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Comparative Study on Vibrational Dynamics of poly(L-Histidine) and poly(L-Glutamine)

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Abstract
A comparative study has been performed on the Vibrational Dynamics of the bio-polymers poly(L-Histidine) and poly(L-Glutamine). We have compared the Fourier Transform Infra-Red (FTIR) spectra and the dispersion curves reported for these polymers which help us in comparing the amide modes of these polymers and a comparison of their density curves.
Keywords *– poly(L-Histidine), poly(L-Glutamine), FT-IR Spectroscopy, Dispersion Curves, Amide Modes, Bio-Polymers.*

I. Introduction

Poly(L-Histidine)

Poly(L-Histidine) is a biopolymer that has gotten a lot of interest because of its unusual features and many uses in industries ranging from healthcare to materials science. It is a synthetic or modified biopolymer that is made up of repeating units of the natural amino acid L-Histidine. It is a particular kind of polypeptide, which is a chain-like molecule made up of several amino acids connected by peptide bonds. The building blocks of proteins, which are vital macromolecules in living things and are in charge of a variety of biological processes, are polypeptides. The amino acid L-Histidine has an imidazole group as part of its side chain. Poly(L-Histidine) exhibits a pH-responsive behavior because of its imidazole group.

Bio-Medical Advantages of Poly(L-Histidine)

It exhibits special pH-responsive properties that have piqued the interest of researchers in a variety of scientific and technical fields. Because it undergoes reversible protonation and deprotonation transitions in response to pH changes, this biopolymer is a versatile molecule with applications in tissue engineering, drug delivery systems, and other fields.

Because of its pH-responsive behavior, poly(L-histidine) may switch between hydrophilic and hydrophobic states, affecting its solubility, charge, and conformation. This property has been used in the creation of pH-sensitive drug delivery systems, allowing for the controlled and precise release of therapeutic medications in certain situations, such as cancer tissues with lower pH values[1-4].

The pH-dependent optical and electrical properties of Poly(L-histidine) have also been used in biosensing and diagnostic applications. This makes it possible to create sensors that can track biological activity and detect pH changes in real-time[5-6].

Poly(L-Glutamine)

Poly(L-Glutamine) is a biopolymer made up of repeated amino acid l-glutamine units. It is a form of polypeptide with many uses due to its unique characteristics and biocompatibility. Poly(L-Glutamine), like other polypeptides, is a chain-like molecule generated by peptide bonds connecting numerous L-Glutamine amino acids. L-Glutamine is a non-essential amino acid that is required for protein synthesis, energy generation, and the maintenance of cellular homeostasis. Poly(L-Glutamine) has gained popularity due to its biocompatibility, minimal immunogenicity, and ability to degrade in biological settings under regulated conditions.

Bio-Medical Advantages of Poly(L-Histidine)

Poly(L-glutamine) is widely regarded as biocompatible and immunogenic, lowering the likelihood of unfavorable immunological responses when utilized in medicinal applications[7].

Because of its biocompatibility and capacity to encapsulate and release diverse compounds, researchers have investigated its potential in medication delivery systems, tissue engineering scaffolds, and as a carrier for gene delivery[7-9].

Poly(l-glutamine) can also be utilized to generate coatings, hydrogels, and other materials with customized characteristics in the field of biomaterials. Because of its biodegradability, it is an appealing

possibility for producing materials that may progressively degrade in vivo, decreasing the need for surgical removal[10-11].

Comparative Study of Vibrational Dynamics for PLH and PLGn

We have previously reported the vibrational dynamics for bio-polymeric systems having α, β, ω, and three-fold helical conformations[12-22]. Also, researchers have already reported the FT-IR Graph and the Dispersion Curves in accordance with the Vibrational Dynamics of PLH and PLGn. In continuation of these studies, we report a comparison between these two bio-polymers. Fig. 1 and Fig. 2 show the chemical repeat units of poly(L-Histidine) and poly(L-Glutamine).

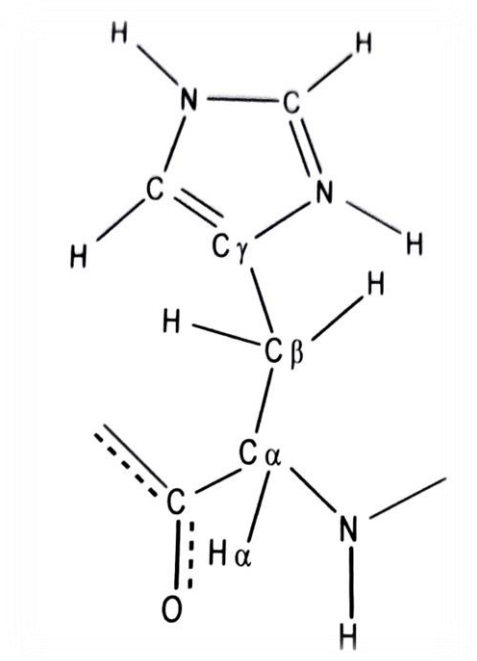

Fig. 1: Chemical repeat unit of Poly(L-histidine)[23]

Experimental and Theoretical Approach

Normal Mode Calculation

In experiments performed by La'Verne et al.[23-24] for PLH and PLGn, the well-known Wilson's GF matrix method[25], as modified by Higgs[26], was used to determine the normal mode frequencies. The inverse kinetic energy matrix G and the potential energy matrix F must be expressed in terms of internal coordinates R. In the case of infinite isolated helical polymers, there are infinitely many internal coordinates, resulting in infinitely ordered G and F matrices. The infinite problem may be condensed to a finite set of dimensions thanks to the screw symmetry of the polymer, which allows for a transformation identical to that described by Born and Von Karman[27].

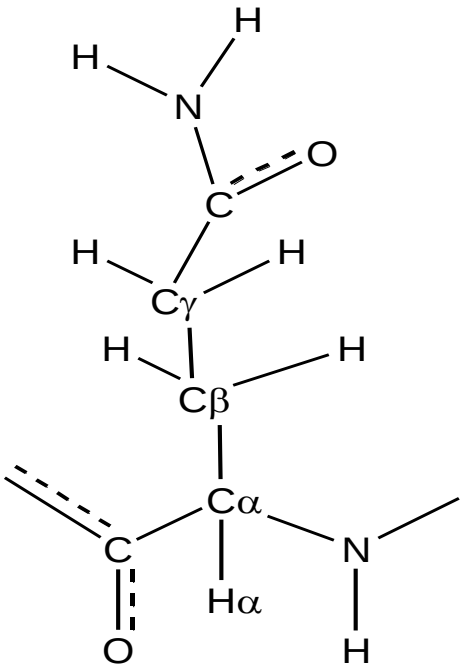

Fig. 2: Chemical repeat unit of Poly(L-Glutamine)[24]

The vibrational secular equation, which has the form:

$$G(\delta)F(\delta) - \lambda(\delta)\, I = 0, \qquad 0 \leq \delta \leq \pi \tag{1}$$

gives the normal mode frequencies and their dispersion as a function of phase angle.

The interrelation between the vibrational frequencies ν(δ) (in cm^{-1}) and eigenvalues λ(δ) by the relation:

$$\lambda(\delta) = 4\pi^2 c^2 \nu^2(\delta) \tag{2}$$

Experiment:

In the experiments performed by La'Verne et. al., the samples were analyzed to obtain the FTIR spectra of PLH and PLGn shown in Figure 3 and Figure 4, recorded on the Perkin Elmer RX-1 in the range 4000-400 cm^{-1} at a resolution better than 1 cm^{-1}.

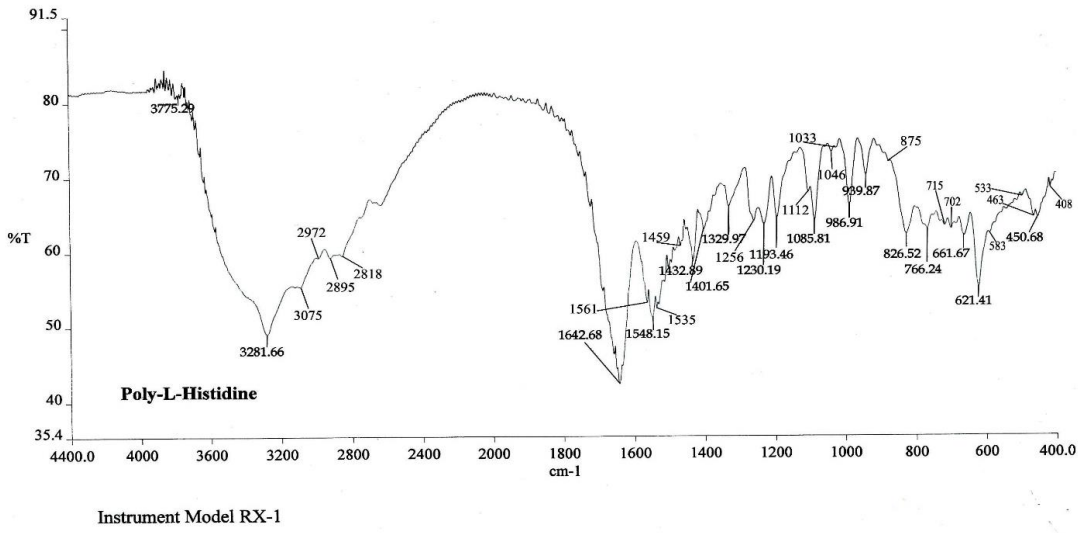

Figure 3: FTIR spectra of poly(L-Histidine)[23]

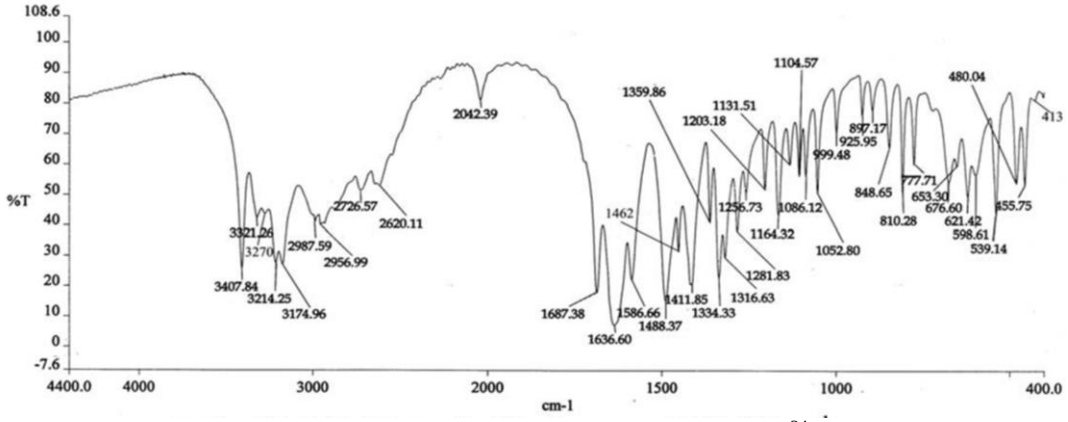

Figure 4: FTIR spectra of poly(L-Glutamine)[24]

II. Results and Discussion:

PLH and PLGn, both exist in α-helical form. There are 17 atoms in one residue which give rise to 51 dispersion curves.

Amide Mode Analysis:

The observed and calculated values for the Amide Modes of the polymers PLH and PLGn are given in brief, in the Table 1 and Table 2.

Table 1: - Observed and Calculated values for different modes of PLH:[12]

S.NO.	*AMIDE*	*OBSERVED*	*CALCULATED*
1.	Amide **A**	3282	3277
2.	Amide **I**	1642	1651
3.	Amide **II**	1549	1546
4.	Amide **III**	1269	1281
5.	Amide **IV**	463	486
6.	Amide **V**	621	633
7.	Amide **VI**	767	759

All frequencies are in cm^{-1}.

It is seen that the Amide modes of both these polymers are in good comparison with the other poly-peptides already published in journals.

We see that for PLH the Amide A mode appears at 3282 in the IR characteristic curve and is calculated at 3277, while for PLGn it is observed that the Amide A mode is observed at 3321 in the IR curve and is calculated at 3318, which is in good comparison.

Considering the Amide I mode for PLH, we observe it at 1642 in the IR Curve and is calculated at 1651, whereas for PLGn the Amide I mode is observed at 1687 in the IR characteristic curve and is calculated at 1583, which is again in close comparison.

Table 2: - Observed and Calculated values for different modes of PLGn:[13]

S. NO.	AMIDE	OBSERVED	CALCULATED
1.	Amide **A**	3321	3318
2.	Amide **I**	1687	1683
3.	Amide **II**	1587	1591
4.	Amide **III**	1317	1313
5.	Amide **IV**	480	488
6.	Amide **V**	539	535
7.	Amide **VI**	777	776

All frequencies are in cm^{-1}.

Moving on to the Amide II mode of PLH, it has been observed at 1549 in the IR Curve and is calculated at 1546, while the Amide II Mode for PLGn has been observed at 1587 in the IR characteristic curve and is calculated at 1591, which is also in close comparison.

Now for the Amide III mode for PLH, it appears at 1269 in the IR characteristic curve and calculated at 1281, whereas for PLGn the Amide III mode appears at 1317 in the IR curve and is calculated at 1313 and this is also in good comparison.

Considering the Amide IV mode for PLH, it is observed at 463 in the IR characteristic curve and is calculated at 486, while the Amide IV mode for PLGn is observed at 480 in the IR curve and is calculated at 488, which is again in close comparison.

Moving on to the Amide V mode for PLH, it has been observed at 621 in the IR curve and is calculated at 633 which is also in close comparison with the Amide V mode of PLGn, which is has been observed at 539 in the IR curve and is calculated at 535.

Taking into account the Amide VI mode for PLH, it is observed at 767 in the IR curve and is calculated at 759, while for PLGn, Amide VI mode appears at 777 in the IR curve and is calculated at 776, which is also in good comparison.

Hence it is observed that for the Polymers poly(L-Histidine) and poly(L-Glutamine), the Amide modes are in good comparison.

Dispersion Curves:

In the region below 1350 cm^{-1}, the modes are mostly coupled and, depending on the degree of coupling, conformation and chemical species, show some characteristic features. The dispersion curves for the polymer PLH are shown in Figure 5, 6 and 7 while dispersion curves for PLGn are shown in Figure 8, 9 and 10.

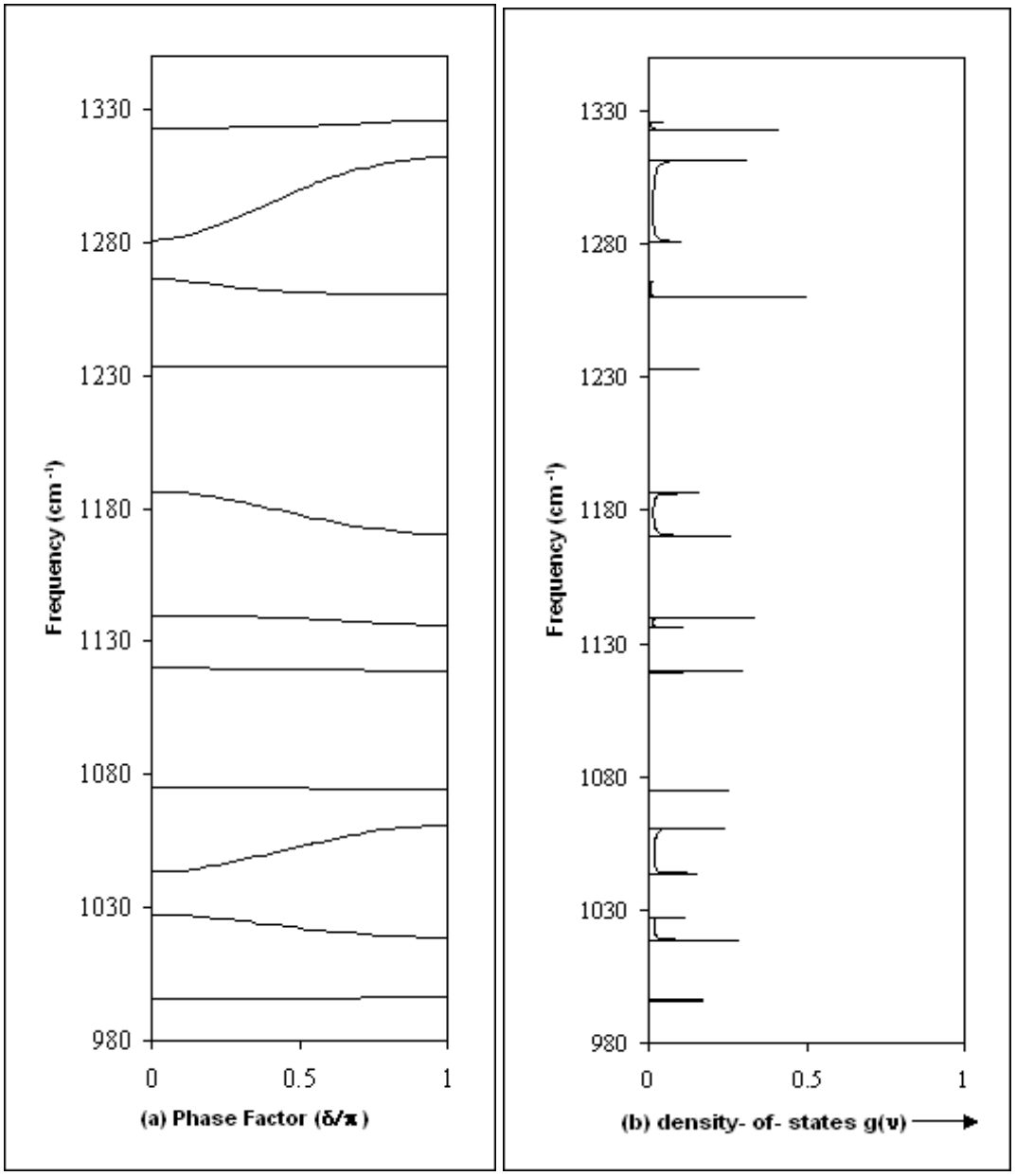

Figure 5: (a) Dispersion curves for PLH (1350-980 cm^{-1}); (b) density-of-states g(ν) (1350-980 cm^{-1})[23]

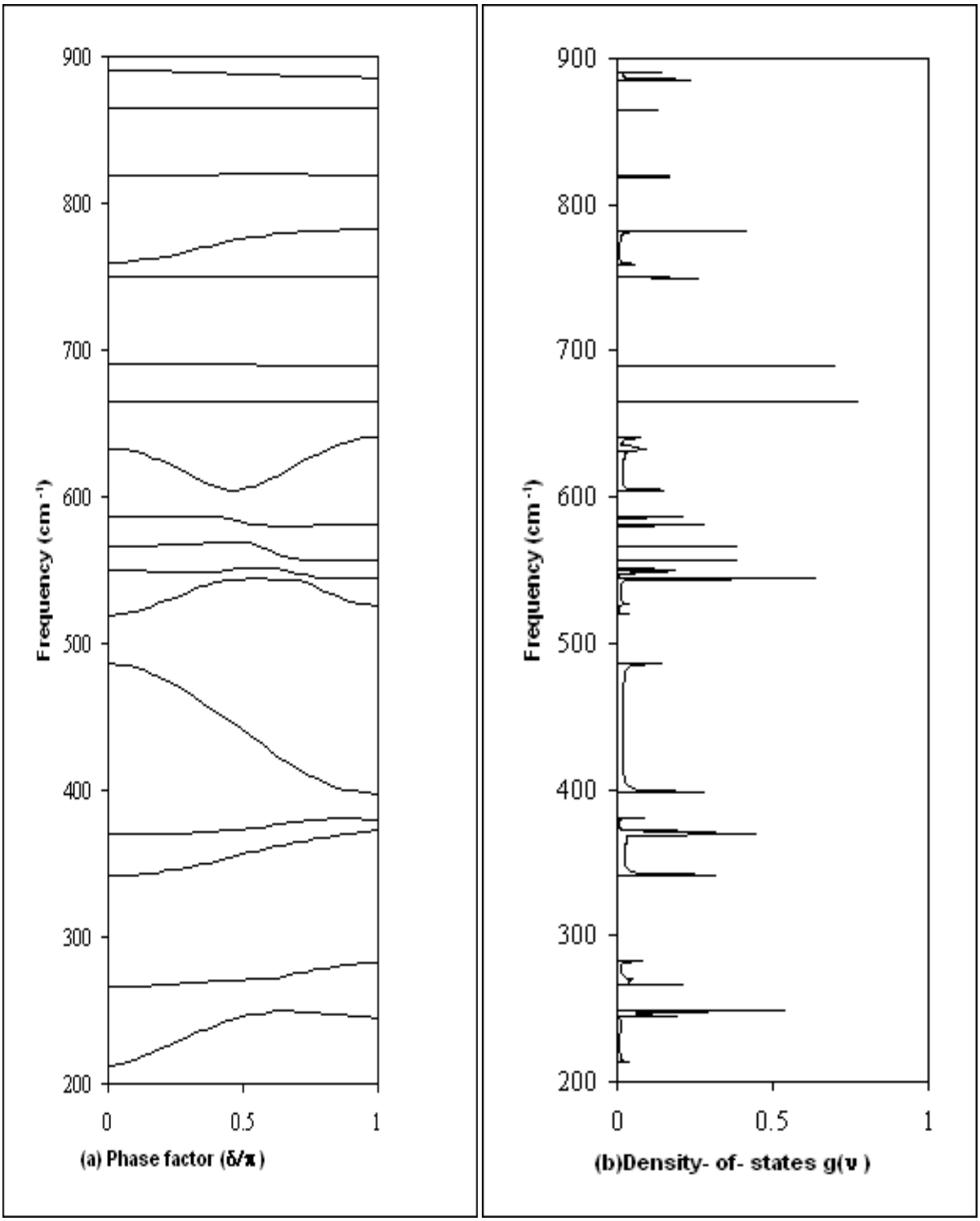

Figure 6: (a) Dispersion curves for PLH (900-200 cm^{-1}); (b) density-of-states g(ν) (900-200 cm^{-1})[23]

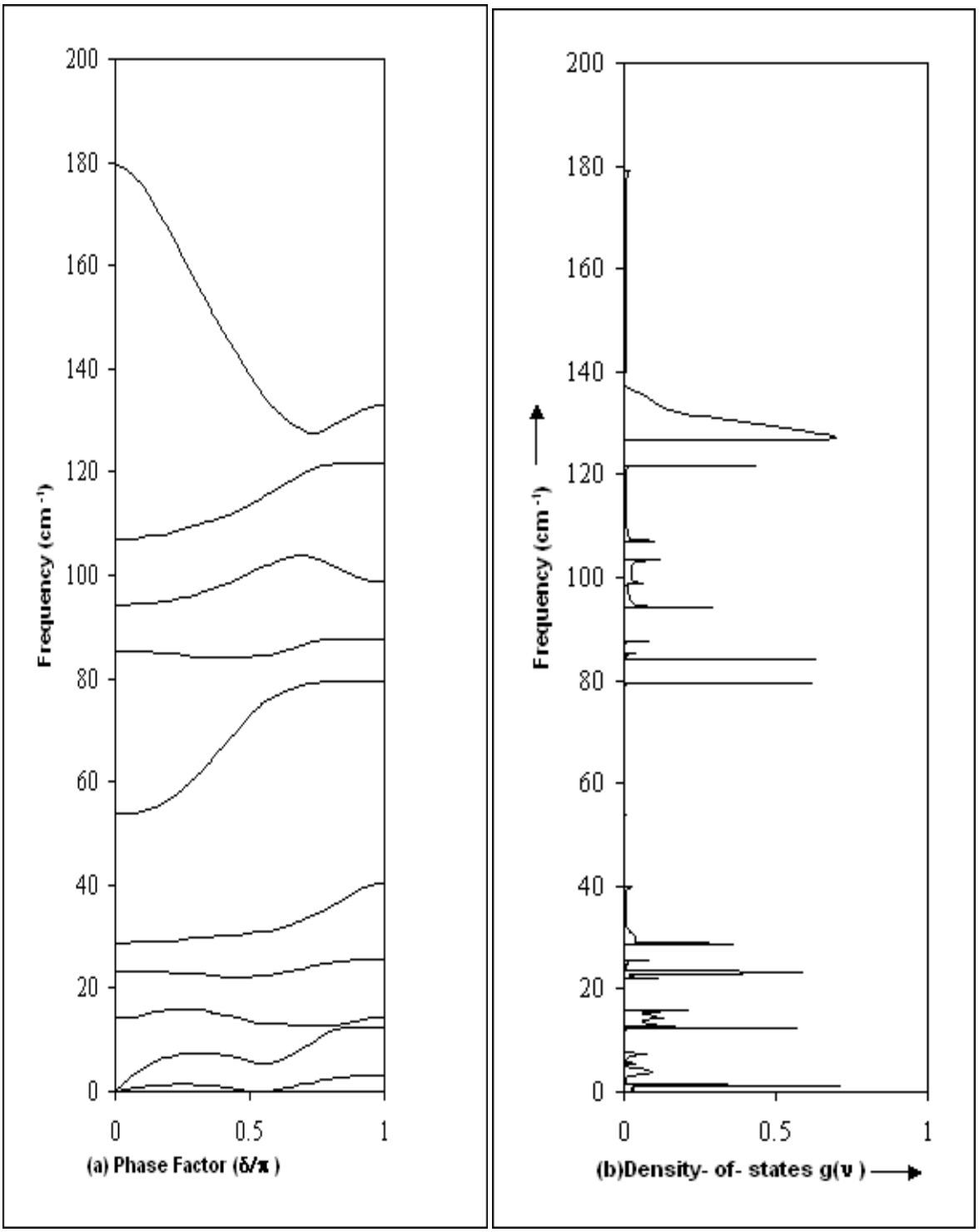

Figure 7: (a) Dispersion curves for PLH (below 200 cm^{-1}); (b)density-of-states g(ν)(below 200 cm^{-1})[23]

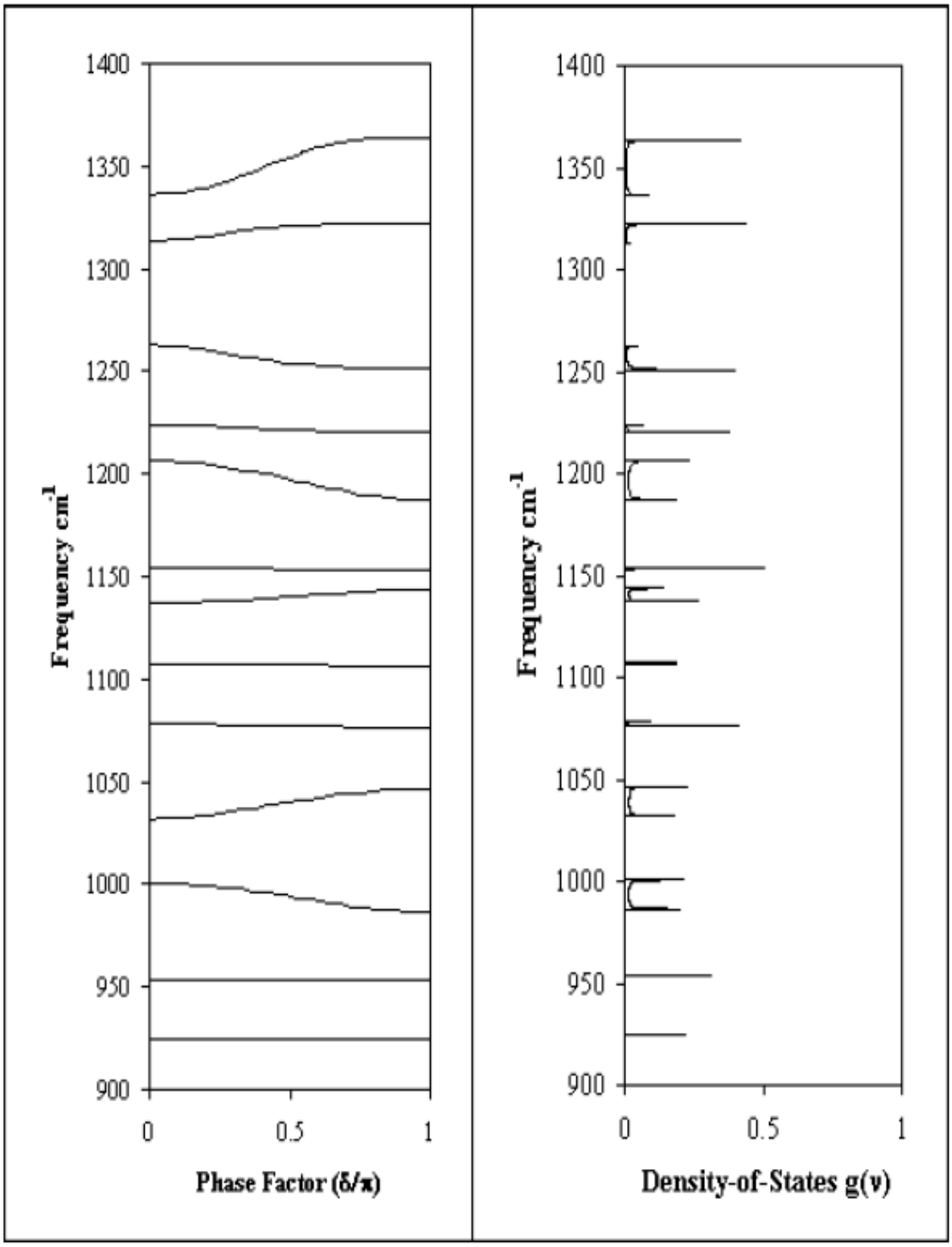

Figure 8: (a) Dispersion curves for PLGn (900-200 cm^{-1}); (b) Density-of-States g(ν) (900-200 cm^{-1})[24]

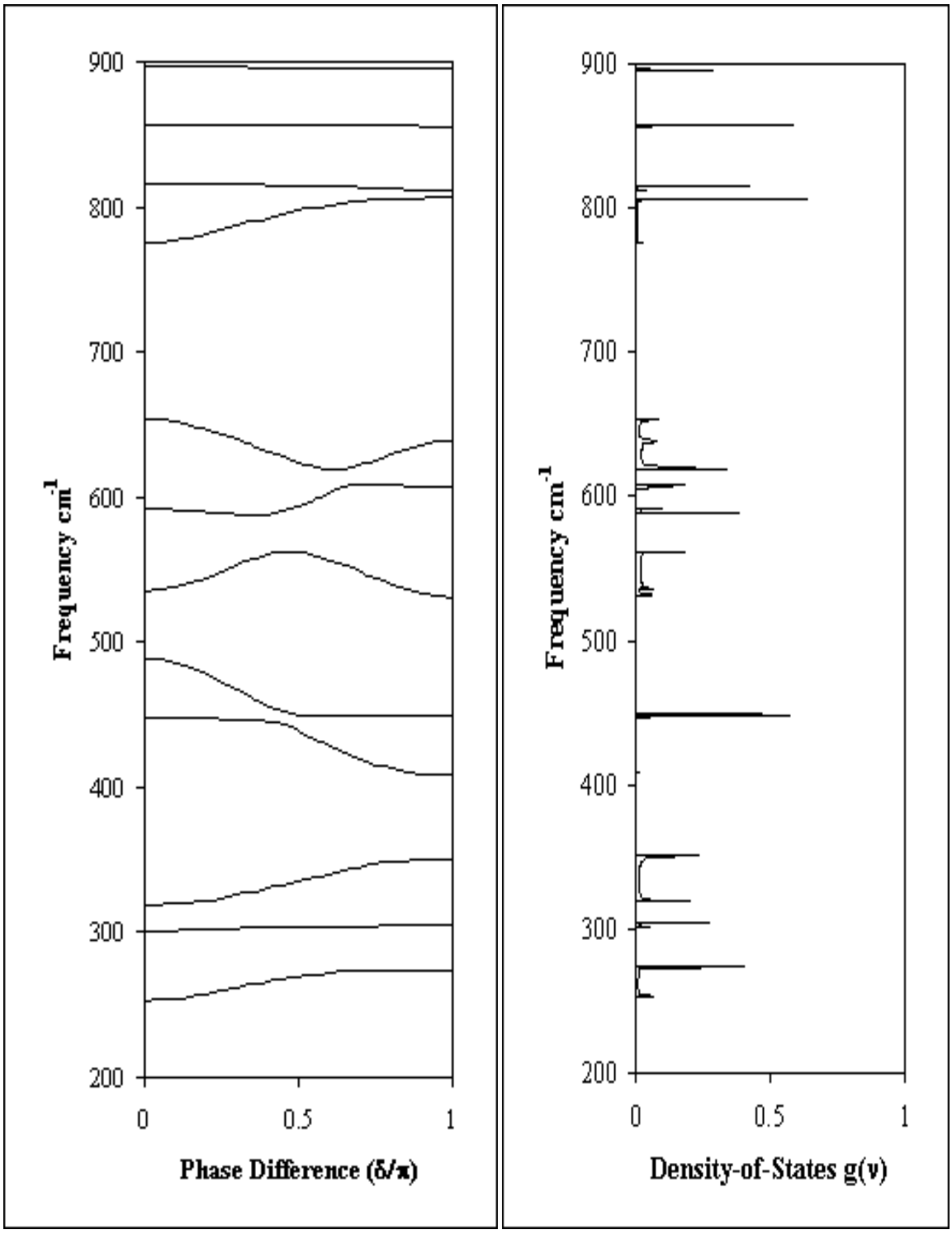

Figure 9: (a) Dispersion curves for PLGn (900-200 cm^{-1}); (b) Density-of-States g(ν) (900-200 cm^{-1})[24]

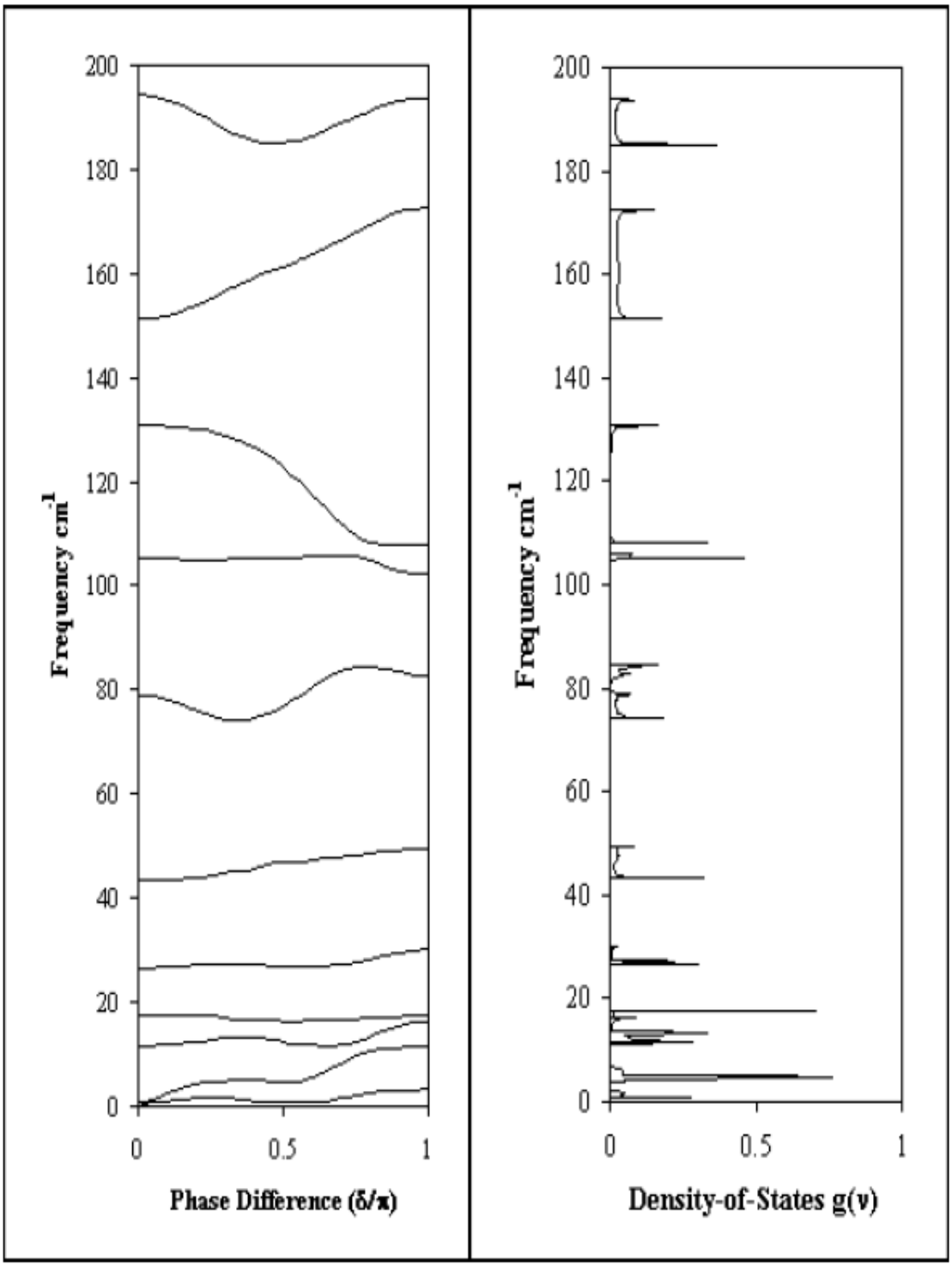

Figure 10: (a) Dispersion curves for PLGn (200-0 cm^{-1}); (b) Density-of-States g(ν) (200-0 cm^{-1})[24]

In the figure 7 and figure 10, it can be observed that the first four dispersion curves for the polymers poly(L-Histidine) and poly(L-Glutamine) are is a close comparision. The fifth and sixth curves, observed for PLH and PLGn, tend to repel.

Taking into account Figures 6 and 9, it is observed that the first and second dispersion curve for PLH tend to attract, and the first and second dispersion curve for PlGn also tend to attract. Also, the third and fourth dispersion curves for both PLH and PLGn tend to attract. A repulsion is observed between the second and third dispersion curves for PLH and PLGn. The last three dispersion curves for PLH and PLGn are almost a straight

line which suggests that both the polymers are having a constant phase factor between the frequency range 800-900 cm^{-1}.

From Figures 5 and 8, it is observed that the dispersion curves lying between the frequency range 900-1000 cm^{-1}, for the polymers PLH and PLGn, are almost a straight line indicating a constant phase factor.

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