{C}-\text{O}-\text{H}$) bending with the $\text{C}_\gamma\text{H}_2$ scissor. It can be assigned to the observed peak at 1414 cm^{-1} . Our assignment do not agree with Krimm *et al.* for this mode. In their case 1414 cm^{-1} band has been assigned to H_α bending mode. Our calculation is supported by the observed frequency at 1405 cm^{-1} in poly(L-aspartic acid).²² CH_2 rocking calculated at 792 cm^{-1} corresponds to the 797 cm^{-1} band in the IR spectra.³ This mode is nondispersive.

CHARACTERISTIC FEATURES OF DISPERSION CURVES

One of the interesting feature of the dispersion curves is the exchange of character between various modes. This feature is observed among the modes corresponding to $\omega(\text{C}=\text{O})$ (amide VI), $\omega(\text{C}_\delta=\text{O}_{\delta 1})$ and $\phi(\text{O}=\text{C}=\text{N})$ (amide IV) which are calculated at 654 , 615 , and 549 cm^{-1} at $\delta=0.0$. All these three modes are observed in a highly mixed form at $\delta=0.0$. On increasing the value of δ , $\text{O}=\text{C}=\text{N}$ bending mode increases while the other two modes remain constant upto $\delta=0.4\pi$ after which the contribution of $\omega(\text{C}_\delta=\text{O}_{\delta 1})$ starts mixing with the amide IV. At $\delta=0.7\pi$ the mode at 549 cm^{-1} becomes ($\text{C}_\delta=\text{O}_{\delta 1}$) wagging mode and $\omega(\text{C}=\text{O})$ starts mixing with the 615 cm^{-1} mode and finally at $\delta=\pi$ the mode at 654 cm^{-1} becomes a highly mixed mode (Table IV). The mode at 615 cm^{-1} is now mainly ($\text{C}=\text{O}$) wagging mode. Besides this the mode at 549 cm^{-1} increases to 617 cm^{-1} and becomes a pure mode of $\text{C}_\delta=\text{O}_{\delta 1}$ wag. Thus it is seen that exchange of character is taking place among these modes.

HEAT CAPACITY

Recently heat capacities of various polyamino acids have been reported by Wunderlich *et al.*²⁸⁻³¹ They have reported the heat capacity of Na-poly(L-glutamate) without mentioning the conformation. The sodium salt

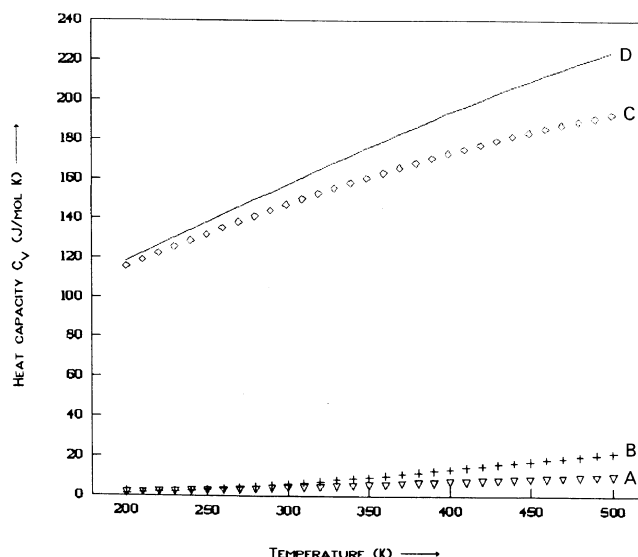


Figure 5. Heat capacity vs. temperature plot of poly(L-glutamic acid). (A) the contribution of backbone modes; (B) the contribution of side chain modes; (C) the contribution of mixed modes; (D) total heat capacity.

is generally the random coil state, or a mixture of states. They have analysed their data on the basis of Tarasov model.²⁸⁻³¹ However their approach has its own limitations when the side chain and backbone modes are heavily mixed up. This has been found to be true in our case. The heat capacity calculated by us is for β_2 conformation of PLG. The density of states are shown in Figures 2(b), 3(b), and 4(b). The contributions of the purely skeletal, purely side chain and mixed modes to the heat capacity are shown in Figure 5.

The contribution from the lattice modes is bound to make an appreciable difference to the heat capacity because of its sensitivity to these modes. At the moment, the calculation for dispersion curves for a unit cell are extremely difficult because even if we assume a minimum of two chains in unit cell then there would be 64 atoms leading to a matrix of 192×192 . It would also bring in an enormous number of interactions which are difficult to visualize and two together make the problem somewhat intractable. Thus in spite of several limitations involved in the calculation of specific heat, the present work does provide a good starting point for further basic studies on thermodynamical behaviour of polypeptides and proteins which go into well-defined conformations.

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