Normal Modes of Poly(L-valine) in Relation to Spectra of Oligovalines

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(Received September 5, 1994)

ABSTRACT: Poly(L-valine) (PLV) belongs to the class of polyamino acids having a bulky side chain. It preferably adopts β -sheet conformation, although high molecular weight PLV may form an α helix as well. In the present communication we report a detailed study of the phonons and their dispersion for β -PLV and the spectra of oligovalines in relation to its polymeric form. The *N*-deuterated analog of β -PLV has also been studied to confirm the correctness of assignments and force-field. Density-of-states and heat capacity have been obtained. The heat capacity is in very good agreement with the experimental measurements of Roles *et al.*

KEY WORDS Conformation / Phonon Dispersion / Specific Heat / Normal Mode Analysis / Poly(L-valine) / Density of States / Oligovalines /

Poly(L-valine) (PLV) is an example of a polyamino-acid having hydrophobic side chain (Figure 1) and it is preferably found to exist in an antiparallel β sheet conformation. Conformational calculations on various degree of polymerization^{1,2} and X-ray structure data³ have demonstrated that high molecular weight poly(L-valine) may form an α helix as well. β -PLV has an orthogonal lattice of unit cell dimensions $a = 4.80 \text{ \AA}$, $b = 19.14 \text{ \AA}$, and $c = 6.59 \text{ \AA}$ with space group P_{212121} and D_2 point group.⁴ It has a two fold screw axis and the chains are packed in an antiparallel arrangement. The neighbouring chains are hydrogen bonded *via* $N-H \cdots O=C$. There is a strong coupling of main chain vibrations with the side chain vibrations in the low frequency region and a detailed vibrational analysis is essential for definite assignment of the bands.

In some recent publications Wunderlich and Bu,⁵ Bu *et al.*,⁶ Roles and Wunderlich,⁷ and Roles *et al.*⁸ have reported experimental and theoretical studies of heat capacities of a

variety of polymeric systems, synthetic as well as biopolymeric. In most of the cases, their analysis is based on separation of the vibrational spectrum into group and skeletal vibrations. The former are taken from computations fitted to IR and Raman data and the latter by

Figure 1. Chemical repeat unit of Poly(L-valine).

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using the two parameter Tarasov model and fitting to low temperature heat capacities. However, in a few cases, where detailed dispersion curves of the vibrational spectrum are available,⁹⁻¹³ they have been used for obtaining group and skeletal vibrations and number of vibrators of each type. In some cases, dispersion curves for one polymeric system have been used to obtain the number of vibrators and frequencies of box oscillators for polymers with identical backbone. This approach is allowed when full dispersion curves are not available. However, it has its own limitations, specially when the side-chain and backbone modes are strongly coupled. In the present communication we report a comprehensive study of the normal mode analysis of β -PLV using Urey Bradley force field, its *N*-deuterated analog, phonon dispersion curves, spectra of oligovalines in relation to the polymeric form and specific heat from the density-of-states derived from the dispersion curves.

THEORY AND EXPERIMENT

Calculation of Normal Mode Frequencies

The calculation of normal mode frequencies has been carried out according to Wilson's G.

F. matrix method¹⁴ as modified by Higgs¹⁵ for an infinite chain. The vibrational secular equation which gives normal mode frequencies and their dispersion as a function of phase angles has the form:

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

where G is the inverse of the kinetic energy matrix, F is the force field matrix, δ is the vibrational phase difference between the corresponding modes of the adjacent residue units.

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

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

The calculated frequencies at $\delta=0$ are matched with the observed infrared frequencies. The FT-IR spectrum (Figure 2) of β -PLV, obtained from Sigma Chemicals, U.S.A. (Lot 111H5536, $DP(\text{vis})$ 82 and $MW(\text{vis})$ 8100) has been recorded in the $4000\text{--}450\text{ cm}^{-1}$ frequency range in CsI on a Perkin Elmer 1800 spectrophotometer, which was purged with dry nitrogen gas before recording the spectrum.

The FT-IR spectra of poly(L-valine) and oligovalines have been obtained in the solid state. It is well studied and established that

Figure 2. F.T.I.R. spectra of Poly(L-valine) ($4000\text{--}450\text{ cm}^{-1}$).

Table I. Internal coordinates and force constants (md Å⁻¹)^a

$\nu(\text{C}=\text{N})$	5.600	$\phi(\text{O}=\text{C}-\text{C}\alpha)$	0.200(0.60)
$\nu(\text{C}\alpha-\text{N})$	2.800	$\phi(\text{O}=\text{C}=\text{N})$	0.330(0.90)
$\nu(\text{C}\alpha-\text{C}\beta)$	2.600	$\phi(\text{C}\alpha-\text{C}=\text{N})$	0.210(0.60)
$\nu(\text{C}\beta-\text{C}\gamma_1)$	2.000	$\phi(\text{C}\gamma_1-\text{C}\beta-\text{C}\gamma_2)$	0.340(0.20)
$\nu(\text{C}\beta-\text{C}\gamma_2)$	2.000	$\phi(\text{C}\gamma_1-\text{C}\beta-\text{H}\beta)$	0.510(0.22)
$\nu(\text{H}-\text{H})$	5.360	$\phi(\text{C}\gamma_2-\text{C}\beta-\text{H}\beta)$	0.510(0.22)
$\nu(\text{H}\alpha-\text{C}\alpha)$	4.155	$\phi(\text{H}\beta-\text{C}\beta-\text{C}\alpha)$	0.440(0.22)
$\nu(\text{H}\beta-\text{C}\beta)$	4.410	$\phi(\text{C}\beta-\text{C}\gamma_1-\text{H}\gamma_1)$	0.420(0.22)
$\nu(\text{H}\gamma_1-\text{C}\gamma_1)$	4.210	$\phi(\text{C}\beta-\text{C}\gamma_2-\text{H}\gamma_2)$	0.420(0.22)
$\nu(\text{H}\gamma_2-\text{C}\gamma_2)$	4.210	$\phi(\text{H}\gamma_1-\text{C}\gamma_1-\text{H}\gamma_1)$	0.425(0.24)
$\nu(\text{C}\alpha-\text{C})$	2.200	$\phi(\text{H}\gamma_2-\text{C}\gamma_2-\text{H}\gamma_2)$	0.425(0.24)
$\nu(\text{C}=\text{O})$	8.225	$\phi(\text{C}\gamma_1-\text{C}\beta-\text{C}\alpha)$	0.210(0.20)
		$\phi(\text{C}\gamma_2-\text{C}\beta-\text{C}\alpha)$	0.210(0.20)
$\phi(\text{H}-\text{N}=\text{C})$	0.380(0.60)	$\omega(\text{N}-\text{H})$	0.155
$\phi(\text{H}-\text{N}-\text{C}\alpha)$	0.345(0.50)	$\omega(\text{C}=\text{O})$	0.445
$\phi(\text{C}=\text{N}-\text{C}\alpha)$	0.650(0.35)		
$\phi(\text{N}-\text{C}\alpha-\text{H}\alpha)$	0.290(0.80)	$\tau(\text{C}\alpha-\text{C})$	0.067
$\phi(\text{C}-\text{C}\alpha-\text{H}\alpha)$	0.270(0.48)	$\tau(\text{C}=\text{N})$	0.027
$\phi(\text{N}-\text{C}\alpha-\text{C})$	0.320(0.50)	$\tau(\text{C}\beta-\text{C}\alpha)$	0.047
$\phi(\text{N}-\text{C}\alpha-\text{C}\beta)$	0.100(0.50)	$\tau(\text{C}\beta-\text{C}\gamma_1)$	0.008
$\phi(\text{C}-\text{C}\alpha-\text{C}\beta)$	0.440(0.20)	$\tau(\text{C}\beta-\text{C}\gamma_2)$	0.008
$\phi(\text{C}\beta-\text{C}\alpha-\text{H}\alpha)$	0.270(0.22)	$\tau(\text{N}-\text{C}\alpha)$	0.031

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

for the degree of polymerization below 500, poly(L-valine) goes into β form.^{2,16} In the present case the degree of polymerization is 80. The sample is highly crystalline as evinced by X-ray diffraction and in β -form as seen from the characteristic Bragg reflections and amide bands, in particular amide III and V. Full use has been made of the dichroic information and our assignments are in complete agreement both at the zone centre (A species) and at the zone boundry (E species) with the observed data. Since the optically active modes correspond to phase values $\delta=0$ and $\delta=\pi$, a reasonably good matching is automatically obtained at $\delta=\pi$ by matching the observed frequencies at $\delta=0$. The frequencies below 450 cm⁻¹ are matched with the FT-IR and Raman frequencies reported by Fanconi.¹⁷ The final force constants are shown in Table I. The dispersion curves below 1400 cm⁻¹ are shown in Figures 3(a), 4(a), and 5(a).

Theory of Interpretation of Spectra of Oligomers

One of the important uses of the dispersion curves is to interpret the spectra of short chain molecules or oligomers which have the same structure as the polymeric form. The infrared spectra of macromolecules containing a finite chain of identical structural units is characterized by a series of absorption bands. It can be shown that the normal modes responsible for a component absorption can be specified by an appropriate phase difference.¹⁸ They are denoted by k values related to the phase difference δ along the chain between adjacent residue units and are given by

$$\delta = (k\pi/n), \quad k=0, 1, 2, \dots, n-1 \quad (3)$$

where n is the number of repeat units in the chain and k is an integer which represents the number of loops in a stationary wave representing the chain vibrations. The above equation holds good for finite chain having free ends. In the present paper, the dispersion

curves are used to calculate the normal frequencies of oligomers of valine upto hexamer for phase values given by eq 3.

Calculation of Heat Capacity

Another use of dispersion curves is that microscopic behaviour of a crystal can be correlated with its macroscopic properties such as specific heat. 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

$$g(\nu) = \sum_j (\partial \nu_j / \partial \delta)^{-1} \big|_{\nu_j(\delta) = \nu} \quad (4)$$

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, specific heat, and enthalpy. The heat capacity, which can give information about the proportion of a protein which is in α -helical or β sheet structure and is necessary in evaluating the basic thermodynamics of enzyme reaction,¹⁹ has been calculated using Debye's relation

$$C_v = \sum_j g(\nu_j) k N_A (h\nu_j/kT)^2 \frac{\exp(h\nu_j/kT)}{[\exp(h\nu_j/kT) - 1]^2} \quad (5)$$

with

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

The constant volume heat capacity C_v , given by eq 5 is converted into constant pressure heat capacity C_p using the Nernst-Lindemann approximation²⁰:

$$C_p - C_v = 3RA_0(C_p^2 T/C_v T_m^0) \quad (6)$$

where A_0 is a constant of a universal value 3.9×10^{-3} (kmol J⁻¹) and T_m^0 is the estimated equilibrium melting temperature, which is taken to be 573 K.

RESULTS AND DISCUSSION

The unit cell of PLV chain consists of two repeat units. Since there are 16 atoms per residue, there would be $(3 \times 32 - 4) = 92$ normal modes of vibrations. 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 π . The four zero frequencies [Figure 5(a)] correspond the acoustic modes, three representing three translations and one rotation of the chain. Assignments of modes are based not only on the concept of group vibrations and potential energy distribution but also take into account line intensity, line profile, and second derivative spectra. For the sake of simplicity, it is convenient to discuss the normal vibrational frequencies under two heads *viz.* side chain modes and backbone modes.

Backbone Modes

The modes involving the motions of amide group and N-C α and C-C α stretches, C-C α -N bending motions, and their mixtures are regarded as skeletal or backbone modes. The pure backbone modes, pure side chain modes and the mix modes along with their assignments are given in Table II, Table III, and Table IV, respectively. On comparison of the spectra of polyglycine I,¹⁰ β -poly(L-alanine)¹⁴ and poly(L-valine), it is inferred that there is very little interaction between the main chain vibrations and side chain vibrations in the 1700–1200 cm⁻¹ region (Table V). Below 1200 cm⁻¹ there is a large influence of side chain vibrations on the vibrations of the main chain (Table IV).

The amide I absorption in the IR spectrum of β -poly(L-valine) is reported at 1638 cm⁻¹ by Yamashita and Yamashita¹ and at 1625 cm⁻¹ by Koenig and Sutton.²¹ The corresponding line in the Raman spectrum appears at 1666 cm⁻¹. We have observed amide I line at 1638 cm⁻¹ in the FT-IR spectra of β -PLV. Second derivative spectra showed splitting of

Table II. Pure back-bone modes^a

Calcd	Obsd	Assignment (% P.E.D. ^b) ($\delta=0$)	Calcd	Obsd	Assignment (% P.E.D.) ($\delta=\pi$)
3289	3290	$\nu(\text{N-H})(99)$ {Amide A}	3289	3290	$\nu(\text{N-H})(100)$ {Amide A}
1629	1638	$\nu(\text{C=N})(20) + \nu(\text{C=O})(64)$ {Amide I}	1631	1638	$\nu(\text{C=N})(19) + \nu(\text{C=O})(63) +$ $\phi(\text{C=N-H})(5)$ {Amide I}
1537	1545	$\nu(\text{C=N})(20) + \phi(\text{C=N-H})(37) +$ $\phi(\text{C}\alpha\text{-N-H})(36)$ {Amide II}	1531	1545	$\nu(\text{C=N})(21) + \phi(\text{C=N-H})(35) +$ $\phi(\text{C}\alpha\text{-N-H})(35)$ {Amide II}

^a All frequencies are in cm^{-1} .^b P.E.D., potential energy distribution.**Table III.** Pure side-chain modes^a

Calcd	Obsd	Assignment (% P.E.D.) ($\delta=0$)
2968	2967	$\nu(\text{C}\alpha\text{-H}\alpha)(99)$
2930	2935	$\nu(\text{C}\beta\text{-H}\beta)(76) + \nu(\text{C}\gamma_1\text{-H}\gamma_1)(12) + \nu(\text{C}\gamma_2\text{-H}\gamma_2)(12)$
2922		$\nu(\text{C}\gamma_1\text{-H}\gamma_1)(52) + \nu(\text{C}\gamma_2\text{-H}\gamma_2)(47)$
2920		$\nu(\text{C}\beta\text{-H}\beta)(25) + \nu(\text{C}\gamma_1\text{-H}\gamma_1)(35) + \nu(\text{C}\gamma_2\text{-H}\gamma_2)(39)$
2880	2876	$\nu(\text{C}\gamma_1\text{-H}\gamma_1)(57) + \nu(\text{C}\gamma_2\text{-H}\gamma_2)(43)$
2880		$\nu(\text{C}\gamma_1\text{-H}\gamma_1)(64) + \nu(\text{C}\gamma_2\text{-H}\gamma_2)(36)$
2879		$\nu(\text{C}\gamma_1\text{-H}\gamma_1)(35) + \nu(\text{C}\gamma_2\text{-H}\gamma_2)(65)$
2879		$\nu(\text{C}\gamma_1\text{-H}\gamma_1)(44) + \nu(\text{C}\gamma_2\text{-H}\gamma_2)(56)$
1471	1470	$\phi(\text{H}\gamma_1\text{-C}\gamma_1\text{-H}\gamma_1)(45) + \phi(\text{H}\gamma_2\text{-C}\gamma_2\text{-H}\gamma_2)(49)$
1470		$\phi(\text{H}\gamma_1\text{-C}\gamma_1\text{-H}\gamma_1)(28) + \phi(\text{H}\gamma_2\text{-C}\gamma_2\text{-H}\gamma_2)(67)$
1469		$\phi(\text{H}\gamma_1\text{-C}\gamma_1\text{-H}\gamma_1)(67) + \phi(\text{H}\gamma_2\text{-C}\gamma_2\text{-H}\gamma_2)(28)$
1467		$\phi(\text{H}\gamma_1\text{-C}\gamma_1\text{-H}\gamma_1)(50) + \phi(\text{H}\gamma_2\text{-C}\gamma_2\text{-H}\gamma_2)(45)$
1391	1394	$\phi(\text{C}\beta\text{-C}\gamma_1\text{-H}\gamma_1)(24) + \phi(\text{C}\beta\text{-C}\gamma_2\text{-H}\gamma_2)(24) + \phi(\text{H}\gamma_2\text{-C}\gamma_2\text{-H}\gamma_2)(23) + \phi(\text{H}\gamma_1\text{-C}\gamma_1\text{-H}\gamma_1)(23)$
1370	1372	$\phi(\text{C}\beta\text{-C}\gamma_1\text{-H}\gamma_1)(24) + \phi(\text{C}\beta\text{-C}\gamma_2\text{-H}\gamma_2)(24) + \phi(\text{H}\gamma_1\text{-C}\gamma_1\text{-H}\gamma_1)(23) + \phi(\text{H}\gamma_2\text{-C}\gamma_2\text{-H}\gamma_2)(23)$
1006	1006	$\phi(\text{C}\beta\text{-C}\gamma_1\text{-H}\gamma_1)(40) + \phi(\text{C}\beta\text{-C}\gamma_2\text{-H}\gamma_2)(38)$
970	981	$\nu(\text{C}\beta\text{-C}\gamma_1)(13) + \nu(\text{C}\beta\text{-C}\gamma_2)(14) + \phi(\text{C}\beta\text{-C}\gamma_2\text{-H}\gamma_2)(26) + \phi(\text{C}\beta\text{-C}\gamma_1\text{-H}\gamma_1)(33)$
918	907	$\phi(\text{C}\beta\text{-C}\gamma_1\text{-H}\gamma_1)(48) + \phi(\text{C}\beta\text{-C}\gamma_2\text{-H}\gamma_2)(45)$
845	852	$\nu(\text{C}\beta\text{-C}\gamma_1)(27) + \nu(\text{C}\beta\text{-C}\gamma_2)(31) + \phi(\text{C}\beta\text{-C}\gamma_2\text{-H}\gamma_2)(14) + \phi(\text{C}\beta\text{-C}\gamma_1\text{-H}\gamma_1)(19)$
199	200	$\tau(\text{C}\beta\text{-C}\gamma_1)(31) + \tau(\text{C}\beta\text{-C}\gamma_2)(63)$

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

amide I mode into four components *viz.* 1635, 1652, 1670, and 1687cm^{-1} . This splitting is due to intrachain and interchain hydrogen bonding between adjacent groups in the same chain and in the neighbouring chain.²² The amide II mode appears as a strong band at 1545cm^{-1} . Koenig and Sutton²¹ in their studies on poly(L-valine) initially suggested the splitting of amide III into four components *viz.* 1287, 1276, 1231, and 1224cm^{-1} , later they revised the assignment of amide III after observing the shift in *N*-deuterated PLV²³ and they assigned the mode at 1231cm^{-1} to amide III. They observed that the line at 1231 and

1276cm^{-1} disappear at equal rate on deuteration. We disagree with this finding as the potential energy distribution of 1270cm^{-1} mode indicates that it is purely a side chain mode. Our result agrees with the Fasman *et al.*,² as the 1270cm^{-1} line, which is mainly $\text{H}\beta$ bending mode according to normal mode analysis, is found in the spectra of a monomer and this cannot be due to peptide group as monomer has no peptide group. The line at 1270cm^{-1} does not disappear on deuteration but shifts down to 1264cm^{-1} in accordance with the Fasman *et al.*²

We observe a strong band at 1228cm^{-1} ,

Table IV. Mixed modes^a

Calcd	Obsd	Assignment (% P.E.D.) ($\delta = 0$)	Calcd	Obsd	Assignment (% P.E.D.) ($\delta = \pi$)
1350	1343	$\phi(\text{N}-\text{C}\alpha-\text{H}\alpha)(45) + \phi(\text{C}-\text{C}\alpha-\text{H}\alpha)(14) + \phi(\text{C}_{71}-\text{C}\beta-\text{H}\beta)(15) + \phi(\text{C}_{72}-\text{C}\beta-\text{H}\beta)(9) + \tau(\text{C}\beta-\text{C}\alpha)(6)$	1345	1343	$\phi(\text{N}-\text{C}\alpha-\text{H}\alpha)(39) + \phi(\text{C}-\text{C}\alpha-\text{H}\alpha)(11) + \phi(\text{C}_{71}-\text{C}\beta-\text{H}\beta)(19) + \tau(\text{C}\beta-\text{C}\alpha)(6) + \phi(\text{C}_{72}-\text{C}\beta-\text{H}\beta)(11)$
1310	1319	$\phi(\text{N}-\text{C}\alpha-\text{H}\alpha)(22) + \phi(\text{C}_{71}-\text{C}\beta-\text{H}\beta)(33) + \phi(\text{C}_{72}-\text{C}\beta-\text{H}\beta)(21)$	1308	1319	$\phi(\text{N}-\text{C}\alpha-\text{H}\alpha)(27) + \phi(\text{C}_{71}-\text{C}\beta-\text{H}\beta)(29) + \phi(\text{C}_{72}-\text{C}\beta-\text{H}\beta)(19)$
1279	1270	$\phi(\text{H}\beta-\text{C}\beta-\text{C}\alpha)(30) + \phi(\text{C}_{72}-\text{C}\beta-\text{H}\beta)(18) + \nu(\text{C}=\text{N})(9) + \nu(\text{C}\alpha-\text{C})(10) + \nu(\text{C}\alpha-\text{C}\beta)(10)$	1274	1270	$\nu(\text{C}\alpha-\text{C}\beta)(16) + \phi(\text{H}\beta-\text{C}\beta-\text{C}\alpha)(38) + \phi(\text{C}_{72}-\text{C}\beta-\text{H}\beta)(21)$
1256	1228	$\nu(\text{C}=\text{N})(30) + \nu(\text{C}\alpha-\text{C})(11) + \nu(\text{C}=\text{O})(10) + \phi(\text{C}\alpha-\text{N}-\text{H})(6) + \phi(\text{H}\beta-\text{C}\beta-\text{C}\alpha)(11)$	1249	1228	$\nu(\text{C}=\text{N})(37) + \nu(\text{C}\alpha-\text{C})(19) + \nu(\text{C}=\text{O})(13) + \phi(\text{C}\alpha-\text{N}-\text{H})(6) + \nu(\text{N}-\text{C}\alpha)(9) + \phi(\text{O}=\text{C}=\text{N})(6)$
1161	1158	$\phi(\text{C}\beta-\text{C}\alpha-\text{H}\alpha)(30) + \phi(\text{C}-\text{C}\alpha-\text{H}\alpha)(33) + \nu(\text{C}\alpha-\text{C})(7) + \nu(\text{C}\alpha-\text{C}\beta)(8)$	1157	1158	$\nu(\text{C}\alpha-\text{C}\beta)(10) + \phi(\text{C}-\text{C}\alpha-\text{H}\alpha)(34) + \phi(\text{C}\beta-\text{C}\alpha-\text{H}\alpha)(33)$
1086	1090	$\nu(\text{N}-\text{C}\alpha)(64) + \nu(\text{C}\alpha-\text{C})(12)$	1052	1056	$\nu(\text{N}-\text{C}\alpha)(35) + \nu(\text{C}\alpha-\text{C}\beta)(18) + \phi(\text{H}\beta-\text{C}\beta-\text{C}\alpha)(8) + \phi(\text{C}\beta-\text{C}_{72}-\text{H}_{72})(7)$
1038	1037	$\nu(\text{C}\alpha-\text{C}\beta)(22) + \phi(\text{C}\beta-\text{C}_{71}-\text{H}_{71})(17) + \phi(\text{C}\beta-\text{C}_{72}-\text{H}_{72})(19) + \phi(\text{C}\beta-\text{C}\alpha-\text{H}\alpha)(8) + \phi(\text{H}\beta-\text{C}\beta-\text{C}\alpha)(12)$	1021	—	$\nu(\text{N}-\text{C}\alpha)(34) + \phi(\text{C}\beta-\text{C}_{71}-\text{H}_{71})(18) + \phi(\text{C}\beta-\text{C}_{72}-\text{H}_{72})(10)$
949	954	$\nu(\text{C}\alpha-\text{C})(35) + \nu(\text{C}=\text{O})(11) + \phi(\text{C}=\text{N}-\text{C}\alpha)(8) + \phi(\text{N}-\text{C}\alpha-\text{C})(8)$	923	928	$\nu(\text{C}\alpha-\text{C})(34) + \nu(\text{C}=\text{O})(6) + \nu(\text{C}\alpha-\text{C}\beta)(8) + \phi(\text{C}\beta-\text{C}_{71}-\text{H}_{71})(12) + \phi(\text{C}\beta-\text{C}_{72}-\text{H}_{72})(16)$
873	868	$\nu(\text{C}\alpha-\text{C}\beta)(23) + \phi(\text{C}\beta-\text{C}_{71}-\text{H}_{71})(13) + \phi(\text{C}\beta-\text{C}_{72}-\text{H}_{72})(24)$	820	822	$\nu(\text{C}\alpha-\text{C})(20) + \nu(\text{C}\alpha-\text{C}\beta)(17) + \phi(\text{C}\beta-\text{C}_{71}-\text{H}_{71})(18) + \nu(\text{C}\beta-\text{C}_{72})(24)$
784	775	$\omega(\text{N}-\text{H})(21) + \omega(\text{C}=\text{O})(19) + \nu(\text{C}\beta-\text{C}_{72})(16) + \phi(\text{C}\beta-\text{C}_{72}-\text{H}_{72})(5) + \nu(\text{C}\beta-\text{C}_{71})(10) + \phi(\text{C}\beta-\text{C}_{71}-\text{H}_{71})(6)$	755	765	$\omega(\text{N}-\text{H})(12) + \omega(\text{C}=\text{O})(14) + \nu(\text{C}\beta-\text{C}_{71})(20) + \phi(\text{C}=\text{N}-\text{C}\alpha)(9) + \nu(\text{C}\beta-\text{C}_{72})(9) + \phi(\text{C}-\text{C}\alpha-\text{C}\beta)(8)$
708	715	$\omega(\text{N}-\text{H})(22) + \nu(\text{C}\alpha-\text{C}\beta)(10) + \nu(\text{C}\beta-\text{C}_{71})(24) + \nu(\text{C}\beta-\text{C}_{72})(17) + \omega(\text{C}=\text{O})(6)$	724	715	$\omega(\text{H}-\text{N})(42) + \omega(\text{C}=\text{O})(16) + \nu(\text{C}\beta-\text{C}_{71})(6) + \nu(\text{C}\beta-\text{C}_{72})(6)$
606	615	$\omega(\text{N}-\text{H})(26) + \omega(\text{C}=\text{O})(35) + \tau(\text{N}-\text{C}\alpha)(13) + \tau(\text{C}=\text{N})(11)$	681	684	$\phi(\text{O}=\text{C}-\text{N})(19) + \phi(\text{C}=\text{N}-\text{C}\alpha)(13) + \nu(\text{N}-\text{C}\alpha)(10) + \phi(\text{N}-\text{C}\alpha-\text{C})(10) + \phi(\text{C}\alpha-\text{C}=\text{O})(7) + \nu(\text{C}\alpha-\text{C}\beta)(5) + \nu(\text{C}\beta-\text{C}_{71})(6) + \nu(\text{C}\beta-\text{C}_{72})(9) + \omega(\text{C}=\text{O})(6)$
551	548	$\phi(\text{C}\alpha-\text{C}=\text{O})(25) + \phi(\text{N}=\text{C}=\text{O})(33) + \phi(\text{C}-\text{C}\alpha-\text{C}\beta)(7)$	627	628	$\omega(\text{N}-\text{H})(19) + \omega(\text{C}=\text{O})(32) + \tau(\text{N}-\text{C}\alpha)(12) + \tau(\text{C}=\text{N})(8) + \nu(\text{C}\alpha-\text{C}\beta)(5) + \phi(\text{N}-\text{C}\alpha-\text{C})(6)$
371	364	$\phi(\text{N}-\text{C}\alpha-\text{C}\beta)(11) + \phi(\text{C}\alpha-\text{C}=\text{O})(8) + \phi(\text{C}_{71}-\text{C}\beta-\text{C}\alpha)(14) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}\alpha)(8) + \phi(\text{C}_{71}-\text{C}\beta-\text{H}\beta)(11) + \phi(\text{H}\beta-\text{C}\beta-\text{C}\alpha)(10) + \tau(\text{C}\alpha-\text{C})(5) + \phi(\text{C}_{72}-\text{C}\beta-\text{H}\beta)(8)$	482	472	$\phi(\text{C}\alpha-\text{C}=\text{O})(12) + \phi(\text{C}\alpha-\text{C}=\text{N})(28) + \phi(\text{N}-\text{C}\alpha-\text{C})(9)$
337	332	$\phi(\text{C}_{72}-\text{C}\beta-\text{C}_{71})(26) + \phi(\text{N}-\text{C}\alpha-\text{C}\beta)(8) + \phi(\text{C}_{71}-\text{C}\beta-\text{C}\alpha)(7) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}\alpha)(8) + \phi(\text{C}=\text{N}-\text{C}\alpha)(5)$	346	332	$\phi(\text{C}_{72}-\text{C}\beta-\text{C}_{71})(25) + \phi(\text{C}_{71}-\text{C}\beta-\text{H}\beta)(14) + \phi(\text{H}\beta-\text{C}\beta-\text{C}\alpha)(14) + \phi(\text{C}_{72}-\text{C}\beta-\text{H}\beta)(14) + \phi(\text{C}\alpha-\text{C}=\text{N})(5)$
312	308	$\phi(\text{N}-\text{C}\alpha-\text{C}\beta)(24) + \phi(\text{C}-\text{C}\alpha-\text{C}\beta)(9) + \phi(\text{C}_{71}-\text{C}\beta-\text{C}\alpha)(6) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}_{71})(14) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}\alpha)(11)$	374	365	$\phi(\text{N}-\text{C}\alpha-\text{C})(25) + \phi(\text{N}-\text{C}\alpha-\text{C}\beta)(17) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}_{71})(6) + \tau(\text{N}-\text{C}\alpha)(11) + \tau(\text{C}\alpha-\text{C})(12) + \tau(\text{C}=\text{N})(10)$
233	239	$\phi(\text{N}-\text{C}=\text{N})(13) + \phi(\text{N}-\text{C}\alpha-\text{C})(14) + \phi(\text{C}\alpha-\text{C}=\text{O})(5) + \tau(\text{C}\alpha-\text{C})(12) + \phi(\text{N}-\text{C}\alpha-\text{H}\alpha)(7) + \omega(\text{C}=\text{O})(8) + \tau(\text{C}\beta-\text{C}\alpha)(11)$	269	275	$\phi(\text{C}=\text{N}-\text{C}\alpha)(13) + \phi(\text{C}\alpha-\text{C}=\text{O})(18) + \phi(\text{O}=\text{C}=\text{N})(26) + \phi(\text{C}_{71}-\text{C}\beta-\text{C}\alpha)(10) + \phi(\text{N}-\text{C}\alpha-\text{C})(7)$
209	200	$\phi(\text{C}=\text{N}-\text{C}\alpha)(9) + \phi(\text{N}=\text{C}=\text{O})(5) + \phi(\text{C}\alpha-\text{C}=\text{N})(6) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}\alpha)(22) + \tau(\text{N}-\text{C}\alpha)(13) + \omega(\text{C}=\text{O})(7) + \phi(\text{C}_{71}-\text{C}\beta-\text{C}\alpha)(6) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}_{71})(6)$	234	239	$+ \phi(\text{C}_{71}-\text{C}\beta-\text{C}\alpha)(16) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}_{71})(37) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}\alpha)(11) + \phi(\text{N}=\text{C}=\text{O})(6) + \phi(\text{C}\alpha-\text{C}=\text{O})(6)$
203	—	$\phi(\text{N}=\text{C}=\text{O})(6) + \tau(\text{C}\beta-\text{C}_{71})(52) + \tau(\text{C}\beta-\text{C}_{72})(17)$	200	200	$\tau(\text{C}\beta-\text{C}_{71})(51) + \tau(\text{C}\beta-\text{C}_{72})(47)$
181	—	$\phi(\text{C}-\text{C}\alpha-\text{H}\alpha)(6) + \phi(\text{C}-\text{C}\alpha-\text{C}\beta)(15) + \phi(\text{N}=\text{C}=\text{O})(7) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}_{71})(15) + \tau(\text{C}\beta-\text{C}_{71})(12) + \tau(\text{C}\beta-\text{C}_{72})(10)$	208	—	$\phi(\text{C}_{71}-\text{C}\beta-\text{C}\alpha)(24) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}\alpha)(36) + \phi(\text{C}-\text{C}\alpha-\text{C}\beta)(6)$
150	150	$\phi(\text{C}=\text{N}-\text{C}\alpha)(5) + \phi(\text{N}-\text{C}\alpha-\text{C})(11) + \phi(\text{C}_{71}-\text{C}\beta-\text{C}\alpha)(28)$	148	150	$\tau(\text{C}\alpha-\text{C})(43) + \phi(\text{C}-\text{C}\alpha-\text{C}\beta)(11) + \omega(\text{C}=\text{O})(12) + \tau(\text{C}=\text{N})(6) + \tau(\text{N}-\text{C}\alpha)(9) + \tau(\text{N}-\text{C}\alpha)(7)$
126	132	$\phi(\text{C}-\text{C}\alpha-\text{C}\beta)(12) + \tau(\text{C}\alpha-\text{C})(26) + \tau(\text{C}=\text{N})(7) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}\alpha)(13) + \tau(\text{C}\beta-\text{C}\alpha)(13)$	102	100	$\tau(\text{C}\beta-\text{C}\alpha)(69) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}\alpha)(6) + \phi(\text{C}-\text{C}\alpha-\text{C}\beta)(5)$
91	100	$\phi(\text{C}=\text{N}-\text{C}\alpha)(7) + \phi(\text{C}\alpha-\text{C}=\text{N})(9) + \tau(\text{C}\beta-\text{C}\alpha)(47) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}\alpha)(7)$	67	64	$\phi(\text{N}-\text{C}\alpha-\text{C}\beta)(20) + \phi(\text{C}-\text{C}\alpha-\text{C}\beta)(28) + \tau(\text{N}-\text{C}\alpha)(8) + \tau(\text{C}\beta-\text{C}\alpha)(13) + \phi(\text{C}_{72}-\text{C}\beta-\text{C}\alpha)(11) + \phi(\text{C}_{71}-\text{C}\beta-\text{C}\alpha)(5)$
51	—	$\phi(\text{N}-\text{C}\alpha-\text{C}\beta)(6) + \phi(\text{C}-\text{C}\alpha-\text{C}\beta)(7) + \omega(\text{H}-\text{N})(14) + \tau(\text{N}-\text{C}\alpha)(9) + \tau(\text{C}=\text{N})(22) + \tau(\text{C}\alpha-\text{C})(16) + \tau(\text{C}\beta-\text{C}\alpha)(6)$	66	—	$\phi(\text{N}-\text{C}\alpha-\text{C}\beta)(12) + \phi(\text{C}\beta-\text{C}\alpha-\text{H}\alpha)(12) + \phi(\text{C}_{72}-\text{C}=\text{N})(8) + \phi(\text{C}_{71}-\text{C}\beta-\text{C}\alpha)(6) + \tau(\text{N}-\text{C}\alpha)(18) + \tau(\text{C}\alpha-\text{C})(9) + \tau(\text{C}=\text{N})(8)$

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

the characteristic frequency of amide III for the β sheet conformation of poly(L-valine). The corresponding calculated frequency is at 1258 cm^{-1} . In spite of our best efforts, this frequency could not be adjusted better. When PLV is deuterated the amide III mode shifts down to 1023 cm^{-1} (a shift of 235 cm^{-1}) but the potential energy distribution of the shifted mode has small contribution of N-C α stretch also (Table VI). This is consistent with the fact that the line shape of the deuterated mode of amide III which shifts from 1231 cm^{-1} to 993 cm^{-1} (a shift of 238 cm^{-1}) does not remain the same as is clear from the *N*-deuterated spectra of β -PLV reported by Koenig and Sutton.²¹ The N-H stretching vibration which is observed at 3290 cm^{-1} in the nondeuterated samples shifts to N-D mode at 2399 cm^{-1} .

The amide V mode which is characteristic of

β conformation in polyglycine, poly(L-valine) is assigned at 715 cm^{-1} . The frequency of amide V mode does not depend solely on main chain conformation but hydrogen bond strength and side chain structure in question also play an important role.²² Likewise the frequency of CO in-plane-bend (amide IV), CO out-of-plane bend (amide VI), and CN torsion (amide VII) also vary with structure. On *N*-deuteration the amide V mode in β -PLV disappears and $\omega(\text{N-D})$ mode appears at 530 cm^{-1} . This agrees well with the finding of Itoh *et al.*²⁴ A mixed mode of amide V + amide VI is assigned at 615 cm^{-1} . The band observed at 472 cm^{-1} which is characteristic of β -PLV and is sensitive to the conformation of main chain, is calculated at 482 cm^{-1} ($\delta = \pi$). It is mainly (C α -C-N) bending mode. Itoh and Fasman¹⁶ have observed two modes at 262 and 235 cm^{-1} in IR spectra of β -PLV and have tentatively assigned these modes as main chain deformation. These modes are reproduced reasonably well as main chain deformation in our normal mode analysis.

An intense band at 132 cm^{-1} in the Raman spectrum is assigned to the torsional motion around the peptide C-N bond (amide VII). This frequency belongs to $\delta = 0$ as shown in Table IV. The corresponding frequency belonging to $\delta = \pi$ is calculated at 148 cm^{-1} .

A normal mode involving (N-C α) (64%) and (C α -C) (12%) stretches is calculated at 1086

Table V. Amide modes of polypeptides in β conformation^a

	PGI	PLA	PLV
Amide I	1690	1695	1666
	1630	1634	1638
Amide II	1514	1524	1545
	1524		
Amide III	1240	1224	1228
	1220	1241	

^a PGI, polyglycine I; PLA, poly(L-alanine); PLV, poly(L-valine).

Table VI. Shifts on *N*-deuteration^a

Freq. ^b of the N-H mode	Assinment (% P.E.D.)	Freq. ^b of the N-D mode	Assignment (% P.E.D.)
3289	$\nu(\text{N-H})(99)$ {Amide A}	2399	$\nu(\text{N-D})(98)$ {Amide A}
1537	$\nu(\text{C}=\text{N})(20) + \phi(\text{C}=\text{N-H})(37) + \phi(\text{C}\alpha-\text{N-H})(36)$ {Amide II}	1380	$\nu(\text{C}=\text{N})(39) + \nu(\text{N-C}\alpha)(12) + \phi(\text{C}=\text{N-D})(15) + \phi(\text{C}\alpha-\text{N-D})(27) + \nu(\text{C}=\text{O})(8) + \nu(\text{C}\alpha-\text{C})(7)$ {Amide II}
1256	$\nu(\text{C}=\text{N})(30) + \nu(\text{C}\alpha-\text{C})(11) + \nu(\text{C}=\text{O})(10) + \phi(\text{C}\alpha-\text{N-H})(6) + \phi(\text{H}\beta-\text{C}\beta-\text{C}\alpha)(11)$ {Amide III}	1023	$\nu(\text{N-C}\alpha)(26) + \phi(\text{C}=\text{N-D})(15) + \phi(\text{C}\alpha-\text{N-D})(27)$ {Amide III}
708	$\omega(\text{N-H})(22) + \nu(\text{C}\beta-\text{C}\gamma)(41) + \omega(\text{C}=\text{O})(6) + \nu(\text{C}\alpha-\text{C}\beta)(10)$ {Amide V}	536	$\omega(\text{N-D})(47) + \omega(\text{C}=\text{O})(7) + \phi(\text{N-C}\alpha-\text{C})(16) + \tau(\text{C}=\text{N})(5)$ {Amide V}

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

cm^{-1} corresponding to observed band at 1090 cm^{-1} .

Side Chain Modes

Side chain of poly(L-valine) has a gem dimethyl group. Side chain modes mostly consist of rocking, wagging, twisting modes of CH_3 and $\text{C}\beta\text{--C}\gamma$, $\text{C}\beta\text{--H}\beta$, $\text{C}\gamma\text{--H}\gamma$ stretching modes. The strong line in the FT-IR spectrum at 1470 cm^{-1} is assigned to asymmetric CH_3 deformation of the gem dimethyl group. The doublet observed at 1394 and 1372 arise from symmetric CH_3 deformation of the gem dimethyl group and is calculated at 1391 and 1370 cm^{-1} . Methyl rocking modes are calculated at 1038, 1006, 970, 918, and 873 cm^{-1} corresponding to observed frequencies at 1037, 1006, 981, 907, and 868 cm^{-1} respectively. Out of these five modes two modes at 1006 and 918 cm^{-1} are pure rocking modes and three modes are mixed modes. The modes at 1038 and 868 cm^{-1} have small contribution from ($\text{C}\alpha\text{--C}\beta$) stretch while the mode at 970 cm^{-1} is mixed with ($\text{C}\beta\text{--C}\gamma$) stretch. The modes calculated at 1350 cm^{-1} and 1310 cm^{-1} corresponding to the observed bands at 1343 cm^{-1} and 1319 cm^{-1} respectively, are mixture of $\text{H}\alpha$ and $\text{H}\beta$ bendings. In the first case $\text{H}\alpha$ bend is dominant while in the other one $\text{H}\beta$ bend is dominant. The doublet calculated at 203 and 199 cm^{-1} corresponds to ($\text{C}\beta\text{--C}\gamma_1$) and ($\text{C}\beta\text{--C}\gamma_2$) torsions.

Dispersion Curves

The dispersion of modes below 1400 cm^{-1} are plotted in Figures 3(a), 4(a), and 5(a). The mode at 371 cm^{-1} shows maximum dispersion. This mode involves the motion of both, backbone and side-chain atoms and its potential energy distribution (P.E.D.) at $\delta=0$ is $\phi(\text{N--C}\alpha\text{--C}\beta)(11\%) + \phi(\text{H}\beta\text{--C}\beta\text{--C}\alpha)(10\%) + \phi(\text{C}\gamma_1\text{--C}\beta\text{--C}\alpha)(10\%) + \phi(\text{C}\gamma_1\text{--C}\beta\text{--H}\beta)(11\%)$. As δ increases the contributions of side chain motion decreases and at $\delta=\pi$ it becomes a pure backbone mode having $\phi(\text{C}\alpha\text{--C}=\text{O})(12\%) + \phi(\text{C}\alpha\text{--C}=\text{N})(28\%)$ and $\phi(\text{N--C}\alpha\text{--C})(9\%)$. The

Figure 3. (a) Dispersion curves of Poly(L-valine) and spectral data of oligovalines [$\bullet$, $\blacksquare$, $\blacklozenge$, and $\blacktriangle$ indicate dimer, trimer, tetramer, and hexamer, respectively] ($1400\text{--}900\text{ cm}^{-1}$). (b) Density-of-states $g(v)$ ($1400\text{--}900\text{ cm}^{-1}$).

Figure 4. (a) Dispersion curves of Poly(L-valine) and spectral data of oligovalines [$\bullet$, $\blacksquare$, $\blacklozenge$, and $\blacktriangle$ indicate dimer, trimer, tetramer, and hexamer, respectively] ($900\text{--}500\text{ cm}^{-1}$). (b) Density-of-states $g(v)$ ($900\text{--}500\text{ cm}^{-1}$).

frequencies that show dispersion are mainly the backbone and side chain-backbone junction modes. The backbone stretching mode calculated at 1086 cm^{-1} shows a dispersion of 34 wavenumbers. The frequency of the mode

Figure 5. (a) Dispersion curves of Poly(L-valine) and spectral data of oligovalines [$\bullet$, $\blacksquare$, $\blacklozenge$, and $\blacktriangle$ indicate dimer, trimer, tetramer, and hexamer, respectively] below 500 cm^{-1} . (b) Density-of-states $g(\nu)$ below 500 cm^{-1} .

at 784 cm^{-1} which consists of a mixture of N-H wag and C=O wag, decreases as the value of δ increases, this mode come closer to the amide V mode (708 cm^{-1}), the energy of which is continuously increasing with δ value. At $\delta \approx 0.65\pi$, percentage contribution of N-H wag and C=O wag start decreasing in the higher mode (784 cm^{-1}) and goes into the lower mode (708 cm^{-1}). The percentage contribution of N-H wag increases very sharply in the lower mode and the energy of this mode starts decreasing while the higher mode takes up a constant value. A repulsion also occurs in the modes at 606 and 551 cm^{-1} . The frequency of 551 cm^{-1} mode increases very sharply as δ increases and percentage contributions of $\phi(\text{C}\alpha\text{--C=O})$ and $\phi(\text{O}\cdots\text{C}\cdots\text{N})$ decrease. The frequency of 606 cm^{-1} mode increases very slowly and % contributions of N-H and C=O wag decrease. At $\delta \approx 0.5\pi$, $\omega(\text{N-H})$ starts mixing with 551 cm^{-1} mode while $\phi(\text{O}\cdots\text{C}\cdots\text{N})$ starts mixing with 606 cm^{-1} at $\delta = 0.55\pi$. At $\delta = 0.6\pi$ the two modes exchange their character and the 606 cm^{-1} mode is repelled up while the lower mode takes

up nearly constant value. The mode at 312 cm^{-1} crosses the 337 cm^{-1} mode belonging to different symmetry species at $\delta \approx 0.7\pi$. The mode at 181 cm^{-1} which is a bending mode of C-C α -C β and C γ_1 -C β -C γ_2 cross the (C β -C γ) torsional mode at $\delta = 0.65\pi$. This type of crossing is possible in polymers where the backbone lies on a mirror plane of symmetry.²⁵

Interpretation of Spectra of Oligomers from Dispersion Curves

In the absence of inelastic neutron scattering data one of the easiest ways to test the meandering part of the dispersion curves is to look at the spectra of various oligomers. As discussed earlier the spectra of oligomers are related to the dispersion profile of the polymer modes through the phase relationship given by expression (3) and provided both the oligo- and polymers are conformationally connected. The Raman scattering data on oligomers of valine upto hexamer as reported by Fasman *et al.*² have been used. The observed modes are assigned at appropriate phase values on the corresponding branch of the dispersion curve from all possible k values and are plotted in Figure 3(a), 4(a), and 5(a) along with the dispersion curve of $(\text{Val})_n$. A comparison of some important modes in various oligomers has been given in Table VII. A good agreement of observed frequencies for oligovalines on the corresponding dispersion curves for allowed phase values show that the oligomers of valine upto hexamer have a structure closer to the extended β form. In case of divalene there are significant deviations, these could be due to the end group interactions arising due to out of plane conformation of the COO^- group with respect to the plane of the atoms in the skeleton (N-C α -C-N). The interactions decay rapidly as chain length increases.

Frequency Distribution Function and Heat Capacity of Poly(L-valine)

Frequency distribution function as obtained from the dispersion curves is shown in Figures

Table VII. A comparison of amide and some other modes in oligovalines and Poly(L-valines)^a

Mode	<i>n</i> =2	<i>n</i> =3	<i>n</i> =4	<i>n</i> =6	β -PLV
Amide I	1622(1630) 1660	1655(1637) 1668	1634(1631) 1663	— 1663	1629
Amide II	1551(1531)	1560(1537)	1565(1537)	1565(1537)	1537
Amide III	1254(1256)	1253(1255)	1238(1253)	1228(1250)	1256
Amide IV	564(551)	560(551)	566(566)	—	551
Amide V	744(726)	720(715)	720(713)	—	708
Amide IV	622(619)	618(606)	618(609)	—	606
Amide VII	133(127)	132(127)	102(106)	—	126
$\nu(\text{N}-\text{C}\alpha) + \nu(\text{C}\alpha-\text{C})$	1072(1066) 1031(1034)	1070(1076) 1032(1037)	1087(1080) —	1092(1086) —	1086 1038
Methyl rock	1003(1006)	1005(1006)	1014(1006)	1017(1005)	1006
$\nu(\text{C}\alpha-\text{C}) + \nu(\text{C}=\text{O})$	936(934) 847(843)	944(941) 850(845)	954(944) 835(832)	954(947) 844(845)	949 845
$\omega(\text{N}-\text{H}) + \omega(\text{C}=\text{O})$	766(771)	784(784)	754(753)	756(760)	784
Main-chain def.	269(269)	265(263)	272(268)	269(267)	270
Side-chain def.	— 375(371)	— 368(371)	147(146) 400(398)	141(143) 403(398)	150 371

^a All frequencies are in cm^{-1} and the figures in parenthesis are the predicted values from the dispersion curves of β -PLV for *n*=2, 3, 4, and 6.

Figure 6. Variation of heat capacity C_p with temperature. [A ----, B ·····, C - · - ·, and D, —●— indicate backbone contribution, side-chain contribution, mixed mode contribution, and total contribution where ● represents experimental points.

3(b), 4(b), and 5(b). The peaks in the frequency distribution curves correspond to the regions of high density-of-states. The observed frequencies compare well with these peak posi-

tions. From this knowledge of density-of-states, heat capacity of PLV chain has been calculated from 230–390 K. Experimental measurements have been reported by Roles and

Wunderlich.⁷ They have fitted the data using approximate group vibrations and dispersion curves of polyglycine I, poly(L-alanine) (β form) reported by this group. Such an approximation is valid only in the high frequency region. The low frequency modes are much more sensitive to actual conformation of the chain and side groups and there is strong coupling between these modes. Specific heat in the low temperature region is sensitive to $g(v)$ in the low frequency region. Modes which are purely skeletal, purely side chain and mixture of these two are given in Table II, Table III, and Table IV, respectively. Their contributions to the heat capacities are shown in Figures 6A, 6B, and 6C, respectively in the temperature range 230–390 K. The sum of these three contributions *i.e.*, total heat capacity is shown in Figure 6D and the experimental data of Roles and Wunderlich⁸ is represented by $\bullet$'s. Our calculations agree well with the experimental data in the whole temperature range. It is clear from Figure 6 that major contribution to the heat capacity comes from backbone and side chain coupled modes.

Acknowledgement. Financial assistance to L.B. and P.T. from the University Grants Commission and to V.D.G. from C.S.I.R. under the Emeritus Scientist Scheme is gratefully acknowledged.

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