Solid−Solid Phase Transitions in DL-Norvaline Studied by Differential Scanning Calorimetry and Raman Spectroscopy

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The structural modifications of the amino acid DL-Norvaline have been studied using differential scanning calorimetry (DSC) and Raman spectroscopy. DSC results showed that this amino acid undergoes two solid−solid phase transitions at −116.9 and −76.1 °C in the temperature range −130 to +300 °C. Raman spectroscopy was applied to complement DSC results. The combination of the two methodologies point out that the observed phase transitions correspond to an increment of disordering in the aliphatic side chain of amino acid, an augmentation of the rotational motion of the amino group and a decrease of the strength of the intramolecular hydrogen bonding of the initial dimers at low temperatures. The observed phase transitions of DL-norvaline are compared with those found in DL-norleucine.

1. Introduction

Amino acids are the basic "building blocks" that are combined to form proteins. In every species, proteins are constructed from the same set of 22 amino acids. Not only are they necessary to form proteins, enzymes, and other body tissues, but also they are found in a wide variety of chemical reactions throughout the body. In addition, amino acids are vital for basic energy production in cycles for energy transfers and muscle activity. Much attention has been directed to polymorphic transition of aliphatic α-amino acids. Aliphatic amino acids with normal alkyl chain are known to undergo solid-state phase transitions during which the alkyl chains change their conformations. The structural variations in the solid state constitute a simple model for conformational dependence in biochemical processes. In particular, the thermal analysis on solid−solid phase transitions between crystalline amino acids brings suggestive information on transition phenomena of biological systems, especially of biomembranes.[1−5]

The information about the structure and the conformational changes of amino acids can be deduced from the spectral parameters like band positions, band intensity, and absorption coefficient. Thus, IR and Raman spectroscopic methods can be used as a tool to study the interesting features, which are useful in understanding their structure either in the crystalline state and in solution, where they are present as zwitterions, or in the gaseous state and isolated in a noble gas matrix at low temperature, where the molecular, nonionic forms are more stable.[6−15]

Recently, our group has been working on the conformational changes of biological systems (e.g., natural and synthetic amino acids and their derivatives, drugs, etc.) and their effects on model lipid membranes.[16−22]

The present study is a continuation of our previous studies to characterize important molecules. More specifically, DSC and Raman techniques are applied to characterize in detail the solid−solid phase conformations in DL-norvaline. DL-norvaline $\{NH_3^+CH(CH_2CH_2CH_3)COO^-\}$ as well as DL-norleucine $\{NH_3^+CH(CH_2CH_2CH_2CH_3)COO^-\}$ are two aliphatic amino acids. Conformational changes of DL-norleucine are extensively studied since the molecular coordinates in the crystal are known. On the other hand, DL-norvaline is one of the amino acids rarely found and discussed in literature. This is presumably due to the absence of detailed crystal structure data for it, making thus, rather difficult the characterization of its different structural modifications.[5,6,23]

2. Experimental Methods

2.1. Materials. Amino acid DL-norvaline $\{NH_3^+CH(CH_2CH_2CH_3)COO^-\}$ chromatographically homogeneous purity grade (99%) was purchased in polycrystalline form from Fluka and was used with no further purification.

2.2. Instruments. A Perkin-Elmer DSC-4 was used to obtain differential scanning calorimetry (DSC) curves. Known weights (5−10 mg) of dry samples, stored either at room temperature or in a freezer at −20 °C, were sealed under drybox conditions at room temperature into DSC aluminum pans. Samples were usually heated or cooled at 10 °C min^{-1}. The DSC curves were analyzed by using the Thermal Analysis Data Station (TADS) of the DSC-4. Transition temperatures T_{tr} were obtained from the temperatures at the peaks of the endotherms or exotherms (±0.5 °C), and enthalpies of transition ΔH_{tr} were obtained from peak areas (±0.2 $kJmol^{-1}$). The power and temperature scales of the calorimeter were calibrated against the enthalpy of fusion and melting temperature of indium. The correction for thermal lag was based on the examination of certain standards at different heating rates and the extrapolation to zero heating rate through plots of T_m against root heating rate. Thermal treatment of samples was carried out in the instrument by successive constant rate heating−cooling cycles.

Raman spectra were recorded with a Perkin-Elmer GX Fourier Transform spectrometer. A diode pumped Nd:YAG laser at 1064 nm was used as the excitation source. The scattered radiation was collected at an angle of 180° to the incident beam. Spectra were recorded at a laser power of 300 mW on sample

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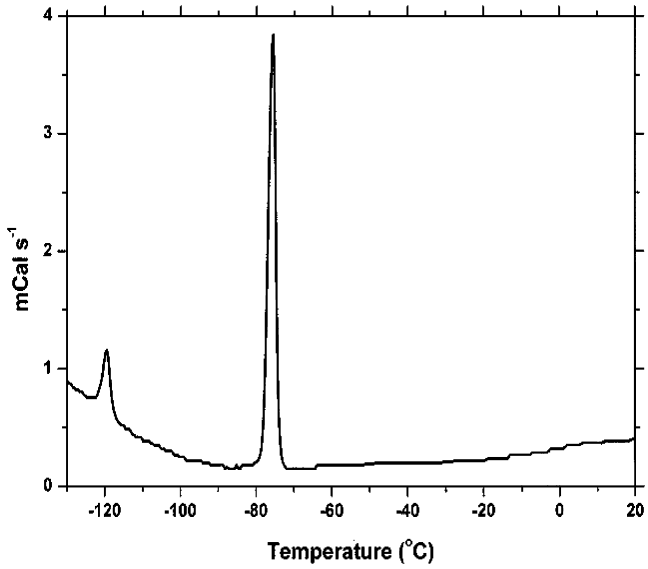

Figure 1. DSC heating curve of DL-norvaline.

TABLE 1: Transition Temperatures, Enthalpies and Entropies of DL-Norvaline

process	temperature (T) (°C)	enthalpy (ΔH) (kJmol^{-1})	entropy (ΔS) (kJ K^{-1} mol^{-1}) × 10^{-3}
heating	−116.9	0.36	2.31
	−76.1	1.59	8.07
cooling	−119.9	0.24	1.57
	−84.5	1.50	7.95

with a resolution of 2 cm^{-1}. To obtain a good signal-to-noise ratio, 250 scans were coadded for the spectra. The temperature increment of Raman spectra was taken by using the low-temperature cell from Ventacon Ltd. The intensity of a Raman band was observed over a period of time to ensure equilibration of the sample at the given temperature. Analysis of the spectra was carried out using the Perkin-Elmer Spectrum Software. Raman spectra of DL-norvaline were obtained in the frequency region 3500−100 cm^{-1} and in the temperature range −130 to 300 °C.

3. Results and Discussion

3.1. Thermal Analysis. The obtained DSC curve of DL-norvaline during heating process is shown in Figure 1. In the temperature range −130 to 300 °C (decomposition temperature) two endotherms at −116.9 and −76.1 °C were observed during heating, while the corresponding exotherms at −119.9 and −84.5 °C were observed during cooling.

The phase transitions are thermodynamically stable as they retain at the same temperatures with the same enthalpy requirements, after a number of successive constant rate heating−cooling cycles. Table 1 summarizes the temperatures, enthalpies, and entropies of DL-norvaline's phase transitions.

Studying by DSC the phase transitions of naturally neutral aliphatic amino acids in the temperature range −40 to 150 °C, Grunenberg et al.[1] found a number of solid−solid phase transitions in most of them. They attributed the observed phase transitions to the change of the alkyl chain conformation and to the translations of their double layers. For DL-norvaline they observed only one phase transition at 0 °C with $\Delta H = 0.04$ kJmol^{-1}, which has not been observed in our measurements. Our research team also found solid−solid phase transitions in racemic synthetic α-amino acids[16] with a number of carbon atoms 6 to 22 and in long chain synthetic amino alcohols.[18]

3.2. Raman Spectroscopy. Raman spectroscopic studies reveal several interesting features, which are useful in understanding the structure and the conformational changes of natural and synthetic α-amino acids, as well as of their derivatives. In the present study Raman spectra of DL-norvaline were obtained in the temperature range −130 to 300 °C. These spectra showed significant changes at specific temperatures in which the DSC heating treatment revealed phase transitions. The observed frequencies and their assignments are listed in Table 2. This table summarizes conformationally sensitive bands which are showed differences during phase transition and will be discussed in the text. Bands were assigned by comparison with similar compounds.[2,7,9,12,14,20,24−30,32,33]

Norvaline's structure (Figure 2) shows several modifications that were monitored by measuring changes in the frequencies and intensities of Raman bands. Three important spectral regions, the 3100−2800 cm^{-1} C−H stretching modes, the 1500−1300 cm^{-1} alkyl chain deformation and bending modes and finally, the 1200−1000 cm^{-1} alkyl chain C−C stretching modes, sensitively reflect modifications in chain packing properties and in intrachain trans/gauche rotamer formation.

3.2.1. Spectral Region 3100−2800 cm^{-1}. C−H stretching bands dominate in Raman spectra in this spectral region; their

TABLE 2: Observed Raman Bands of DL-Norvaline and Their Assignment in the Spectral Region 3500−100 cm^{-1} at Four Different Temperatures

−130 °C	−90 °C	−60 °C	25 °C	assignment
		829	829	$C^{\alpha}-CO2^{-}$ wagging (ω)
879	877			$C^{\alpha}-CO2^{-}$ wagging (ω)
1052	1052	1050	1050	C−C asymmetric stretching (υ_{asym})
1076	1076	1076	1076	C−C symmetric stretching (υ_{sym})
		1080	1080	C−C symmetric stretching (υ_{sym})
1120	1119	1117	1117	C−C symmetric stretching (υ_{sym})
1313	1313	1307	1307	C^{α}−H symmetric deformation (δ_{sym})
1331	1331	1323	1323	N−H deformation (δ_{sym})
1376	1376	1372	1372	CH_3 symmetric deformation (δ_{sym})
1428	1427	1424	1423	CH_2 bending (δ_{sym})
1449	1449	1447	1447	CH_3 asymmetric deformation (δ_{asym})
2868	2868	2870	2870	CH_2 symmetric stretching (υ_{sym})
2908	2908	2914	2914	CH_3 symmetric stretching (υ_{sym})
2932	2932	2934	2935	CH_2 asymmetric stretching (υ_{asym})
		2959	2959	CH_3 asymmetric stretching (υ_{asym})
2978	2978	2978	2978	NH_3^{+} asymmetric stretching (υ_{asym})
2990	2990			NH_3^{+} asymmetric stretching (υ_{asym})
2994	2994			NH_3^{+} asymmetric stretching (υ_{asym})

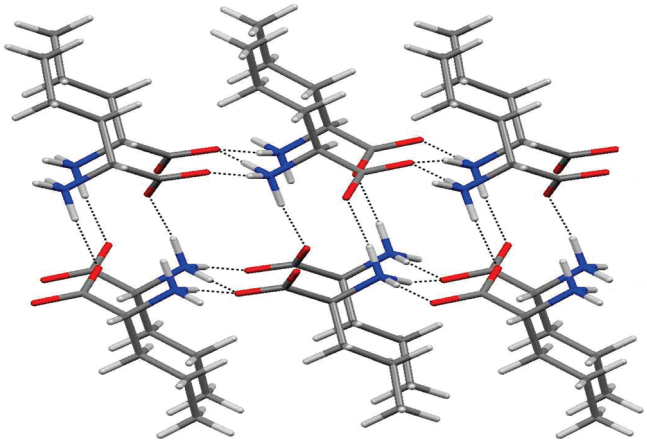

Figure 2. Molecular structure of DL-norvaline.

temperature dependence provides a qualitative indicator of changes in chain packing and conformational order.

Bands at 2870 and 2935 cm^{-1} were assigned to methylene C−H symmetric and asymmetric stretching modes respectively,[28−30] while bands at 2914 and 2959 cm^{-1} correspond to chain terminal methyl C−H symmetric and asymmetric stretching modes respectively.[28,29] In addition, the band at 2978, 2990, and 2994 cm^{-1} represents the asymmetric stretching mode of N−H of protonated amino group (Figure 3, Table 2).

C−H stretching bands shift to higher frequencies during heating from −130 to +25 °C, showing an abrupt increase of the frequency at about −76 °C, where an endothermic phase transition is observed by DSC. This observation is interpreted as an increase of chain−chain interactions caused by the decrease of strength of the hydrogen bonds as will be discussed in Section 3.2.4. To illustrate this, an example of the temperature profile of the symmetric methyl C−H stretching band at 2914 cm^{-1}.

On the other hand, changes in the peak height intensity ratios of bands described above provide convenient means for constructing temperature profiles for amino acids reflecting phase transitions. Of interest are the peak height intensity ratios

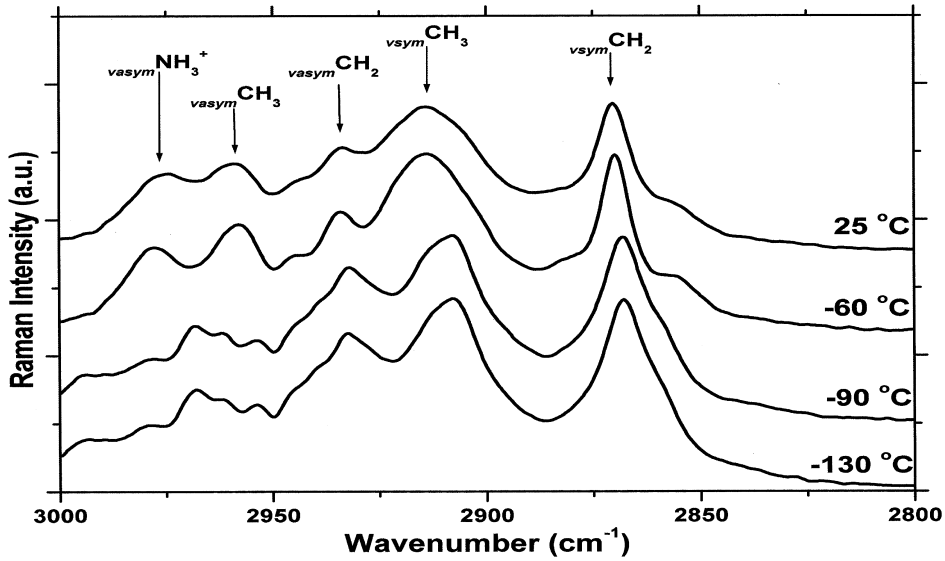

Figure 3. Normalized Raman spectra (3000−2800 cm^{-1}) of DL-norvaline at several temperatures as indicated.

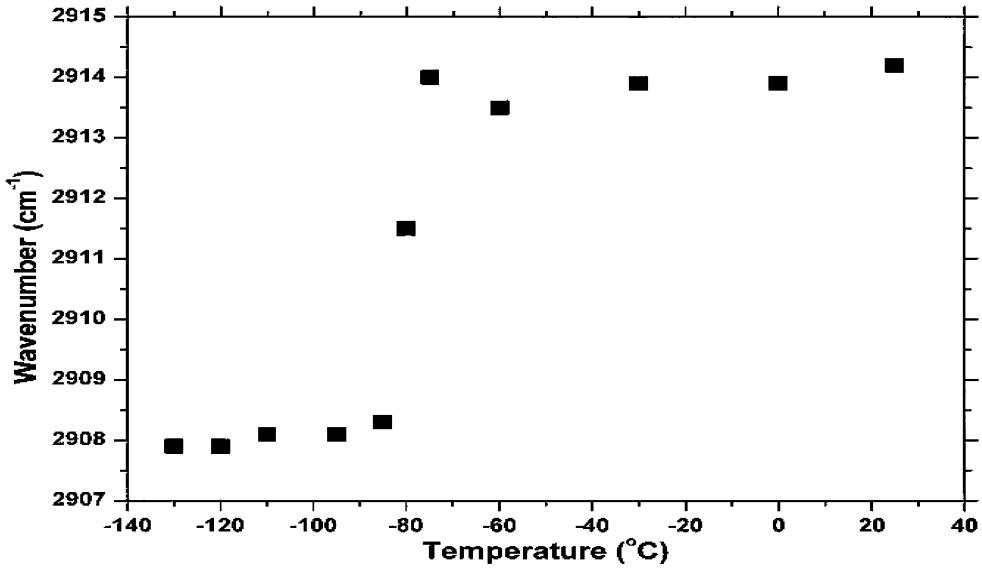

Figure 4. Temperature dependence of the symmetric methyl stretching band at 2914 cm^{-1}.

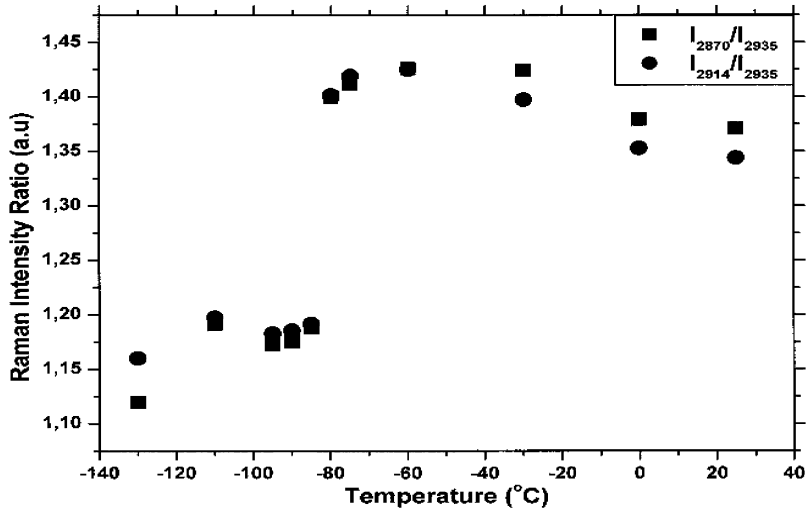

Figure 5. Temperature dependence of Raman peak height intensity ratios I_{2870}/I_{2935} and I_{2914}/I_{2935}.

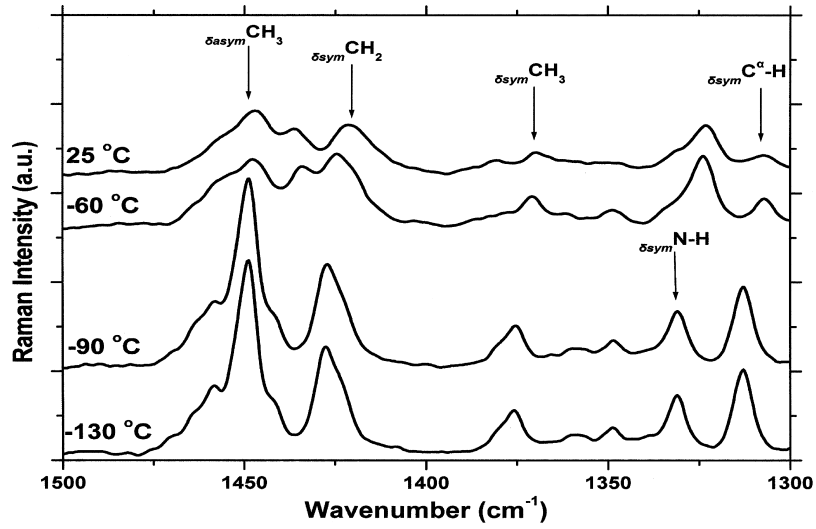

Figure 6. Normalized Raman spectra (1500−1300 cm^{-1}) of DL-norvaline at temperature range of −130 to +25 °C.

I_{2870}/I_{2935} and I_{2914}/I_{2935}. The first ratio is assumed to be sensitive to lateral chain−chain interactions and the second ratio is sensitive to intermolecular interactions, but also it should reflect the mobility of the methyl terminal group of hydrocarbon chains. Thus, the lower the intensity ratio is, the higher the conformational order of the alkyl chain and the lower mobility of the methyl end group is obtained.[2,18,34] Figure 5 represents the changes in Raman peak height intensity ratios in relation to temperature of DL-norvaline. It is shown clearly that there are two temperature regions at about −120 and −76 °C, in which an increase of the intensity ratios is observed that almost corresponds to the phase transitions observed by DSC. These observations reveals that the phase transitions of DL-norvaline includes contributions of rearrangement of molecular layers due to intermolecular interactions between constituent molecules and conformational change due to the rotation of carbon−carbon bonds in alkyl chains.[31]

3.2.2. Spectral Region 1500−1300 cm^{-1}. The bands at 1372 and 1447 cm^{-1} are attributed to symmetric and asymmetric $-CH_3$ deformation respectively, while the band 1423 cm^{-1} is assigned to $-CH_2$ bending. C−H deformation and bending bands shift to lower frequencies during heating, showing a dramatic decrease of the frequency at about −76 °C, where a phase transition is observed by DSC. It is worth mentioning that the downshifting of the wavenumbers of $-CH_2$ or $-CH_3$ deformation and bending modes and the corresponding upshifting of the wavenumbers of stretching bands of vibration indicate an extensive change of intramolecular hydrogen bonding.[9] Comparing the spectra features of bending modes of methylene and methyl groups in Figure 6, which are connected with changes in structure, it is concluded that above the second endothermic phase transition temperature at −76 °C, the system has less ordered chain packing due to the augmentation of the gauche conformers and the increment of chain mobility. The above are clarified in Figure 7, which shows a representative temperature profile of the $-CH_2$ bending band at 1423 cm^{-1}.

In addition, we observed a downshifting of wavenumber of the $C^{\alpha}-H$ symmetric deformation peak from 1313 (at −130 °C) to 1307 cm^{-1} (at +25 °C) and the N−H deformation band from 1331 to 1323 cm^{-1}, respectively, revealing the decrease of hydrogen bonding strength (Figure 8).[14]

3.2.3. Spectral Region 1200−1000 cm^{-1}. This spectral region also provides an overall measure of the degree of alkyl chain disorder. Three C−C stretching modes representative of all-trans hydrocarbon segments, correspond to the spectral frequencies at approximately 1117, 1076, and 1050 cm^{-1} (Table 2).[20,29,33] The intense 1050 cm^{-1} band, that is assigned to the C−C asymmetric stretching mode, is almost independent of temperature. Frequencies of the intense bands at 1117 and 1076 cm^{-1} are assigned to the C−C symmetric stretching modes. The

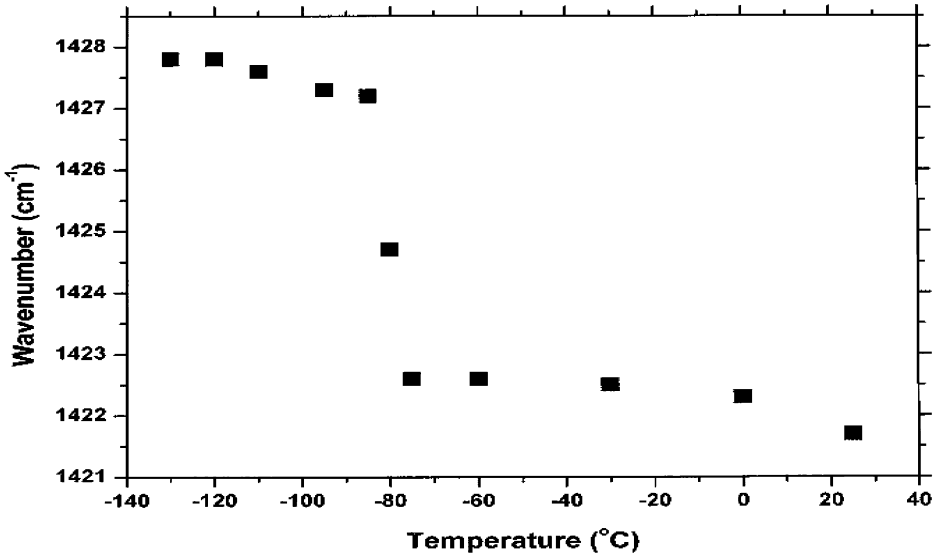

Figure 7. Temperature dependence of $-CH_2-$ bending band at 1423 cm^{-1}.

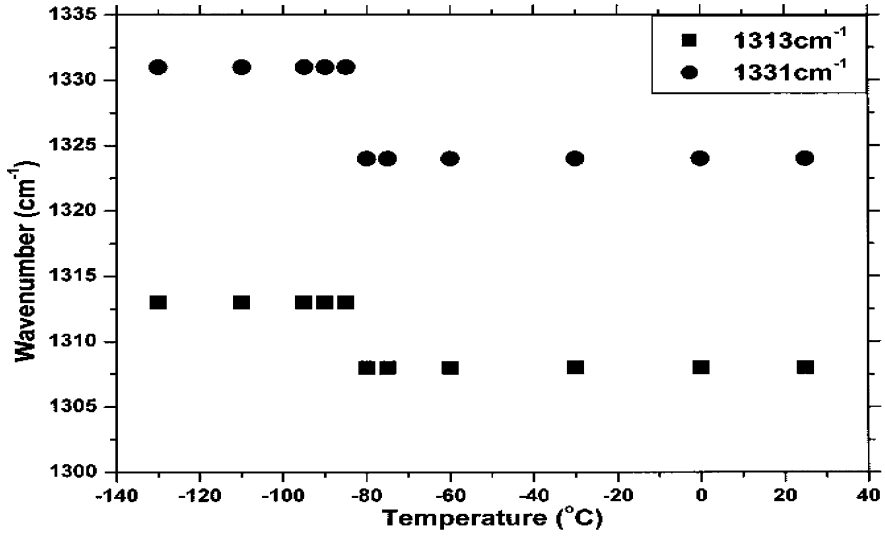

Figure 8. Temperature dependence of $C^{\alpha}-H$ and $N-H$ deformation bands at 1313 and 1331 cm^{-1}, respectively.

first one is a methyl-sided chain, while the second one corresponds to the carboxyl-sided chain and their frequencies are related to the temperature. By increasing the temperature, the band of the all-trans conformers at 1120 shifts to 1117 cm^{-1}. This fact indicates disordering of the alkyl side chain.

Simultaneously, a new band appears at about 1080 cm^{-1}, which is specifically assigned to the gauche $C-C$ stretching mode[28] (Figure 9). The 1117 cm^{-1} $C-C$ stretching mode is coupled with the chain $C-C-C$ angle bending modes and terminal methyl rocking mode. Frequency shift in this vibration is expected as the motions of methyl rotor are not only involved but also become less restricted.[35] The analogous temperature dependence of the 1076 cm^{-1} mode suggests that this $C-C$ mode may also be coupled to the same skeletal and terminal methyl vibrations. Thus, both all-trans $C-C$ stretching mode bands shift to lower frequencies as the number of all-trans segments decrease.[33]

3.2.4. Hydrogen Bonding Effect. In the spectral region 940−800 cm^{-1} were observed important changes relative to structural modifications (Figure 10). The 879 cm^{-1} band at −130 °C, assigned to $C^{\alpha}-COO^{-}$ wagging mode, and any change of the intermolecular hydrogen bonding influences the frequency of this band.[8,32] The band shifts to 829 cm^{-1} after the transition temperature at about −76 °C, as the strength of hydrogen bonds is getting lower.[9,36,37]

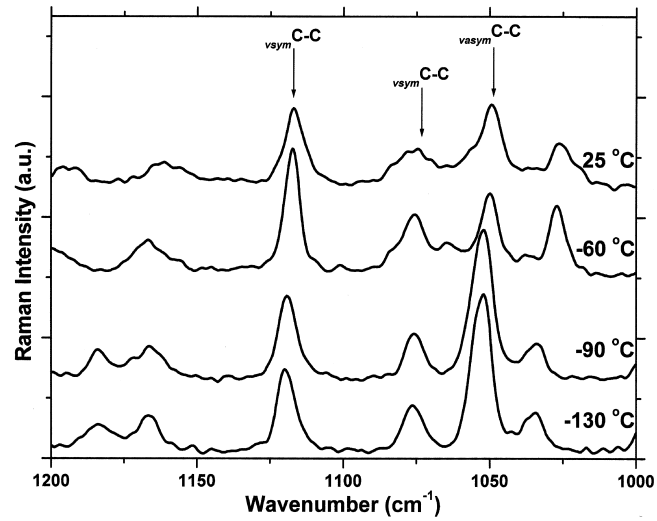

Figure 9. Normalized Raman spectra (1200−1000 cm^{-1}) of DL-norvaline at temperature range of −130 to +25 °C.

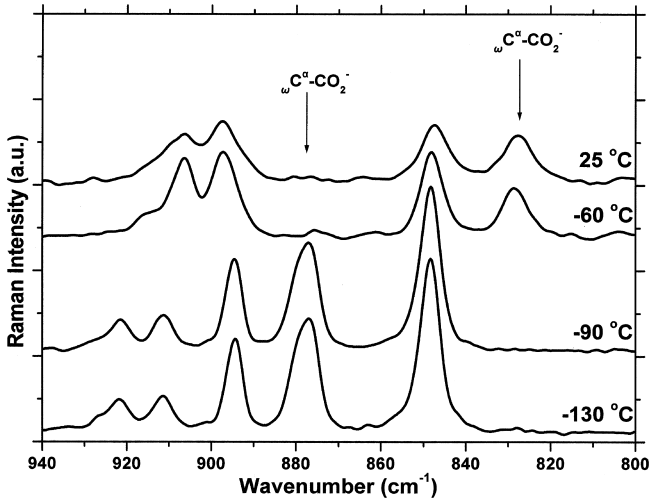

Figure 10. Normalized Raman spectra (940−800 cm^{-1}) of DL-norvaline at temperature range of −130 to +25 °C.

At higher temperatures, the intensity of the band increases gradually, whereas the intensity of the initial band decreases showing that the number of dimers that remain in their initial state is decreasing.

3.2.5. Comparison between DL-Norvaline and DL-Norleucine. DL-Norleucine undergoes[38−40] three polymorphic reversible crystalline forms α, β, and γ. In terms of stability, the β-form is the stable form at −150 °C, the α-form is stable at ambient conditions, and the γ-form is stable above 117 °C. The lattice energy difference for the β- to α−γ transition was calculated to be $\Delta H_{\beta\rightarrow\alpha} = 0.74$ $kJmol^{-1}$ and the corresponding energy difference from α- to γ-phase transition $\Delta H_{\gamma\rightarrow\alpha} = 4.92$ $kJmol^{-1}$ (experimental value). In an attempt to explain their results on β- to α-transition in which they used molecular dynamics simulation on a martensitic-type transformation in crystals of DL-norleucine, Anwar et al. in a recent study[39] suggest concerted molecular displacements, involving entire bilayer shifts during the transition. It is worth mentioning here that the crystal structure of γ-phase is still unknown.

The transition enthalpies of the observed phases in DL-norvaline shows similar values, that is, 0.36 and 1.59 kJ mol^{-1}, respectively, with those of DL-norleucine. Also, the spectral feature of DL-norvaline above −60 °C is almost the same with that of norleucine at 117 °C, revealing less ordered chain packing. According to these results, it can be concluded that the phases observed in DL-norvaline correspond to that of DL-norleucine, assuming that DL-norvaline exists in three different solid states. At lower temperatures, its aliphatic chain is in the extended zigzag conformation as in the crystals of norleucine,[41] while at higher temperatures the gauche conformers are predominant.

The verification of the above conclusions awaits a detailed X-ray study of DL-norvaline at different temperatures, as among the previous results there was not in agreement.[5]

4. Conclusions

In this study, differential scanning calorimetry and Raman spectroscopy are applied to examine the structural modifications of amino-acid DL-norvaline. Raman results, obtained from the peak height intensity ratios at C−H spectral region (Figure 5), are showing intermolecular chain interactions, which should also reflect the mobility of the methyl terminal group of hydrocarbon side chains. These observations reveal that the phase transitions of DL-norvaline include contributions of rearrangement of molecular layers due to intermolecular interactions between constituent molecules and conformational change due to the rotation of carbon−carbon bonds in alkyl chains. This is in agreement with the increment of ΔH and ΔS values obtained from calorimetric results. In addition, the results from the spectral region of C−C stretching modes and C−H deformation and bending modes show the disorder of alkyl chain during heating, which leads to a conformation with less ordered packing. Finally, the absence of the asymmetric stretching modes of N−H of protonated amino group at 2990 and 2994 cm^{-1} bands (Figure 3, Table 2) in the spectra at higher temperatures above the transition temperature; the decrease of hydrogen bonding strength, which is discussed on the relevant section, and the features quality of Raman spectra at temperatures above the transition temperature, agree with the above conclusion.

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