Phonon Dispersion and Heat Capacity in β -Sheet Poly(L-alanine)

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ABSTRACT: Earlier work on β -sheet poly(L-alanine) (β PLA) reported by Krishnan and Gupta suffers from several infirmities such as the replacement of the dynamic methyl group by a mass unit, which has resulted both in wrong assignments and incorrect profile of dispersion curves. In the present communication we report the phonon dispersion, density-of-states and heat capacity as a function of temperature in the range 200–400 K, in β PLA with all the atoms in the chemical repeat. Such studies have been already reported for the α PLA. The heat capacity is in good agreement with the measurements reported by Roles and Wunderlich. [DOI 10.1295/polymj.37.30]

KEY WORDS Poly(L-alanine) / β Conformation / Phonon Dispersion / Heat Capacity / Density-of-States /

Synthetic homopolypeptides are a class of materials that form model compounds for the study of proteins. They are capable of taking up a variety of conformations. For example, poly(β -benzyl-L-aspartate) depending on the conditions of preparation, is capable of going into left-handed α -helix, ω -helix and β -pleated sheet.¹ Similarly, glycine, proline and hydroxyproline are known to be helix breaker² but their polymeric forms *i.e.*, polyglycine II, poly(L-proline II) and poly(L-hydroxyproline) form left-handed 3-fold helix. Further these amino acids in collagen combine to form 3-fold right-handed helix. Thus a study of the dynamical behaviour of polypeptides is very important in order to unravel the behaviour of proteins. Vibrational spectroscopy is an important tool for probing conformation through conformationally sensitive modes. The infrared absorption (IR), Raman spectra and inelastic neutron scattering (INS) from polymers in general and polypeptides in particular are very complex and can not be unraveled without the full knowledge of dispersion curves. One cannot appreciate without it the origin of both symmetry dependent and symmetry independent spectral feature. Analysis of infrared and Raman spectra calculated by the molecular dynamical method has also been recently reported.³ As in case of β poly(L-valine)⁴ (β PLV), dispersion curves also provide information on the extent of coupling along the chain together with an understanding of the dependence of the frequency of a given mode upon the sequence length of ordered conformation.

Next to polyglycine, poly(L-alanine) ($-\text{NH}-\text{C}_\alpha\text{H}-\text{CH}_3-\text{CO}-$)_n is the simplest polypeptide. It exists in two crystalline forms differing in their chain conformations. One consists of α -helices in a hexagonal close-packed arrangement with interchain bonds

formed between N–H and C=O groups of alanine units three residue apart.⁵ The other form, known as a β form, consists of antiparallel-pleated sheet having hydrogen bonds between N–H and C=O groups of adjacent polypeptide chains.⁶

In continuation to our work on the vibrational dynamics and phonon dispersion in polymers in general and polypeptides^{1,4,7–12} in particular, we report in the present communication phonon dispersion in β PLA. Several workers^{12–14} have reported studies on this simple homopolypeptide. However, all these studies have one or the other infirmity. For example, Krishnan and Gupta¹² have replaced CH₃ group by an atom of mass 15. This is a serious approximation because it hides all modes coupled with the dynamics of CH₃ group. Moore and Krimm¹³ have reported normal modes analysis of β PLA using only valence force field. Vandana and Krimm reported the phonon dispersion relation, density-of-states and heat capacity only for the α form of PLA.¹⁵ Such complete studies have not yet been reported in the literature for the β form of PLA. Hence, it was felt that for a fuller understanding of the vibrational dynamics of β PLA, a fresh look at it is necessary. In the present communication, we have critically reexamined the problem and removed all the infirmities as far as possible. We report here, phonon dispersion, density-of-states and heat capacity in β PLA. Our calculations are based on Urey–Bradley force field, which in addition to valence force field accounts for the non-bonded interactions in the gem and cis configuration and tension terms. The normal mode frequencies obtained are found to be in better agreement with observed infrared and Raman bands than had been the case for the previous calculations.¹²

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THEORY

Calculation of Normal Mode Frequencies

Normal mode calculation for a polymeric chain was carried out using Wilson's GF matrix method¹⁶ as modified by Higgs¹⁷ for an infinite polymeric chain. The vibrational secular equation to be solved is:

$$|G(\delta)F(\delta) - \lambda(\delta)I| = 0 \quad 0 \leq \delta \leq \pi \quad (1)$$

where δ is the phase difference between the modes of adjacent chemical units, $G(\delta)$ is the inverse kinetic energy matrix and $F(\delta)$ is the force field matrix for a certain phase value. The frequencies ν_i in cm^{-1} are related to eigen values by $\lambda_i(\delta) = 4\pi^2 c^2 \nu_i^2(\delta)$.

A plot of $\nu_i(\delta)$ vs. δ gives the dispersion curve for the i th mode. The use of the type of force field is generally a matter of one's chemical experience and intuition.¹⁸ As stated earlier, in the present work we have used Urey-Bradley force field.¹⁹ Potential energy for this force field can be written as

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

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.

Recently spectroscopically effective molecular mechanics model have been used for inter and intra molecular interactions consisting of charges, atomic dipoles and van der Waals interactions.²⁰

The force constants, including those for the interaction of first and third non-bonded atoms, which give the "best fit", are given in the Table I and have been obtained by least squares fitting. In order to obtain the "best fit" with the observed IR, Raman, and INS spectra^{14,21-24} the following procedure is adopted.

Force constants were initially transferred from the molecules (polyglycine I (PG I)¹⁰ and β PLV⁴) having similar groups placed in the similar environment.

Table I. Internal coordinates and force constants for β -sheet poly(L-alanine) (mydn/Å)

Internal coordinates	Force constants	Internal coordinates	Force constants
$\nu(\text{C=O})$	8.500	$\varphi(\text{O=C=N})$	0.580 (0.120)
$\nu(\text{C=N})$	5.200	$\varphi(\text{C=N-H})$	0.330 (0.570)
$\nu(\text{N-H})$	5.170	$\varphi(\text{C=N-C}_\alpha)$	0.620 (0.370)
$\nu(\text{N-C}_\alpha)$	3.050	$\varphi(\text{H-N-C}_\alpha)$	0.320 (0.570)
$\nu(\text{C}_\alpha\text{-H}_\alpha)$	3.940	$\varphi(\text{N-C}_\alpha\text{-H}_\alpha)$	0.386 (0.810)
$\nu(\text{C}_\alpha\text{-C}_\beta)$	3.350	$\varphi(\text{N-C}_\alpha\text{-C}_\beta)$	0.130 (0.500)
$\nu(\text{C}_\beta\text{-H}_\beta)$	4.350	$\varphi(\text{N-C}_\alpha\text{-C})$	0.540 (0.520)
$\nu(\text{C}_\alpha\text{-C})$	2.750	$\varphi(\text{C}_\beta\text{-C}_\alpha\text{-C})$	0.440 (0.200)
$\omega(\text{N-H})$	0.146	$\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})$	0.480 (0.200)
$\omega(\text{C=O})$	0.415	$\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta)$	0.480 (0.220)
$\tau(\text{N-C}_\alpha)$	0.031	$\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)$	0.425 (0.200)
$\tau(\text{C}_\alpha\text{-C}_\beta)$	0.013	$\varphi(\text{H}_\beta\text{-C}_\beta\text{-H}_\beta)$	0.400 (0.270)
$\tau(\text{C}_\alpha\text{-C})$	0.008	$\varphi(\text{C}_\alpha\text{-C=O})$	0.520 (0.800)
$\tau(\text{C=N})$	0.040	$\varphi(\text{C}_\alpha\text{-C=N})$	0.500 (0.600)
Off-diagonal interactions			
$\nu(\text{C=N}) - \varphi(\text{O=C=N})$		0.560	
$\nu(\text{C=N}) - \varphi(\text{C=N-H})$		-0.100	

Note. ν , φ , ω and τ denote stretch, angle bend, wag and torsion respectively. Non-bonded force constants are given in parenthesis.

Thus starting with the approximate F matrix F_0 and observed frequencies λ_{obs} (related through a constant), one can solve the secular matrix equation:

$$GF_0L_0 = L_0\lambda_0 \quad (3)$$

Let $\Delta\lambda_i = \lambda_{i \text{ obs}} - \lambda_{i 0}$ in the above equation. It can be shown that in the direct order of approximation

$$\Delta\lambda = J\Delta F \quad (4)$$

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 used the theory of least squares and calculate

$$J'P\overline{\Delta\lambda} = (J'PJ)\overline{\Delta F} \quad (5)$$

where P is the weighting matrix and J' is the transposition of J . The solution of this equation is obtained by inverting $J'PJ$ to give

$$\overline{\Delta F} = (J'PJ)^{-1}J'P\overline{\Delta\lambda} \quad (6)$$

If the number of frequencies is greater than the number of F matrix elements, the matrix $J'PJ$ should be non-singular and we obtain the corrections ΔF , which will minimize the sum of the weighted squares of the residuals. This minimum sum provides the "best fit". If the corrections ΔF are fairly large, the linear relation between force constant and frequency term in the matrix equation (3) breaks down. In such a situation, further refinement using higher order terms in the Taylor's series expansion of $\Delta\lambda_i$ is needed. King *et al.*²⁵ developed this procedure.

Table II. Normal modes and their dispersion in β -sheet poly(L-alanine)

Calc. freq.	Obs. freq.		Assignment ($\delta = 0$)	
	IR	Raman	PED (%)	
3242	3242	—	$\nu(\text{N-H})(100)$	(Amide A)
2985	2985	—	$\nu(\text{C}_\beta\text{-H}_\beta)(100)$	
2927	2930	2933	$\nu(\text{C}_\beta\text{-H}_\beta)(100)$	
2927	2930	2933	$\nu(\text{C}_\beta\text{-H}_\beta)(100)$	
2871	2883	2871	$\nu(\text{C}_\alpha\text{-H}_\alpha)(99)$	(Amide I)
1671	—	1669	$\nu(\text{C=O})(64)+\nu(\text{C-N})(17)+\varphi(\text{C}_\alpha\text{-C-N})(5)$	
1536	—	1538	$\varphi(\text{H-N-C}_\alpha)(38)+\varphi(\text{C-N-H})(34)+\nu(\text{C-N})(14)$	
1446	1446	1451	$\varphi(\text{H}_\beta\text{-C}_\beta\text{-H}_\beta)(88)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(5)$	
1444	1446	1451	$\varphi(\text{H}_\beta\text{-C}_\beta\text{-H}_\beta)(94)$	(Amide II)
1404	1400	1399	$\varphi(\text{N-C}_\alpha\text{-H}_\alpha)(40)+\varphi(\text{H}_\beta\text{-C}_\beta\text{-H}_\beta)(12)+\nu(\text{C}_\alpha\text{-C}_\beta)(9)+$ $\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(9)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta)(8)+\nu(\text{N-C}_\alpha)(8)$	
1392	1380	—	$\varphi(\text{H}_\beta\text{-C}_\beta\text{-H}_\beta)(27)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(27)+\varphi(\text{N-C}_\alpha\text{-H}_\alpha)(17)+$ $\nu(\text{C}_\alpha\text{-C}_\beta)(10)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})(10)$	
1330	1332	1335	$\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta)(26)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})(19)+\nu(\text{C}_\alpha\text{-C})(14)+$ $\nu(\text{C-N})(10)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(9)+\varphi(\text{H}_\beta\text{-C}_\beta\text{-H}_\beta)(7)$	
1224	1223	1221	$\nu(\text{C-N})(34)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})(12)+\nu(\text{N-C}_\alpha)(10)+\nu(\text{C}_\alpha\text{-C})(8)+$ $\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta)(7)+\varphi(\text{H-N-C}_\alpha)(7)+\nu(\text{C=O})(6)+$ $\varphi(\text{O=C-N})(6)$	(Amide III)
1173	1167	1165	$\nu(\text{N-C}_\alpha)(44)+\nu(\text{C}_\alpha\text{-C})(17)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(7)+\varphi(\text{C}_\alpha\text{-C=O})(5)$	
1060	1050	1069	$\nu(\text{C}_\alpha\text{-C})(17)+\nu(\text{C}_\alpha\text{-C}_\beta)(16)+\nu(\text{C=O})(12)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})(8)+$ $\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta)(8)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(8)+\nu(\text{C-N})(6)+\varphi(\text{C-N-C}_\alpha)(6)$	
981	967	967	$\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(58)+\nu(\text{C}_\alpha\text{-C}_\beta)(17)$	
896	906	909	$\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(77)+\nu(\text{N-C}_\alpha)(8)+\nu(\text{C}_\alpha\text{-C})(8)$	(Amide IV)
891	—	—	$\nu(\text{C}_\alpha\text{-C}_\beta)(29)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(27)+\varphi(\text{O=C-N})(13)+$ $\nu(\text{N-C}_\alpha)(6)+\varphi(\text{C-N-C}_\alpha)(6)$	
775	771	775	$\omega(\text{N-H})(37)+\omega(\text{C=O})(26)+\varphi(\text{N-C}_\alpha\text{-C})(9)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(8)$	
631	622	—	$\omega(\text{N-H})(30)+\tau(\text{C-N})(18)+\tau(\text{N-C}_\alpha)(13)+\omega(\text{C=O})(13)+$ $\varphi(\text{N-C}_\alpha\text{-C})(5)$	
528	528	531	$\varphi(\text{C}_\alpha\text{-C=O})(29)+\varphi(\text{O=C-N})(24)+\omega(\text{C=O})(20)+$ $\nu(\text{C}_\alpha\text{-C})(11)+\nu(\text{C}_\alpha\text{-C}_\beta)(7)$	(Amide IV + Amide VI)
392	372	375	$\omega(\text{C=O})(21)+\varphi(\text{N-C}_\alpha\text{-C}_\beta)(13)+\varphi(\text{C}_\alpha\text{-C=O})(10)+$ $\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta)(8)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})(7)+\varphi(\text{C}_\alpha\text{-C-N})(7)+$ $\varphi(\text{C}_\beta\text{-C}_\alpha\text{-C})(6)+\nu(\text{N-C}_\alpha)(6)$	
326	326	332	$\varphi(\text{N-C}_\alpha\text{-C}_\beta)(32)+\varphi(\text{C}_\beta\text{-C}_\alpha\text{-C})(31)+\varphi(\text{C}_\alpha\text{-C-N})(9)+$ $\varphi(\text{C-N-C}_\alpha)(9)+\varphi(\text{O=C-N})(7)$	
259	—	266	$\tau(\text{C}_\alpha\text{-C}_\beta)(88)$	
187	—	185	$\tau(\text{N-C}_\alpha)(33)+\omega(\text{C=O})(12)+\omega(\text{N-H})(12)+\varphi(\text{N-C}_\alpha\text{-C})(11)+$ $\tau(\text{C}_\alpha\text{-C}_\beta)(8)+\tau(\text{C-N})(6)$	(Amide V)
182	—	185	$\varphi(\text{C}_\beta\text{-C}_\alpha\text{-C})(26)+\varphi(\text{N-C}_\alpha\text{-C})(24)+\varphi(\text{C}_\alpha\text{-C-N})(15)+$ $\varphi(\text{C}_\alpha\text{-C=O})(10)+\varphi(\text{N-C}_\alpha\text{-C}_\beta)(6)$	
137	—	135	$\varphi(\text{C-N-C}_\alpha)(33)+\varphi(\text{N-C}_\alpha\text{-C}_\beta)(23)+\varphi(\text{O=C-N})(9)+$ $\varphi(\text{C}_\alpha\text{-C-N})(8)+\varphi(\text{C-N-H})(6)+\varphi(\text{H-N-C}_\alpha)(5)$	
83	—	91	$\tau(\text{C-N})(43)+\tau(\text{C}_\alpha\text{-C})(24)+\omega(\text{N-H})(12)+\varphi(\text{N-C}_\alpha\text{-C})(6)$	

Continued on next page.

Calculation of Specific Heat

Dispersion curves can be used to calculate the specific heat of a polymeric system. For a one-dimensional system the density-of-state 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

$$g(\nu) = \Sigma (\partial \nu_j / \partial \delta)^{-1}]_{\nu_j(\delta) = \nu_j} \quad (7)$$

The sum is over all the branches j . Considering a solid as an assembly of harmonic oscillators, the frequency distribution $g(\nu)$ is equivalent to a partition function. The constant volume heat capacity can be calculated using Debye's relation

$$C_v = \Sigma g(\nu_j) K N_A (h \nu_j / K T)^2 \times [\exp(h \nu_j / K T) / \{\exp(h \nu_j / K T) - 1\}]^2 \quad (8)$$

with

Continued.

Calc. freq.	Obs. freq.		Assignment ($\delta = \pi$) PED (%)	
	IR	Raman		
3242	3242	—	$\nu(\text{N-H})(100)$	(Amide A)
2985	2985	—	$\nu(\text{C}_\beta\text{-H}_\beta)(100)$	
2927	2930	2933	$\nu(\text{C}_\beta\text{-H}_\beta)(100)$	
2927	2930	2933	$\nu(\text{C}_\beta\text{-H}_\beta)(100)$	
2871	2883	2871	$\nu(\text{C}_\alpha\text{-H}_\alpha)(99)$	
1663	—	1669	$\nu(\text{C=O})(68)+\nu(\text{C-N})(14)$	(Amide I)
1536	—	1538	$\varphi(\text{H-N-C}_\alpha)(36)+\varphi(\text{C-N-H})(34)+\nu(\text{C-N})(17)$	(Amide II)
1446	1446	1451	$\varphi(\text{H}_\beta\text{-C}_\beta\text{-H}_\beta)(87)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(5)$	
1444	1446	1451	$\varphi(\text{H}_\beta\text{-C}_\beta\text{-H}_\beta)(94)$	
1406	1400	1399	$\varphi(\text{N-C}_\alpha\text{-H}_\alpha)(42)+\varphi(\text{H}_\beta\text{-C}_\beta\text{-H}_\beta)(10)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta)(8)+$ $\nu(\text{C}_\alpha\text{-C}_\beta)(7)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(7)+\nu(\text{N-C}_\alpha)(6)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})(5)$	
1389	1380	—	$\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(32)+\varphi(\text{H}_\beta\text{-C}_\beta\text{-H}_\beta)(32)+\varphi(\text{N-C}_\alpha\text{-H}_\alpha)(14)+$ $\nu(\text{C}_\alpha\text{-C}_\beta)(11)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})(7)$	
1312	1308	1311	$\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta)(34)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})(32)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(6)+$ $\nu(\text{C}_\alpha\text{-C}_\beta)(6)$	
1236	1243	1241	$\nu(\text{C-N})(29)+\nu(\text{C}_\alpha\text{-C})(21)+\nu(\text{N-C}_\alpha)(15)+\varphi(\text{O=C-N})(7)+$ $\varphi(\text{H-N-C}_\alpha)(6)+\nu(\text{C=O})(5)$	(Amide III)
1092	—	1096	$\nu(\text{N-C}_\alpha)(32)+\nu(\text{C}_\alpha\text{-C}_\beta)(14)+\nu(\text{C-N})(13)+\nu(\text{C}_\alpha\text{-C})(9)+$ $\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})(6)+\varphi(\text{N-C}_\alpha\text{-C})(5)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(5)$	
1005	1017	—	$\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(27)+\nu(\text{C}_\alpha\text{-C}_\beta)(27)+\nu(\text{C}_\alpha\text{-C})(9)+\nu(\text{C-N})(8)+$ $\nu(\text{N-C}_\alpha)(7)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta)(6)$	
991	—	—	$\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(47)+\nu(\text{C}_\alpha\text{-C})(12)+\nu(\text{C}_\alpha\text{-C}_\beta)(8)+\nu(\text{C-N})(5)$	
920	926	—	$\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(53)+\varphi(\text{O=C-N})(12)+\nu(\text{C}_\alpha\text{-C})(8)+\varphi(\text{C-N-C}_\alpha)(6)$	
870	—	—	$\Phi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(43)+\nu(\text{N-C}_\alpha)(23)+\nu(\text{C}_\alpha\text{-C})(10)+\nu(\text{C}_\alpha\text{-C}_\beta)(8)$	
703	709	—	$\omega(\text{N-H})(64)+\tau(\text{C-N})(10)+\omega(\text{C=O})(7)$	(Amide V)
699	—	698	$\varphi(\text{O=C-N})(13)+\nu(\text{C}_\alpha\text{-C})(11)+\omega(\text{C=O})(10)+\varphi(\text{C}_\alpha\text{-C}_\beta\text{-H}_\beta)(9)+\nu(\text{N-}$ $\text{C}_\alpha)(8)+\varphi(\text{N-C}_\alpha\text{-C})(7)+\varphi(\text{C-N-C}_\alpha)(7)+\omega(\text{N-H})(7)+\nu(\text{C-N})(5)$	(Amide IV)
646	657	—	$\omega(\text{C=O})(50)+\tau(\text{N-C}_\alpha)(12)+\varphi(\text{N-C}_\alpha\text{-C})(8)$	(Amide VI)
507	—	—	$\varphi(\text{C}_\alpha\text{-C-N})(22)+\varphi(\text{C}_\alpha\text{-C=O})(19)+\varphi(\text{N-C}_\alpha\text{-C})(18)+\tau(\text{N-C}_\alpha)(7)+$ $\nu(\text{C}_\alpha\text{-C}_\beta)(6)+\omega(\text{C=O})(6)+\varphi(\text{C}_\beta\text{-C}_\alpha\text{-C})(5)$	
438	432	437	$\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta)(14)+\varphi(\text{N-C}_\alpha\text{-C}_\beta)(13)+\varphi(\text{C}_\beta\text{-C}_\alpha\text{-C})(12)+\tau(\text{C-N})(10)+$ $\tau(\text{N-C}_\alpha)(8)+\varphi(\text{H}_\alpha\text{-C}_\alpha\text{-C})(7)+\varphi(\text{C}_\alpha\text{-C-N})(7)+\varphi(\text{N-C}_\alpha\text{-H}_\alpha)(6)$	
299	—	300	$\varphi(\text{O=C-N})(26)+\varphi(\text{N-C}_\alpha\text{-C})(19)+\varphi(\text{C}_\alpha\text{-C=O})(19)+\varphi(\text{C-N-C}_\alpha)(16)+$ $\varphi(\text{N-C}_\alpha\text{-C}_\beta)(7)$	
247	240	235	$\tau(\text{C}_\alpha\text{-C}_\beta)(96)$	
182	—	185	$\varphi(\text{C}_\beta\text{-C}_\alpha\text{-C})(46)+\varphi(\text{N-C}_\alpha\text{-C}_\beta)(36)+\varphi(\text{C}_\alpha\text{-C-N})(5)$	
117	122	—	$\tau(\text{C}_\alpha\text{-C})(42)+\tau(\text{N-C}_\alpha)(24)+\omega(\text{C=O})(5)$	
101	122	—	$\tau(\text{N-C}_\alpha)(29)+\tau(\text{C-N})(25)+\varphi(\text{C-N-C}_\alpha)(10)+\varphi(\text{N-C}_\alpha\text{-C})(8)+$ $\varphi(\text{N-C}_\alpha\text{-C}_\beta)(8)$	(Amide VII)

All frequencies are in cm^{-1}

$$\int g(v_i)dv_i = 1.$$

The constant-volume heat capacity C_v , given by above equation, can be converted into constant-pressure heat capacity C_p using the Nernst–Lindemann approximation.²⁶

$$C_p - C_v = 3RA_0(C_p^2 T / C_v T_m^0) \quad (9)$$

Where A_0 is a constant often of a universal value [3.90×10^{-3} (K mol)/J] and T_m^0 is the estimated equilibrium melting temperature, which is taken to be 573 K.²⁷

RESULTS AND DISCUSSION

Figure 1 represents the chemical repeat unit of PLA. It has 10 atoms per repeat residue that give rise to 30 dispersion curves. The vibrational frequencies were calculated for values of δ varying from 0 to π in steps of 0.05π . The optically active modes are those for which $\delta = 0$ or $\delta = \pi$. The assignment of various modes along the potential energy distribution (PED) is given in Table II. The assignments have been made on the basis of PED, absorption band shape, band intensity and absorption/scattering in

Figure 1. One chemical repeat unit of β PLA.

similar molecules having groups placed in similar environments. For the sake of simplicity the modes are discussed under two heads, *viz.*, backbone modes and side-chain modes.

Backbone Modes

The mode involving the motions of main chain atoms ($-\text{CO}-\text{C}\alpha-\text{NH}-$) are termed as backbone modes. Amide groups of polypeptides are strong absorber in IR region, and these groups give rise to strong characteristic bands (Amide A, I–VII). These amide modes along with other characteristic modes have been used for the structural diagnosis. Based on such diagnostic correlations, attempts have been made to estimate secondary structural composition in proteins. A comparison of the amide modes of β PLA with the other polypeptides^{4,10,28} having β sheet conformation is given in Table III.

The amide A mode which arises due to the N–H stretch, is not too sensitive to chain conformation and side-chain structure, but is highly sensitive to the strength of the $\text{N}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bond. As seen in Table III, amide A in β PLA has the frequency which is lower than poly(L-serine) (PLS) and PG I. It should be noted that the value of the N–H stretch force constant for β PLA is lower than that for PG I. This is consistent with the stronger hydrogen bond in the pleated sheet structure as compared to the rippled-sheet.^{29,30}

Amide I mode is calculated at 1671 cm^{-1} at $\delta = 0$ and is assigned to the observed peak at 1669 cm^{-1} in Raman spectra. Amide II mode is calculated at 1536 cm^{-1} both at the zone centre and zone boundary and can be assigned to Raman band at 1538 cm^{-1} . The 1555 cm^{-1} peak in Raman and 1524 cm^{-1} peak in polarized IR spectra arise from the crystal field splittings as discussed by Moore and Krimm.¹³ This mode lies in the same range in other polypeptides having β

Table III. Comparison of amide modes of β PLA with other polypeptides in β form

Amide	β PLA		β PLV		β PG I		β PLS	
	$\delta = 0$	$\delta = \pi$	$\delta = 0$	$\delta = \pi$	$\delta = 0$	$\delta = \pi$	$\delta = 0$	$\delta = \pi$
A	3242	3242	3290	3290	3398	3298	3318	3318
I	1669	1669	1638	1638	1650	1628	1637	1628
II	1538	1538	1545	1545	1520	1520	1532	1537
III	1223	1243	1228	1228	1300	1281	1249	1270
IV	528	698	548	684	628	711	533	773
V	622	709	715	715	705	725	713	685
VI	528	657	615	628	590	600	533	647

All frequencies are in cm^{-1}

PLA: poly(L-alanine) PLV: poly(L-valine)⁴

PG I: poly(L-glycine)¹⁰ PLS: poly(L-serine)²⁸

(Table III) sheet conformation.

The frequency of the amide III mode does not depend solely on main-chain conformation. Side-chain structure also plays an important role.³¹ The amide III mode calculated at 1224 cm^{-1} at the zone centre is assigned to the observed peak at $1221/1223\text{ cm}^{-1}$ in Raman/IR spectra. At the zone boundary it is calculated at 1236 cm^{-1} and matched to the observed band at $1241/1243\text{ cm}^{-1}$ Raman/IR spectra. This matching could be made only when the off-diagonal coupling interaction between $\nu(\text{C}=\text{O})$ and $\varphi(\text{O}=\text{C}=\text{N})$ and $\nu(\text{C}=\text{N})$ and $\varphi(\text{C}=\text{N}-\text{H})$ was taken into consideration. The motion of these internal coordinates becomes coupled *via* the motion of the carbon atom of the carbonyl group and *via* the Nitrogen atom of the peptide group.

The amide IV mode calculated at 528 cm^{-1} at $\delta = 0$ and is assigned to the observed peak at the same value, is coupled mode mixed with amide VI. Krishnan *et al.*¹² have assigned this mode at 594 cm^{-1} . The peak at 594 cm^{-1} is not observed in the spectra of β PLA but in IR spectra and INS of α PLA.

The N–H wagging mode, which give rise to the amide V is calculated at 631 cm^{-1} at the zone centre and is assigned to the observed IR peak at 622 cm^{-1} . Its frequency depends on a combination of main-chain conformation, hydrogen bond strength and side-chain structure. Although interchain interactions through hydrogen bonds are not explicitly used in the present calculations for the isolated chain, but its effects are indirectly taken into account in the search for the “best” force field for the neighbouring alanine residue.

Elliott³² speculated that the observed IR band at 1308 cm^{-1} in β PLA was probably due to the presence of some α -helical conformation in β sample. Actually in the IR spectrum of β PLA, there are two bands in this region, at 1332 and 1308 cm^{-1} . From the spectrum it is not clear if these absorptions are in-

deed spectral contributions from β or are α -helically linked alanine residues. However, in Raman spectrum of β PLA the bands at 1335 and 1311 cm^{-1} have intensities which are too large relative to the intensities of the corresponding bands in the α form. Bands near these frequencies are predicted by our calculations as ($\text{C}_\alpha\text{--H}_\alpha$) bending. The appearance of ($\text{C}_\alpha\text{--H}_\alpha$) bending mode in PLS²⁸ in the same range also supports our assignment.

CH_3 as a Dynamical Unit

The introduction of CH_3 as a dynamical unit brings about significant changes in the assignments and in the dispersive behaviour of normal modes lying below 1400 cm^{-1} . They are shown in Table II. These are the modes, which belong either to the CH_3 group or appear with the CH_3 group as a mixture of several skeletal and non-skeletal modes. The CH_3 symmetric stretch, asymmetric stretch and asymmetric deformation are pure modes. However the symmetric deformation does mix with its neighbouring angle bends ($\text{C}_\alpha\text{--C}_\beta\text{--H}_\beta$). These motions are electrically and mechanically coupled. The main dispersive modes are CH_3 torsion and CH_3 rock, which appear at the zone centre at 266 and 906 cm^{-1} , respectively, and disperse to 300 and 926 cm^{-1} at the zone boundary. However, there are other modes which appear at 1060 and 981 cm^{-1} at $\delta = 0$ and have significant contribution from the CH_3 rock. As the 266 cm^{-1} mode progresses towards the zone boundary, its character starts changing and at $\delta = 0.40\pi$, it suffers repulsion with another mode which appears at 185 cm^{-1} at the zone centre. After repulsion there is an exchange of PE. Such points of repulsion/cross-over generally refer to some internal symmetry points in the energy momentum space. With CH_3 as a dynamical unit some new mode have appeared which are not purely CH_3 mode but are coupled with several other modes. The modes calculated at 1404 and 1330 cm^{-1} at $\delta = 0$ belong to this category. These modes were not observed by Krishnan *et al.*¹² The mode at 1404 cm^{-1} is a skeletal angle bend $\varphi(\text{N--C}_\alpha\text{--H}_\alpha)$ and mixes with ($\text{C}_\alpha\text{--C}_\beta\text{--H}_\beta$) and ($\text{H}_\beta\text{--C}_\beta\text{--H}_\beta$). The other mode is the bending of ($\text{C}_\alpha\text{--H}_\alpha$) and it also mixes with ($\text{C}_\alpha\text{--C}_\beta\text{--H}_\beta$) and ($\text{H}_\beta\text{--C}_\beta\text{--H}_\beta$). Since these modes are dynamically coupled, hence the profile of dispersion curves is also changed.

The introduction of CH_3 as a dynamical unit leads to the revision of some of the assignments made earlier.¹² They have assigned the peak at 1167 cm^{-1} due to angle bends $\varphi(\text{C--C}_\alpha\text{--C}_\beta)$ and $\varphi(\text{N--C}_\alpha\text{--C}_\beta)$. Now, on comparison with other polypeptides, this mode is assigned as skeletal stretching mode of (N--C_α) and (C--C_α). This mode is partially coupled with ($\text{C}_\alpha\text{--C}_\beta\text{--H}_\beta$). Our assignment agrees with that made by Moore and Krimm.¹³ Also this mode appears in the

same range in β PLV.⁴ The $\tau(\text{C--N})$ which was assigned to 247 cm^{-1} at $\delta = 0$ is incorrect and should be assigned to 91 cm^{-1} at $\delta = 0$ and at 122 cm^{-1} at $\delta = \pi$. The mode calculated at 247 cm^{-1} , which appears intense in INS at 230 cm^{-1} , should be assigned to the methyl torsion. Its intensity in INS is due to large amplitude of motion.

Dispersion Curves

The dispersion of modes below 1350 cm^{-1} is plotted in Figures 2a and 3a. All modes above this are non dispersive. As shown in Figure 3a the two lowest lying branches ($\nu = 0$ at $\delta = 0$ and $\delta = \pi$) are the four acoustic modes. At $\delta = 0$ the two acoustic branches correspond to the translational mode along the chain axis and rotational mode about the axis. At $\delta = \pi$, they correspond to the translational modes perpendicular to the rotational axis.

The mode calculated at 1173 cm^{-1} at $\delta = 0$ is assigned to the observed peak at 1167/1165 cm^{-1} in Raman/IR. It shows a dispersion of 81 wave number. This mode has a dominant contribution of skeletal stretches [$\nu(\text{N--C}_\alpha)$ (44%) + $\nu(\text{C}_\alpha\text{--C})$ (17%)] at the zone centre. On moving away from the zone centre contribution of $\nu(\text{N--C}_\alpha)$ and $\nu(\text{C}_\alpha\text{--C})$ decreases and that of $\nu(\text{C--N})$ and $\nu(\text{C}_\alpha\text{--C}_\beta)$ increases. At the zone boundary, this mode reaches 1092 cm^{-1} and is assigned to the peak at 1096 cm^{-1} in Raman spectra.

The mode at 1060 cm^{-1} at the zone centre, assigned to the observed peak at 1050 (Raman) cm^{-1} , shows a dispersion of 55 wave number. This mode has the dominant contribution of skeletal as well as side-chain stretches. The contribution of skeletal stretches decreases with δ and that of side-chain stretches and methyl bending increases. At zone boundary this mode reaches 1005 cm^{-1} and is assigned to the peak at 1017 cm^{-1} in IR spectra.

The mode calculated at 775 cm^{-1} at $\delta = 0$, [$\omega(\text{N--H})$ (37%) + $\omega(\text{C=O})$ (26%)] is assigned to the observed peak at 770 cm^{-1} . The 630 cm^{-1} mode at $\delta = 0$, [$\omega(\text{N--H})$ (30%) + $\tau(\text{C--N})$ (18%) + $\omega(\text{C=O})$ (13%)] is Amide V which is assigned to the observed peak at 622 cm^{-1} . The PED of these two modes shows no appreciable change up to $\delta = 0.40\pi$. Beyond this they start interacting and come closer. In the 775 cm^{-1} mode contribution of $\omega(\text{N--H})$ starts increasing while its frequency decreases with δ and reaches 702 cm^{-1} at $\delta = \pi$, where it is assigned to Amide V mode and corresponds to the observed peak at 709 cm^{-1} in IR spectra. On the other hand, the contribution of the C=O in-plane bending increases in the mode at 630 cm^{-1} . This mode reaches 698 cm^{-1} at $\delta = \pi$ and becomes Amide IV mode.

The mode at 528 cm^{-1} at zone centre has the major contribution from the C=O in-plane bending along

Figure 2. (a) Dispersion curves and (b) density of states of β PLA (1350–800 cm⁻¹).

Figure 3. (a) Dispersion curves and (b) density of states of β PLA below 800 cm⁻¹.

with its out-of-plane bending [$\varphi(\text{C}_\alpha\text{--C=O})(29) + \varphi(\text{O=C--N})(24) + \omega(\text{C=O})(20)$]. It is assigned to the observed peak at the same frequency. The contribution of (C=O) in plane bending decreases and that

of the C=O out-of-plane bending increases in this mode with increasing δ . At $\delta = \pi$, it reaches 646 cm⁻¹ [$\omega(\text{C=O})(50\%) + \tau(\text{N--C}_\alpha)(12\%)$] and is assigned to the observed peak at 657 cm⁻¹ (Amide VI).

Figure 4. Variation of heat capacity of β PLA as a function of temperature [theoretical values (—) and experimental data (●)].

The modes calculated at 392 and 326 cm^{-1} , which arises due to skeletal angle bending modes, are highly dispersive because of strong coupling along the chain.

One of the characteristic features of the dispersion curves is the repulsion and exchange of character between two pairs of modes. Pairs of modes that repel appear at 259 and 187 cm^{-1} at the zone centre. The repulsion occurs in the neighbourhood of 0.40π . It is observed that at this δ value, the modes come close, exchange their PED and then repel. After repulsion, the second mode becomes non dispersive, while the first one disperses progressively with δ . This interesting phenomenon of exchange of character may be viewed as the collision of two phonons approaching to each other and moving apart after exchanging their PED. Such repulsion occurs for modes belonging to same symmetry species.³³

The dispersion curves in the lower frequency region ($150\text{--}400\text{ cm}^{-1}$) fan out from the zone centre towards the zone boundary, appearing to repel each other. This feature is also true of the dispersion curves of PG I,¹⁰ β PLS,²⁸ and polyethylene (PE),³⁴ which take planar zig-zag configuration. This common feature may be due to the absence of strong interchain interactions, stabilizing the structure, in contrast to the case of the hydrogen-bonded α -helix.

An interesting feature in the dispersion curves is the parallelism between the 528 , 392 and 326 cm^{-1} modes. Since the phonon velocity is related to the gradient of the dispersion curve, it shows same velocity for the three phonons.

The lower frequency modes, especially the acoustic modes, are the characteristic of 2-fold helical chain symmetry. The two acoustic branches in the disper-

sion curves are similar in shape to the dispersion of these branches in other 2-fold helical polymers like PE,³⁴ PG I,¹⁰ β PLV⁴ and syndiotactic polystyrene in its two-fold helical form,³⁵ etc. The peaks in the acoustic curves of β PLA occur at $\delta = 0.45\pi$ and $\delta = 0.25\pi$. A comparison with β PLV shows that, although the peaks in the acoustic curves fall at about the same δ value, the peaks heights are different due to different side-chain structure.

Agreement with the experimental values for frequencies at $\delta = 0$ and $\delta = \pi$ shows that basically the profile of dispersion curves is correct.

Density-of-States and Heat Capacity

Frequency distribution function as obtained from the dispersion curves is shown in Figures 2b and 3b. The peaks in the frequency distribution curves correspond to the regions of high density-of-states. The observed frequencies correspond well with these peak positions. From this knowledge of density-of-states heat capacity of β PLA chain has been calculated in the range $200\text{--}400\text{ K}$ (Figure 4). In the figure the solid circles represent experimental data of Roles and Wunderlich²⁷ Our calculations agree well with the experimental data except at the low temperatures.

The discrepancy at the low temperature could arise for two reasons, one the neglect of interchain interactions at low temperature and the other because of force field being temperature independent. The former leads to low frequency lattice modes, which are not included in the present model, and the heat capacity is sensitive to it. The evaluation of lattice modes is not only prohibitive dimensionally but even the enormity of interactions, which are difficult to visualize.

As for the latter, the temperature dependence of force field is difficult to build in the potential field. Such measurement and evaluation of heat capacity can give information about the portion of protein which is in α -helical or β sheet structure and is necessary in evaluating the basic thermodynamics of enzyme reaction.

CONCLUSIONS

The use of CH₃ as a dynamical unit rather than as a mass point has emerged in correcting several assignments both at the zone centre and at the zone boundary. Further, the change in the dispersion profile results in good agreement with the heat capacity measurements on β PLA.

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