

Normal Modes and Their Dispersion in α Form of Nylon-6 (α NY6)

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ABSTRACT: Nylon-6 $[-(\text{CH}_2)_5\text{-NHCO-}]_n$ (α NY6) is a synthetic polymer widely used in industrial applications. It has a planar zigzag conformation. A comprehensive study of the normal modes and their dispersion in α NY6 using Urey Bradley force field is being reported. Crossing between the various pairs of modes of dispersion curves have been explained as arising due to internal symmetry in the energy momentum space. The heat capacity derived from the dispersion curves *via* the density-of-states, is in good agreement with the experimental measurements obtained from the Athas data bank. [doi:10.1295/polymj.PJ2006103]

KEY WORDS Nylon-6 / α -Form / Phonon Dispersion / Heat Capacity / Density-of-States /

The word Nylon has been accepted as generic term for synthetic polyamides, Nylon-6 $[-(\text{CH}_2)_5\text{-NHCO-}]_n$ is one of the most important members of this family. It is highly useful for industrial applications because of its high tensile and impact strength, firm stability at high temperature, good abrasion resistance and self-lubricating properties. It also retains both tough and flexible at low temperatures. Commercially it can be processed by conventional processing methods such as injection molding, extrusion blow molding, and special grade of Nylon-6 are available for rotational molding and thermoforming.

Nylon-6 crystallizes in two different forms namely α and γ forms.^{1,2} Thermodynamically stable α form takes on planar zigzag conformation and the molecular chains are arranged in sheets by means of hydrogen bonding between antiparallel chains, while the γ form takes a helical symmetry with the secondary amide group at 66° with respect to the plane of CH_2 zigzag and sheets of parallel chains are joined by hydrogen bonds. In both the forms the neighbouring chains are arranged in sheets of parallel but oppositely directed molecules. Lattice parameters along the polymer axis are slightly shorter ($b = 16.88 \text{ \AA}$)² in the γ form as comparison to that of the α form ($b = 17.24 \text{ \AA}$).¹

Vibrational spectroscopy plays an important role in the elucidation of polymeric structure. Normal mode analysis besides identification of various modes provides an insight into Infrared absorption (IR), Raman spectra and Inelastic Neutron Scattering (INS). An overall understanding of vibrational dynamics in a polymer involves calculation of the dispersion curves. These curves provide knowledge of degree of uninterrupted sequence lengths in an ordered conformation. The dispersion curves also facilitate correlation of

the microscopic behaviour of the long chain molecule with the macroscopic properties such as entropy, enthalpy, specific heat etc.

We present here a complete normal mode analysis of α NY6 with phonon dispersion in the first Brillouin Zone using Urey Bradley force field (UBFF).^{3,4} This polymer has been subjected to several spectroscopic studies (IR, Raman and INS)^{5–12} by several workers. Tadokoro *et al.*¹¹ have reported normal mode analysis of α NY6 considering methylene group as a point mass thereby neglecting the interaction between carbon and hydrogen atoms where as Jakes and Krimm⁵ have used simple valence force field in their normal mode calculations. Our calculations are based on UBFF, which in addition to valence force field accounts for the non-bonded interactions in the *gem* and *cis* configuration and the tension terms. In this force field the potential energy expression does not have quadratic cross terms. The force constants are supplemented by the repulsive forces between non-bonded atoms, which simulate the van der Waals force¹³ between them. It gives a better description of intra and inter unit interactions, and arbitrariness in choosing the force constants is reduced, thereby enabling us to arrive at a better unique force field.

THEORY

Calculation of Normal Mode Frequencies

Normal mode calculation for a polymeric chain was carried out using Wilson's GF matrix method¹⁴ as modified by Higgs¹⁵ for an infinite polymeric chain. The vibrational secular equation to be solved is

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

where δ is the phase difference between the modes of

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adjacent chemical units, $\mathbf{G}(\delta)$ is the inverse kinetic energy matrix and $\mathbf{F}(\delta)$ is the force field matrix for a certain phase value. The wavenumber $\bar{\nu}_i(\delta)$ in cm^{-1} are related to eigen values by $\lambda_i(\delta) = 4\pi^2 c^2 [\bar{\nu}_i(\delta)]^2$.

A plot of $\bar{\nu}_i(\delta)$ versus 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.¹⁶ In the present work, we have used Urey-Bradley force field as it is more comprehensive than valence force field. The Urey-Bradley takes into account both bonded and non-bonded interactions as well as internal tensions. Potential energy for this force field can be written as

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

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 models have been used for inter and intra molecular interactions consisting of charges, atomic dipoles and van der Waals (non bonded) interactions.¹³

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 wave numbers the following procedure is adopted.

Force constants were initially transferred from the molecules (PCL¹⁷ and β poly (L-valine)¹⁸ in the present case) having similar groups placed in the similar environment. 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:

$$\mathbf{GF}_0\mathbf{L}_0 = \mathbf{L}_0\lambda_0 \quad (3)$$

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

$$\Delta\lambda = \mathbf{J}\Delta\mathbf{F} \quad (4)$$

where \mathbf{J} is computed from \mathbf{L}_0 . We wish to compute

Table I. Internal coordinates and force constants for α NY6 (mydn/Å)

Internal Coordinates	Force Constants	Internal Coordinates	Force Constants
ν (C=O)	7.85	φ (C ₄ -C ₅ -C ₆)	0.470 (.600)
ν (C ₁ -C ₂)	2.85	φ (H-C ₅ -C ₆)	0.470 (.220)
ν (C ₂ -H)	4.18	φ (C ₅ -C ₆ -N)	0.150 (.600)
ν (C ₂ -C ₃)	3.24	φ (C ₅ -C ₆ -H)	0.440 (.220)
ν (C-H)	4.18	φ (H-C ₆ -H)	0.362 (.360)
ν (C-C)	2.98	φ (H-C-N)	0.245 (.780)
ν (C ₅ -C ₆)	3.28	φ (C ₆ -N-H)	0.292 (.520)
ν (C ₆ -H)	3.91	φ (C-N-C)	0.440 (.540)
ν (C ₆ -N)	2.35	φ (H-N-C ₁)	0.453 (.520)
ν (N-H)	5.38	φ (N-C=O)	0.890 (.900)
ν (N-C ₁)	5.75	φ (N-C ₁ -C ₂)	0.400 (.600)
φ (O=C ₁ -C ₂)	0.890 (.900)	ω (N-H)	0.165
φ (C ₁ -C ₂ -H)	0.406 (.215)	ω (C=O)	0.519
φ (H-C ₂ -H)	0.389 (.340)	τ (C ₁ -C ₂)	0.010
φ (H-C ₂ -C ₃)	0.410 (.215)	τ (C ₂ -C ₃)	0.011
φ (C ₁ -C ₂ -C ₃)	0.750 (.500)	τ (C ₃ -C ₄)	0.009
φ (C ₂ -C ₃ -H)	0.440 (.230)	τ (C ₄ -C ₅)	0.019
φ (H-C-C)	0.458 (.230)	τ (C ₅ -C ₆)	0.032
φ (C ₂ -C ₃ -C ₄)	0.480 (.500)	τ (C ₆ -N)	0.011
φ (H-C-H)	0.392 (.340)	τ (N-C ₁)	0.030
φ (C ₃ -C ₄ -C ₅)	0.470 (.600)		

Note: 1. ν , φ , ω and τ denote stretch, angle bend, wag and torsion respectively.

2. Non-bonded force constants are given in parentheses.

the corrections to \mathbf{F}_0 so that the errors $\overline{\Delta\lambda}$ are minimized. We used the theory of least squares and calculate

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

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

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

If the number of frequencies is greater than the number of \mathbf{F} matrix elements, the matrix $\mathbf{J}'\mathbf{P}\mathbf{J}$ should be non-singular and be obtain the corrections $\Delta\mathbf{F}$, which will minimize the sum of the weighted squares of the residuals. This minimum sum provides the "best fit". If the corrections $\Delta\mathbf{F}$ are fairly large, the linear relation between force constant and frequency term in the matrix eq 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.*¹⁹ developed this procedure.

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 expresses the way energy is dis-

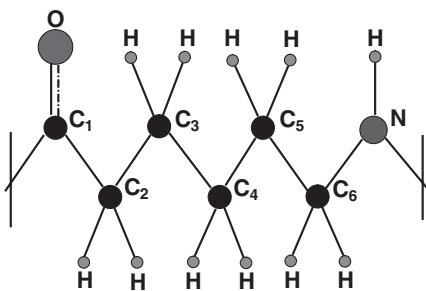


Figure 1. One chemical repeat unit of α NY6.

tributed among the various branches of normal modes in the crystal, is calculated from the relation

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

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

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

With $\int g(\nu_i) d\nu_i = 1$

The constant-volume heat capacity C_v , given by the above equation, can be converted into constant-pressure heat capacity C_p using the Nernst-Lindemann approximation.²⁰

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

Where A_0 is a constant often of a universal value [6.0×10^{-3} (K mol)/J] and T_m^0 is the estimated equilibrium melting temperature, which is taken to be 310 K.²¹

RESULT AND DISCUSSION

One chemical repeat unit of α NY6 (Figure 1) contains 19 atoms, which give rise to 57 dispersion curves. Initially the force constants for CH_2 groups are transferred from poly (ϵ -caprolactone) (PCL)¹⁷ and for amide group from β poly (L-valine)¹⁸ molecules and later modified to give the "best fit" to the observed frequencies. Final sets of constants are given in Table I. The assignments are made on the basis of potential energy distribution (PED), band profile, line intensities and the presence/absence of similar groups in an identical environment in addition to the information obtained from photo acoustic-Fourier transform infrared (PAFTIR-IR)¹² ($1500\text{--}500\text{ cm}^{-1}$), Fourier transform Raman spectrum^{7,8} ($3500\text{--}500\text{ cm}^{-1}$), micro Raman confocal spectra¹² ($3450\text{--}900\text{ cm}^{-1}$) and in-

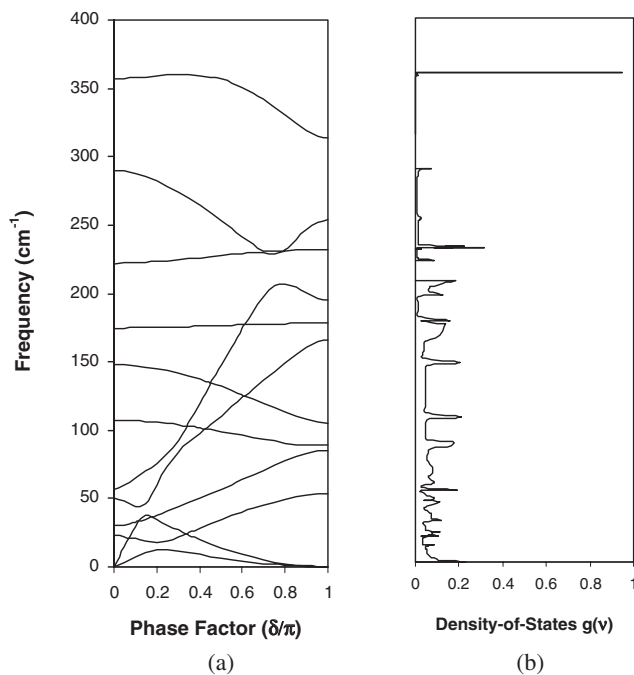


Figure 2. Dispersion curves (a) and density states (b) of α NY6 ($0\text{--}400\text{ cm}^{-1}$).

elastic neutron spectra^{9,10} (below 900 cm^{-1}). The vibrational frequencies have been calculated for the values of δ ranging from 0 to π in steps of 0.05π . The optically active modes correspond to those at $\delta = 0$ and π . Dispersion curves are plotted in Figure 2(a) for the modes below 400 cm^{-1} , because the modes above this are non dispersive in nature. Heat capacities are obtained from the dispersion curves *via* density of states and compared with the experimental data obtained from Athas data bank. Normal mode frequencies are broadly classified under amide modes, methylene modes and others.

Amide Modes

The amide linkage is one of the most fundamental and wide spread chemical linkages in nature. Amide groups of polyamides are strong chromophores in IR absorption, and these groups give rise to strong characteristic bands (Amide A, I to VII). Thus amide modes play a vital role in the vibrational dynamics of polyamides. The observed and calculated frequencies along with the PEDs at the zone center and zone boundary are shown in Table II, III. A comparison of the amide modes of α NY6 with those of other β sheet polypeptides (which also take the planar zig zag conformation) is given in Table IV. This table reflects the spectral differences due to presence of different chemical groups in between amide groups. It would be interesting to compare the amide group modes of PGI²² with those of α NY6. In the former the amide group is flanked by only one CH_2 group. But in α NY6 it is

Table II. Calculated and observed modes of α NY6

Cal. freq.	Obs. Freq.			Assignment (% PED), $\delta = 0$	Cal. freq.	Obs. Freq.			Assignment (% PED), $\delta = \pi$
	IR ^a	Raman ^b	INS ^c			IR ^a	Raman ^b	INS ^c	
2936	2932 ^s	2930 ^s	—	$\nu(\text{C}_6\text{-H})(58) + \nu(\text{C-H})(40)$	2936	2932 ^s	2930 ^s	—	$\nu(\text{C}_6\text{-H})(58) + \nu(\text{C-H})(40)$
2933	2932 ^s	2930 ^s	—	$\nu(\text{C-H})(66) + \nu(\text{C}_6\text{-H})(26) + \nu(\text{C}_2\text{-H})(8)$	2933	2932 ^s	2930 ^s	—	$\nu(\text{C-H})(66) + \nu(\text{C}_6\text{-H})(26) + \nu(\text{C}_2\text{-H})(8)$
2928	2932 ^s	2930 ^s	—	$\nu(\text{C-H})(65) + \nu(\text{C}_2\text{-H})(24) + \nu(\text{C}_6\text{-H})(10)$	2928	2932 ^s	2930 ^s	—	$\nu(\text{C-H})(65) + \nu(\text{C}_2\text{-H})(24) + \nu(\text{C}_6\text{-H})(10)$
2924	2932 ^s	2930 ^s	—	$\nu(\text{C}_2\text{-H})(48) + \nu(\text{C-H})(47)$	2924	2932 ^s	2930 ^s	—	$\nu(\text{C}_2\text{-H})(48) + \nu(\text{C-H})(47)$
2922	2932 ^s	2930 ^s	—	$\nu(\text{C-H})(79) + \nu(\text{C}_2\text{-H})(18)$	2922	2932 ^s	2930 ^s	—	$\nu(\text{C-H})(79) + \nu(\text{C}_2\text{-H})(18)$
2863	2864 ^s	2855 ^s	—	$\nu(\text{C-H})97$	2863	2864 ^s	2855 ^s	—	$\nu(\text{C-H})(97)$
2860	2864 ^s	2855 ^s	—	$\nu(\text{C-H})(91) + \nu(\text{C}_2\text{-H})(7)$	2860	2864 ^s	2855 ^s	—	$\nu(\text{C-H})(91) + \nu(\text{C}_2\text{-H})(7)$
2857	2864 ^s	2855 ^s	—	$\nu(\text{C-H})(87) + \nu(\text{C}_2\text{-H})(7)$	2857	2864 ^s	2855 ^s	—	$\nu(\text{C-H})(87) + \nu(\text{C}_2\text{-H})(7) + \nu(\text{C}_6\text{-H})(5)$
2854	2864 ^s	2855 ^s	—	$\nu(\text{C}_2\text{-H})(83) + \nu(\text{C-H})(16)$	2854	2864 ^s	2855 ^s	—	$\nu(\text{C}_2\text{-H})(83) + \nu(\text{C-H})(17)$
2852	2864 ^s	2855 ^s	—	$\nu(\text{C}_6\text{-H})(92) + \nu(\text{C-H})(8)$	2852	2864 ^s	2855 ^s	—	$\nu(\text{C}_6\text{-H})(93) + \nu(\text{C-H})(7)$
1482	1486 ^s	1480 ^s	—	$\varphi(\text{H-C-H})(76) + \varphi(\text{H-C-C})(11) + \varphi(\text{C}_2\text{-C}_3\text{-H})(6)$	1482	1486 ^s	1480 ^s	—	$\varphi(\text{H-C-H})(76) + \varphi(\text{H-C-C})(11) + \varphi(\text{C}_2\text{-C}_3\text{-H})(6)$
1474	1476 ^s	1480 ^s	—	$\varphi(\text{H-C-H})(72) + \varphi(\text{H-C-C})(9)$	1474	1476 ^s	1480 ^s	—	$\varphi(\text{H-C-H})(70) + \varphi(\text{H-C-C})(10)$
1464	1458 ^s	1468 ^s	—	$\varphi(\text{H-C-H})(66) + \varphi(\text{H-C}_2\text{-H})(6) + \varphi(\text{C}_2\text{-C}_3\text{-H})(7) + \varphi(\text{H-C-C})(6)$	1463	1458 ^s	1468 ^s	—	$\varphi(\text{H-C-H})(70) + \varphi(\text{C}_2\text{-C}_3\text{-H})(7) + \varphi(\text{H-C-C})(6)$
1459	1458 ^s	1468 ^s	—	$\varphi(\text{H-C}_2\text{-H})(66) + \varphi(\text{H-C-H})(11) + \varphi(\text{H-C}_2\text{-C}_3)(7) + \varphi(\text{C}_1\text{-C}_2\text{-H})(7)$	1459	1458 ^s	1468 ^s	—	$\varphi(\text{H-C}_2\text{-H})(68) + \varphi(\text{H-C-H})(9) + \varphi(\text{H-C}_2\text{-C}_3)(7) + \varphi(\text{C}_1\text{-C}_2\text{-H})(7)$
1451	1448 ^s	1443 ^s	—	$\varphi(\text{H-C}_6\text{-H})(64) + \varphi(\text{H-C-N})(12) + \varphi(\text{C}_5\text{-C}_6\text{-H})(6) + \varphi(\text{H-C-H})(6)$	1451	1448 ^s	1443 ^s	—	$\varphi(\text{H-C}_6\text{-H})(64) + \varphi(\text{H-C-N})(12) + \varphi(\text{C}_5\text{-C}_6\text{-H})(6) + \varphi(\text{H-C-H})(5)$
1393	1393 ^s	1395 ^w	—	$\varphi(\text{H-C-C})(27) + \nu(\text{C}_3\text{-C}_4)(22) + \nu(\text{C}_5\text{-C}_6)(14) + \varphi(\text{H-C}_5\text{-C}_6)(13) + \varphi(\text{C}_2\text{-C}_3\text{-H})(10) + \varphi(\text{H-C-N})(7)$	1394	1393 ^s	1395 ^w	—	$\varphi(\text{H-C-C})(26) + \nu(\text{C}_3\text{-C}_4)(20) + \nu(\text{C}_5\text{-C}_6)(15) + \varphi(\text{H-C}_5\text{-C}_6)(13) + \varphi(\text{C}_2\text{-C}_3\text{-H})(9) + \varphi(\text{H-C-N})(8)$
1364	1373 ^m	1377 ^s	—	$\varphi(\text{H-C-C})(19) + \nu(\text{C}_2\text{-C}_3)(17) + \varphi(\text{C}_2\text{-C}_3\text{-H})(16) + \nu(\text{C}_1\text{-C}_2)(9) + \nu(\text{C}_3\text{-C}_4) + (7) + \varphi(\text{H-C}_2\text{-C}_3)(7) + \varphi(\text{C}_1\text{-C}_2\text{-H})(7)$	1371	1373 ^s	1377 ^s	—	$\varphi(\text{H-C-C})(18) + \varphi(\text{C}_2\text{-C}_3\text{-H})(18) + \nu(\text{C}_2\text{-C}_3)(16) + \nu(\text{C}_3\text{-C}_4)(10) + \nu(\text{C}_1\text{-C}_2)(10) + \varphi(\text{H-C}_2\text{-C}_3)(7) + \varphi(\text{C}_1\text{-C}_2\text{-H})(6)$
1346	1340 ^s	1342 ^{sh}	—	$\nu(\text{C}_1\text{-C}_2)(16) + \varphi(\text{H-C-N})(11) + \varphi(\text{C}_2\text{-C}_3\text{-H})(10) + \varphi(\text{H-C-C})(9) + \nu(\text{C}_3\text{-C}_4)(7) + \varphi(\text{C}_5\text{-C}_6\text{-H})(7) + \varphi(\text{C}_6\text{-N-H})(6)$	1326	1340 ^s	1342 ^{sh}	—	$\nu(\text{C}_1\text{-C}_2)(16) + \varphi(\text{H-C-C})(10) + \varphi(\text{H-C-N})(8) + \nu(\text{C}=\text{O})(6) + \nu(\text{C}_5\text{-C}_6)(5) + \varphi(\text{C}_1\text{-C}_2\text{-H})(5) + \varphi(\text{H-C}_2\text{-C}_3)(5)$
1259	1264 ^s	1261 ^s	—	$\varphi(\text{H-C-C})(31) + \varphi(\text{H-C}_5\text{-C}_6)(18) + \varphi(\text{C}_2\text{-C}_3\text{-H})(17) + \varphi(\text{H-C-N})(8) + \varphi(\text{C}_5\text{-C}_6\text{-H})(6)$	1255	1264 ^s	1261 ^s	—	$\varphi(\text{H-C-C})(27) + \varphi(\text{C}_2\text{-C}_3\text{-H})(17) + \varphi(\text{H-C}_5\text{-C}_6)(13) + \varphi(\text{H-C-N})(11) + \varphi(\text{C}_5\text{-C}_6\text{-H})(10) + \nu(\text{N-C}_1)(6)$
1236	1239 ^s	1237 ^s	—	$\varphi(\text{H-C-N})(55) + \varphi(\text{C}_5\text{-C}_6\text{-H})(21) + \varphi(\text{H-C-C})(13)$	1236	1239 ^s	1237 ^s	—	$\varphi(\text{H-C-N})(55) + \varphi(\text{C}_5\text{-C}_6\text{-H})(21) + \varphi(\text{H-C-C})(13)$
1210	1210 ^m	1205 ^m	—	$\varphi(\text{C}_1\text{-C}_2\text{-H})(23) + \varphi(\text{H-C}_2\text{-C}_3)(20) + \varphi(\text{H-C-C})(17) + \varphi(\text{C}_2\text{-C}_3\text{-H})(16) + \nu(\text{N-C}_1)(11)$	1212	1210 ^m	1205 ^m	—	$\varphi(\text{C}_1\text{-C}_2\text{-H})(23) + \varphi(\text{H-C}_2\text{-C}_3)(21) + \varphi(\text{H-C-C})(16) + \varphi(\text{C}_2\text{-C}_3\text{-H})(14) + \nu(\text{N-C}_1)(11)$
1191	1200 ^m	1200 ^m	—	$\varphi(\text{H-C-C})(34) + \varphi(\text{H-C}_5\text{-C}_6)(27) + \varphi(\text{C}_2\text{-C}_3\text{-H})(26) + \varphi(\text{C}_5\text{-C}_6\text{-H})(7)$	1192	1200 ^m	1200 ^m	—	$\varphi(\text{H-C-C})(35) + \varphi(\text{H-C}_5\text{-C}_6)(27) + \varphi(\text{C}_2\text{-C}_3\text{-H})(26) + \varphi(\text{C}_5\text{-C}_6\text{-H})(6)$
1172	1173 ^w	1168 ^m	—	$\varphi(\text{H-C-C})(51) + \varphi(\text{C}_2\text{-C}_3\text{-H})(37) + \varphi(\text{H-C-N})(6)$	1172	1173 ^w	1168 ^m	—	$\varphi(\text{H-C-C})(51) + \varphi(\text{C}_2\text{-C}_3\text{-H})(38) + \varphi(\text{H-C-N})(6)$

Continued on next page.

sandwiched between five CH₂ groups.

Amide A band arising from N-H stretching is characteristic of its functional group. This mode is highly sensitive to the strength of N-H...O=C hydrogen bonding. We have calculated Amide A frequency at 3301 cm⁻¹ corresponding to the observed peak at 3300 cm⁻¹ in IR\Raman.⁵⁻⁸

Amide I mode has significant contribution of C=O and C-N stretches. This localized mode is calculated at 1648 cm⁻¹ corresponding to the observed band at 1647 cm⁻¹ in Raman.⁵ This mode reflects the hydrogen bond strength due to the presence of C=O stretch contributions. Its value plays a decisive role to identify backbone conformation.

Amide II is predominantly a N-H in plane bending mode. It is calculated at 1554 cm⁻¹ and assigned to the peak observed at 1551 cm⁻¹ in Raman.^{5,6}

Amide III is a combination of N-H in plane bend and C-N stretch as in amide II but in opposite phase. This mode has been calculated at 1286 cm⁻¹ at $\delta = 0$ and assigned to the peak observed at 1289\1280 cm⁻¹ in FTIR¹²\Raman.⁸

Amide IV vibration is associated with the in plane bending of C=O band. This mode is calculated at 722 cm⁻¹ and observed at the peak appearing at 734 cm⁻¹ in INS.¹⁰ This mode is quite sensitive to molecular geometry.

Amide V and Amide VI are mainly asymmetric out

Continued.

Cal. freq.	Obs. Freq.			Assignment (% PED), $\delta = 0$	Cal. freq.	Obs. Freq.			Assignment (% PED), $\delta = \pi$
	IR ^a	Raman ^b	INS ^c			IR ^a	Raman ^b	INS ^c	
1154	1162 ^m	1168 ^m	—	$\varphi(\text{H-C-C})(45) + \varphi(\text{C}_2\text{-C}_3\text{-H})(26) + \varphi(\text{H-C}_5\text{-C}_6)(15)$	1153	1162 ^m	1168 ^m	—	$\varphi(\text{H-C-C})(45) + \varphi(\text{C}_2\text{-C}_3\text{-H})(26) + \varphi(\text{H-C}_5\text{-C}_6)(16)$
1114	1121 ^m	1123 ^s	—	$\varphi(\text{H-C}_2\text{-C}_3)(44) + \varphi(\text{C}_1\text{-C}_2\text{-H})(42) + \varphi(\text{C}_2\text{-C}_3\text{-H})(6)$	1114	1121 ^m	1123 ^s	—	$\varphi(\text{H-C}_2\text{-C}_3)(44) + \varphi(\text{C}_1\text{-C}_2\text{-H})(42) + \varphi(\text{C}_2\text{-C}_3\text{-H})(6)$
1070	1067 ^s	1076 ^s	—	$\nu(\text{C}_6\text{-N})(32) + \nu(\text{C}_3\text{-C}_4)(14) + \nu(\text{C}_2\text{-C}_3)(13)$	1054	1067 ^s	1076 ^s	—	$\nu(\text{C}_3\text{-C}_4)(24) + \nu(\text{C}_2\text{-C}_3)(21) + \nu(\text{C}_6\text{-N})(11) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(8) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(8) + \varphi(\text{C}_1\text{-C}_2\text{-C}_3)(6) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(5)$
1028	1028 ^s	—	—	$\nu(\text{C}_6\text{-N})(43) + \nu(\text{C}_2\text{-C}_3)(12) + \nu(\text{C}_5\text{-C}_6)(12) + \nu(\text{C}_3\text{-C}_4)(8)$	1047	1028 ^s	—	—	$\nu(\text{C}_6\text{-N})(62) + \nu(\text{C}_2\text{-C}_3)(6)$
1003	—	1001 ^w	—	$\nu(\text{C}_5\text{-C}_6)(30) + \nu(\text{C}_3\text{-C}_4)(18) + \nu(\text{C}_2\text{-C}_3)(9) + \varphi(\text{C}_5\text{-C}_6\text{-H})(6) + \varphi(\text{C}_5\text{-C}_6\text{-N})(6) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(5)$	1004	—	1001 ^w	—	$\nu(\text{C}_5\text{-C}_6)(49) + \nu(\text{C}_3\text{-C}_4)(16) + \varphi(\text{C}_5\text{-C}_6\text{-H})(7)$
987	980 ^m	989 ^m	—	$\varphi(\text{H-C-C})(27) + \varphi(\text{C}_2\text{-C}_3\text{-H})(26) + \varphi(\text{H-C}_5\text{-C}_6)(14) + \varphi(\text{C}_5\text{-C}_6\text{-H})(11) + \varphi(\text{H-C-N})(9) + \varphi(\text{C}_1\text{-C}_2\text{-H})(6)$	981	980 ^m	989 ^m	—	$\varphi(\text{H-C-C})(28) + \varphi(\text{C}_2\text{-C}_3\text{-H})(28) + \varphi(\text{H-C}_5\text{-C}_6)(15) + \varphi(\text{C}_5\text{-C}_6\text{-H})(10) + \varphi(\text{H-C-N})(10) + \varphi(\text{C}_1\text{-C}_2\text{-H})(7)$
982	973 ^m	980 ^m	—	$\nu(\text{C}_3\text{-C}_4)(48) + \nu(\text{C}_5\text{-C}_6)(15) + \varphi(\text{H-C-C})(9) + \nu(\text{C}_2\text{-C}_3)(5)$	979	973 ^m	980 ^m	—	$\nu(\text{C}_3\text{-C}_4)(52) + \nu(\text{C}_2\text{-C}_3)(10) + \nu(\text{C}_5\text{-C}_6)(10) + \varphi(\text{H-C-C})(10)$
949	955 ^m	955 ^w	—	$\nu(\text{C}_3\text{-C}_4)(41) + \nu(\text{C}_2\text{-C}_3)(17) + \varphi(\text{C}_2\text{-C}_3\text{-H})(8) + \nu(\text{C}_5\text{-C}_6)(8) + \nu(\text{C}_1\text{-C}_2)(7) + \varphi(\text{H-C-C})(6)$	947	955 ^m	955 ^w	—	$\nu(\text{C}_3\text{-C}_4)(44) + \nu(\text{C}_2\text{-C}_3)(12) + \nu(\text{C}_1\text{-C}_2)(12) + \varphi(\text{C}_2\text{-C}_3\text{-H})(7) + \varphi(\text{H-C-C})(7)$
929	927 ^s	930 ^m	934 ^s	$\nu(\text{C}_1\text{-C}_2)(30) + \nu(\text{C}_3\text{-C}_4)(18) + \nu(\text{C}=\text{O})(12) + \nu(\text{N-C}_1)(8) + \varphi(\text{C}_1\text{-C}_2\text{-H})(6)$	938	927 ^s	930 ^m	934	$\nu(\text{C}_1\text{-C}_2)(25) + \nu(\text{C}_3\text{-C}_4)(12) + \nu(\text{C}=\text{O})(11) + \varphi(\text{C}_1\text{-C}_2\text{-H})(8) + \nu(\text{N-C}_1)(7) + \nu(\text{C}_2\text{-C}_3)(6) + \varphi(\text{H-C}_2\text{-C}_3)(5)$
897	887 ^s	898 ^w	—	$\varphi(\text{H-C-C})(31) + \varphi(\text{C}_5\text{-C}_6\text{-H})(18) + \varphi(\text{C}_1\text{-C}_2\text{-H})(14) + \varphi(\text{H-C-N})(12) + \varphi(\text{C}_2\text{-C}_3\text{-H})(10) + \varphi(\text{H-C}_2\text{-C}_3)(9)$	912	887 ^s	898 ^w	—	$\varphi(\text{H-C-C})(27) + \varphi(\text{C}_5\text{-C}_6\text{-H})(19) + \varphi(\text{C}_1\text{-C}_2\text{-H})(12) + \varphi(\text{H-C}_2\text{-C}_3)(11) + \varphi(\text{H-C-N})(9) + \varphi(\text{C}_2\text{-C}_3\text{-H})(9) + \omega(\text{C}=\text{O})(7)$
837	834 ^s	835 ^w	—	$\varphi(\text{H-C-C})(31) + \varphi(\text{C}_5\text{-C}_6\text{-H})(18) + \varphi(\text{C}_1\text{-C}_2\text{-H})(14) + \varphi(\text{H-C-N})(12) + \varphi(\text{C}_2\text{-C}_3\text{-H})(10) + \varphi(\text{H-C}_2\text{-C}_3)(9)$	827	834 ^s	835 ^w	—	$\varphi(\text{C}_5\text{-C}_6\text{-H})(31) + \varphi(\text{H-C}_5\text{-C}_6)(23) + \tau(\text{C}_5\text{-C}_6)(11) + \varphi(\text{H-C-C})(10) + \varphi(\text{H-C-N})(8)$
806	—	—	814 ^s	$\varphi(\text{H-C-C})(34) + \varphi(\text{C}_2\text{-C}_3\text{-H})(13) + \varphi(\text{H-C}_5\text{-C}_6)(11) + \tau(\text{C}_5\text{-C}_6)(9) + \varphi(\text{H-C}_2\text{-C}_3)(8) + \tau(\text{C}_4\text{-C}_5)(8)$	802	—	—	814 ^s	$\varphi(\text{H-C-C})(38) + \varphi(\text{C}_2\text{-C}_3\text{-H})(19) + \varphi(\text{H-C}_2\text{-C}_3)(13) + \varphi(\text{C}_1\text{-C}_2\text{-H})(8) + \tau(\text{C}_4\text{-C}_5)(7)$
749	736 ^s	743 ^s	743 ^s	$\varphi(\text{C}_2\text{-C}_3\text{-H})(34) + \varphi(\text{H-C-C})(28) + \varphi(\text{H-C}_2\text{-C}_3)(13)$	753	736 ^s	743 ^s	736 ^s	$\varphi(\text{C}_2\text{-C}_3\text{-H})(34) + \varphi(\text{H-C-C})(27) + \varphi(\text{H-C}_2\text{-C}_3)(12) + \omega(\text{C}=\text{O})(7) + \omega(\text{N-H})(6)$
531	523 ^m	—	524 ^s	$\varphi(\text{C}_3\text{-C}_4\text{-C}_5)(18) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(17) + \varphi(\text{N-C}_1\text{-C}_2)(15) + \varphi(\text{C}_1\text{-C}_2\text{-C}_3)(8) + \varphi(\text{O}=\text{C}_1\text{-C}_2)(7) + \varphi(\text{C-N-C})(7)$	504	523 ^m	—	524 ^s	$\varphi(\text{N-C}_1\text{-C}_2)(18) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(16) + \varphi(\text{C}_5\text{-C}_6\text{-N})(13) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(11) + \varphi(\text{O}=\text{C}_1\text{-C}_2)(9) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(9)$
431	429 ^m	—	435 ^s	$\varphi(\text{C}_2\text{-C}_3\text{-C}_4)(26) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(18) + \varphi(\text{C}_5\text{-C}_6\text{-N})(17) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(12) + \varphi(\text{H-C-C})(6)$	424	429 ^m	—	435 ^s	$\Phi(\text{C}_3\text{-C}_4\text{-C}_5)(25) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(21) + \varphi(\text{O}=\text{C}_1\text{-C}_2)(9) + \varphi(\text{N-C}=\text{O})(9) + \varphi(\text{C}_1\text{-C}_2\text{-C}_3)(8) + \varphi(\text{C-N-C})(7)$

Note: 1. ^aRef. 5, 6, 11, 12, ^bRef. 7, 8, 12, ^cRef 9, 10.2. All freq. are in cm^{-1} .

3. s = strong, sh = shoulder = medium, w = weak.

of plane wag of N-H and C=O bonds respectively. These vibrational modes are calculated at 698 cm^{-1} and 584 cm^{-1} respectively corresponding to the observed peaks at 701 and 580 cm^{-1} in INS spectra.¹⁰

A comparison of αNY6 and polyethylene shows that the dispersive behaviour of normal modes in αNY6 should resemble those in PE. The perturbation caused by the Amide groups cannot totally delocalize the modes and hence they should continue to display in dispersion. The perturbation would affect most (C-N) torsion because both (C-C) torsion (C-N) will get mixed up. This is what happen to the potential energy distribution. The mode at 217 cm^{-1} is a mix-

ture of $\tau(\text{C}_5\text{-C}_6)(60)\% + \tau(\text{N-C}_1)(14)\% + \tau(\text{C}_4\text{-C}_5)(8)\% + \varphi(\text{C-C-C})(5)\%$.

As for the vibrations of the amide groups, in β -poly (L-Ornithine),²³ β -poly (O-Acetyl, L-Serine),²⁴ β -polyglycine I²² and poly (L-Serine)²⁵ the amide modes of all these polymers are in the same wave number range. The minor differences are because of the number of intervening CH_2 groups that affect the long range interaction.

Methylene Modes

The αNY6 molecule has five methylene groups that are flanked by the rigid amide groups. This linear

Table III. Amide modes of α NY6

Mode	Freq (Calc.)	Obs. Freq.			Potential Energy Distribution at $\delta = 0$	Freq (Calc.)	Obs. Freq.			Potential Energy Distribution at $\delta = \pi$
		IR ^a	Raman ^b	INS ^c			IR ^a	Raman ^b	INS ^c	
Amide A	3301	3300	3300	—	$\nu(\text{N-H})(99)$	3301	3300	3300	—	$\nu(\text{N-H})(99)$
Amide I	1648	1646	1635	—	$\nu(\text{C=O})(57) + \nu(\text{N-C}_1)(24)$	1648	1646	1635	—	$\nu(\text{C=O})(57) + \nu(\text{N-C}_1)(24)$
Amide II	1554	1556	1543	—	$\varphi(\text{H-N-C}_1)(36) +$ $\varphi(\text{C}_6\text{-N-H})(26) + \nu(\text{N-C}_1)(21)$	1554	1556	1543	—	$\varphi(\text{H-N-C}_1)(35) + \varphi(\text{C}_6\text{-N-H})(26) + \nu(\text{N-C}_1)(21)$
Amide III	1286	1280	1280	—	$\varphi(\text{C}_5\text{-C}_6\text{-H})(19) + \varphi(\text{H-C-N})(19) + \varphi(\text{H-C-C})(13) +$ $\varphi(\text{C}_2\text{-C}_3\text{-H})(10) + \nu(\text{C=O})(7)$ $+ \nu(\text{N-C}_1)(7)$	1300	1280	1280	—	$\varphi(\text{H-C-C})(19) + \varphi(\text{H-C-N})(18) + \varphi(\text{C}_5\text{-C}_6\text{-H})(14) +$ $\varphi(\text{C}_2\text{-C}_3\text{-H})(12) + \nu(\text{N-C}_1)(5)$
Amide IV	722	736	—	725	$\varphi(\text{O=C}_1\text{-C}_2)(23) + \varphi(\text{N-C=O})$ $+ \nu(\text{C}_1\text{-C}_2)(12) + \varphi(\text{C}_1\text{-C}_2\text{-C}_3)$ $(11) + \nu(\text{C}_6\text{-N})(6) + \varphi(\text{C-N-C})(6)$	728	736	—	725	$\varphi(\text{O=C}_1\text{-C}_2)(20) +$ $\varphi(\text{N-C=O})(19) + \nu(\text{C}_1\text{-C}_2)(13)$ $+ (\text{C}_1\text{-C}_2\text{-C}_3)(12) +$ $\varphi(\text{C-N-C})(7)$
Amide V	698	693	—	701	$\omega(\text{N-H})(57) + \varphi(\text{C}_1\text{-C}_2\text{-H})(9) +$ $\tau(\text{N-C}_1)(8) + \omega(\text{C=O})(8) +$ $\varphi(\text{H-C}_2\text{-C}_3)(6)$	698	693	—	701	$\omega(\text{N-H})(57) + \varphi(\text{C}_1\text{-C}_2\text{-H})(9) +$ $\omega(\text{C=O})(8) + \tau(\text{N-C}_1)(8) +$ $\varphi(\text{H-C}_2\text{-C}_3)(6)$
Amide VI	584	580	—	580	$\omega(\text{C=O})(56) + \omega(\text{N-H})(12) +$ $\tau(\text{C}_1\text{-C}_2)(10) + \tau(\text{N-C}_1)(8) +$ $\varphi(\text{C}_1\text{-C}_2\text{-H})(6)$	584	580	—	580	$\omega(\text{C=O})(55) + \omega(\text{N-H})(12) +$ $\tau(\text{C}_1\text{-C}_2)(10) + \tau(\text{N-C}_1)(8) +$ $\varphi(\text{C}_1\text{-C}_2\text{-H})(6)$
Amide VII	222	220	—	218	$\tau(\text{C}_5\text{-C}_6)(60) + \tau(\text{N-C}_1)(14) +$ $\tau(\text{C}_4\text{-C}_5)(8) + \varphi(\text{H-C-C})(5)$	232	220	—	218	$\tau(\text{C}_5\text{-C}_6)(53) + \tau(\text{N-C}_1)(15) +$ $\tau(\text{C}_3\text{-C}_4)(7) + \tau(\text{C}_4\text{-C}_5)(7)$

Note: 1. ^aRef. 5, 6, 11, 12, ^bRef. 7, 8, 12, ^cRef 10.

2. All freq. are in cm^{-1} .

Table IV. Comparison of Amide modes of α NY6 (α -form) with other β -sheet polypeptides

Modes	Nylon-6		β -PLO		β -PALS		β -PG1		β -PLS	
	$\delta = 0$	$\delta = \pi$	$\delta = 0$	$\delta = \pi$	$\delta = 0$	$\delta = \pi$	$\delta = 0$	$\delta = \pi$	$\delta = 0$	$\delta = \pi$
Amide A	3301	3301	3286	3286	3303	3303	3274	3274	3318	3318
Amide I	1648	1648	1649	1645	1640	1637	1642	1634	1637	1628
Amide II	1554	1554	1533	1528	1521	1517	1520	1520	1532	1537
Amide III	1286	1299	1275	1228	1229	1217	1306	1287	1249	1270
Amide IV	722	729	510	—	600	—	630	711	533	773
Amide V	698	699	702	705	695	718	720	745	713	685
Amide VI	584	584	594	547	448	515	570	634	533	647

Note: All frequencies are in cm^{-1} .

PLO = Poly(L-Ornithine).²³

PALS = Poly(O-Acetyl, L-Serine).²⁴

PG1 = Polyglycine I.²²

PLS = Poly(L-Serine).²⁵

chain of CH_2 groups has selection rules different from those for an infinite chain. They are related to the dispersion of a given normal mode of an infinite chain and the absorption/scattering occurs at the phase values given by the following relation

$$\delta = k\pi/(m + 1) \quad (10)$$

Where m denotes the number of CH_2 groups in the linear chain linkage and $k = 1, 2, \dots, 5$. Thus the allowed δ for a given mode, would give rise to wave numbers on the corresponding dispersion curve for an infinite system which is polyethylene (PE)²⁶ in this case. The wave numbers thus obtained are given in Table IV. The calculated CH_2 group frequencies of α NY6 are in good agreement with those calculated

from the dispersion curves of PE. Small deviations arise because of the intra and inter chain interactions of CH_2 group with the amide group in α NY6.

The skeletal structure of α NY6 consists of the five-methylene groups, which are flanked by amide group at both the ends. Because of such anchoring, a comparison of the wave numbers obtained from the dispersion curves of PE, corresponding to phase values given by eq 1 is in order in case of CH_2 group modes except for the skeletal modes. These modes in polyethylene mostly consist of coupled motions of $\varphi(\text{C-C-C})$ and $\tau(\text{C-C})$ and are spread over the entire chain. In PE, these modes are acoustical in nature whereas in α NY6, the skeletal modes of $(-\text{CH}_2)_5$ fragments are optical in nature and thus a comparison would not be

in order. Similar phenomena have been observed in PCL.¹⁷ The origin of such optical phonon is explained by the splitting of the longitudinal acoustic phonon band of PE chain into several optical bands due to a periodic perturbation (the presence of the heavier amide groups-NHCO). It is similar to the role played by the (-COO-) end groups in PCL [-(CH₂)₅-COO-]. The CH₂ group modes are in order and in agreement with the modes sequence of CH₂ groups of PCL (Table V). Because of more or less identical situations, the agreement of the CH₂ segmental and others modes with PCL is almost total.

Dispersion Curves

Dispersion curves and frequency distribution function are important for an understanding of thermodynamical and elastic properties of solids. Besides providing knowledge of density-of-states, dispersion curves give information on the extent of the coupling of a mode along the chain in the ordered state. Also a study of these is necessary to appreciate the origin of both symmetry independent and symmetry dependent spectral features. The dispersion curves and the corresponding density of states of α NY6 below 400 cm⁻¹ are shown in Figure 2(a) and 2(b). The lower two branches ($\nu = 0$ at $\delta = 0$ & $\delta = \pi$) correspond to four acoustic modes. Two of them are at the zone center and two are at the zone boundary. They represent three translations (one parallel and two perpendicular to the axis) and one free rotation about the chain axis.

The mode calculated at 357 cm⁻¹ observed at 354 cm⁻¹ (INS studies)¹⁰ at $\delta = 0$ disperses by 44 wave numbers and thus it is calculated at 313 cm⁻¹ at $\delta = \pi$ and observed at 295 cm⁻¹. This mode has prominent contributions from angle bends φ (C₅-C₆-N), φ (N-C₁-C₂) & φ (C₃-C₄-C₅). But beyond $\delta = 0.70\pi$, the contribution of φ (C₃-C₄-C₅) dominates. The wave number of the mode calculated at 290 cm⁻¹ at zone center decreases to 229 cm⁻¹ at $\delta = 0.75\pi$. This mode involves mainly (C-C-C) bending, (C-N-C) bending and (C=O) in plane bending. As the value of δ increases, the contribution of (C=O) in plane bending decreases and at the zone boundary this mode appears at 252 cm⁻¹ [φ (C₅-C₆-N) (28)% + φ (C₂-C₃-C₄) (21)%]. The modes calculated at 148 and 107 cm⁻¹ are pure torsional mode at $\delta = 0$ these modes disperse by 42 & 18 wave numbers respectively at the zone boundary. The vibrational mode calculated at 57 cm⁻¹ at $\delta = 0$ is in plane deformation mode with PED [φ (C₁-C₂-C₃) + φ (C₂-C₃-C₄) + φ (C₃-C₄-C₅) + φ (C₄-C₅-C₆)]. It is a highly dispersive mode and reaches 195 cm⁻¹ at the zone boundary. It is assigned to the observed frequency at 195 cm⁻¹ in IR spectra.⁵ In its journey from the zone center towards zone boundary it crosses three torsional modes (107, 148 &

Table V. Comparison of CH₂ modes of α NY6 with PCL

Modes	Calculated by selection rule from PE ^c dispersion curves	α NY6		Freq (PCL) ^b
		Freq (calc.)	Freq (obs.) ^d	
		2936	2930	
CH ₂		2933	2930	
asymmetric stretch	2919 ^a	2938	2930	2916
		2924	2930	
		2922	2930	
		2863	2855	
CH ₂		2860	2855	
symmetric stretch	2848 ^a	2857	2855	2866
		2854	2855	
		2852	2855	
CH ₂		1482	1486	
scissoring		1473	1476	1470
	1473	1464	1458	1439
	1440	1459	1458	
		1451	1448	
CH ₂ wag	1390	1393	1393	1400
	1360	1364	1364	1367
	1310	1346	1340	1340
	1260	1259	1264	1303
	1210	1210	1210	1195
CH ₂ twist	1300	—	1289	1303
	1280	1287	1239	1280
	1247	1236	1199	1240
	1195	1191	1168	1195
	—	1171,1153	1123	1170
	—	1114	—	—
CH ₂ rock	1005	987	955	—
	935	897	887	930
	835	837	842	835
	770	806	814	770
	740	749	734	734
C-C stretch	1069	1071	1076	1107
	1040	1027	1028	1063
	1040	1002	1001	1033
	1010	981	980	956
	995	950	955	912
	490	531	524	523
C-C-C bend	420	431	435	451
	290	357	354	370
	240	290	290	315
	60	57	—	260
C-C torsion	178	175	173	215
	165	148	141	197
	110	107	—	172
	90	30	—	110
	30	22	24	—

Note: 1. All frequencies are in cm⁻¹.

2. ^a marked frequencies are observed in the spectra of polyethylene.

3. ^bRef. 17, ^cRef. 26, ^dRef. 5–12.

175 cm⁻¹ calculated at $\delta = 0$) at $\delta = 0.341\pi$, 0.452π & 0.612π respectively. Similar phenomenon is observed for another in plane deformation vibrational

mode calculated at 50 cm^{-1} at $\delta = 0$ with the exception that the mode initially decreases by 7 wave number till $\delta = 0.10\pi$. It rises again and crosses the two torsional mode (107 cm^{-1} and 148 cm^{-1} calculated at $\delta = 0$) at $\delta = 0.426\pi$ and $\delta = 0.612\pi$ respectively.

When the approaching modes belong to different symmetry species then they can crossover. Since αNY6 has a mirror plane of symmetry along the chain axis, hence crossings are permissible. All such modes showing crossover are given in Table VI, along with the PED and the δ values at which these features occur. Further since the PED of these two modes remains the same before and after intersection, it confirms that they do not repel.

The intersection of the acoustic and lowest optical modes at $\delta = 0.072\pi$ $\delta = 0.113\pi$ can be similarly interpreted as two collisions in the (ϵ, p) space. A similar feature is observed in the case of PCL. The dispersive behaviour of αNY6 is almost the same as in PCL in the low frequency region ($0\text{--}300$) cm^{-1} .

Frequency Distribution Function and Heat Capacity

A study of dispersion curves provides us with an

understanding of the origin of both symmetry dependent and symmetry independent spectral features. The profiles of these curves also assist in determining the thermodynamic behaviour of the polymer. We have calculated the heat capacity of αNY6 in the temperature range ($70\text{--}310\text{ K}$) (Figure 3) using density-of-states *via* dispersion curves using Debye's formalism. The calculated frequency distribution function (density-of-states) as a function of frequency is shown in Figure 2(b). The flat region in the frequency distribution curves correspond to regions of high density-of-state (Von Hove type singularities). These peaks denote the observed frequencies. The calculated heat capacity data is shown to be in good agreement with the experimental measurements as obtained from the ATHAS data bank 1993²⁷ updated.

As our calculations have been made for an isolated molecular chain, the interpretation of IR\Raman spectra and theoretical calculations are subject to certain limitations. A complete interpretation of the spectra requires calculations for a three dimensional system where interactions play an important role. Special mention may be made of interactions between the

Table VI. Crossing between the pair of modes of αNY6

freq. $\delta = 0$	δ^a/π	δ^b/π	freq.	P.E.D before crossing	δ^b/π	freq.	P.E.D after crossing
290	0.792	0.75	231	$\tau(\text{C}_5\text{-C}_6)(53) + \tau(\text{N-C}_1)(15) + \tau(\text{C}_4\text{-C}_5)(7) + \tau(\text{C}_3\text{-C}_4)(7)$	0.80	232	$\varphi(\text{C}_5\text{-C}_6\text{-N})(6) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(21) + \varphi(\text{C-N-C})(9) + \nu(\text{C}_3\text{-C}_4)(8) + \varphi(\text{C}_1\text{-C}_2\text{-C}_3)(6)$
222	0.792	0.75	229	$\varphi(\text{C}_5\text{-C}_6\text{-N})(21) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(17) + \varphi(\text{C-N-C})(12) + \varphi(\text{C}_1\text{-C}_2\text{-C}_3)(11) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(6) + \nu(\text{C}_3\text{-C}_4)(5)$	0.80	231	$\tau(\text{C}_5\text{-C}_6)(53) + \tau(\text{N-C}_1)(15) + \tau(\text{C}_4\text{-C}_5)(7) + \tau(\text{C}_3\text{-C}_4)(7)$
290	0.709	0.70	236	$\varphi(\text{C}_1\text{-C}_2\text{-C}_3)(16) + \varphi(\text{C-N-C})(14) + \varphi(\text{C}_5\text{-C}_6\text{-N})(12) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(9) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(9) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(8)$	0.75	231	$\tau(\text{C}_5\text{-C}_6)(53) + \tau(\text{N-C}_1)(15) + \tau(\text{C}_4\text{-C}_5)(7) + \tau(\text{C}_3\text{-C}_4)(7)$
222	0.709	0.70	230	$\tau(\text{C}_5\text{-C}_6)(54) + \tau(\text{N-C}_1)(15) + \tau(\text{C}_4\text{-C}_5)(7) + \tau(\text{C}_3\text{-C}_4)(6)$	0.75	229	$\varphi(\text{C}_5\text{-C}_6\text{-N})(21) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(17) + \varphi(\text{C-N-C})(12) + \varphi(\text{C}_1\text{-C}_2\text{-C}_3)(11) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(6) + \nu(\text{C}_3\text{-C}_4)(5)$
175	0.612	0.60	177	$\tau(\text{C}_4\text{-C}_5)(50) + \tau(\text{C}_6\text{-N})(18) + \tau(\text{C}_1\text{-C}_2)(8) + \tau(\text{C}_3\text{-C}_4)(8) + \tau(\text{C}_2\text{-C}_3)(7)$	0.65	186	$\varphi(\text{C}_4\text{-C}_5\text{-C}_6)(13) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(10) + \varphi(\text{C}_5\text{-C}_6\text{-N})(10) + \nu(\text{C}_3\text{-C}_4)(8) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(7) + \varphi(\text{C}_1\text{-C}_2\text{-C}_3)(7) + \nu(\text{C}_6\text{-N})(7) + \varphi(\text{N-C}_1\text{-C}_2)(6) + \varphi(\text{O=C}_1\text{-C}_2)(5)$
57	0.612	0.60	174	$\varphi(\text{C}_4\text{-C}_5\text{-C}_6)(12) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(11) + \varphi(\text{C}_5\text{-C}_6\text{-N})(11) + \nu(\text{C}_3\text{-C}_4)(9) + \nu(\text{C}_6\text{-N})(7) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(6) + \varphi(\text{C}_1\text{-C}_2\text{-C}_3)(6) + \varphi(\text{N-C}_1\text{-C}_2)(6) + \nu(\text{C}_1\text{-C}_2)(5)$	0.65	177	$\tau(\text{C}_4\text{-C}_5)(50) + \tau(\text{C}_6\text{-N})(18) + \tau(\text{C}_1\text{-C}_2)(9) + \tau(\text{C}_3\text{-C}_4)(8) + \tau(\text{C}_2\text{-C}_3)(7)$
148	0.612	0.60	126	$\tau(\text{C}_3\text{-C}_4)(24) + \tau(\text{C}_1\text{-C}_2)(21) + \tau(\text{N-C}_1)(15) + \tau(\text{C}_2\text{-C}_3)(12) + \tau(\text{C}_5\text{-C}_6)(10)$	0.65	130	$\varphi(\text{C}_1\text{-C}_2\text{-C}_3)(16) + \varphi(\text{C-N-C})(13) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(12) + \varphi(\text{C}_5\text{-C}_6\text{-N})(12) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(11) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(8)$
50	0.612	0.60	124	$\varphi(\text{C}_1\text{-C}_2\text{-C}_3)(16) + \varphi(\text{C-N-C})(13) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(12) + \varphi(\text{C}_5\text{-C}_6\text{-N})(12) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(11) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(8)$	0.65	122	$\tau(\text{C}_3\text{-C}_4)(23) + \tau(\text{C}_1\text{-C}_2)(21) + \tau(\text{N-C}_1)(14) + \tau(\text{C}_2\text{-C}_3)(13) + \tau(\text{C}_5\text{-C}_6)(11)$
148	0.452	0.45	135	$\tau(\text{C}_3\text{-C}_4)(29) + \tau(\text{C}_1\text{-C}_2)(22) + \tau(\text{N-C}_1)(15) + \tau(\text{C}_2\text{-C}_3)(10) + \tau(\text{C}_5\text{-C}_6)(7)$	0.50	147	$\varphi(\text{C}_2\text{-C}_3\text{-C}_4)(13) + \varphi(\text{C}_5\text{-C}_6\text{-N})(12) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(12) + \nu(\text{C}_3\text{-C}_4)(9) + \nu(\text{C}_6\text{-N})(7) + \nu(\text{C}_1\text{-C}_2)(6) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(5) + \varphi(\text{N-C}_1\text{-C}_2)(5) + \varphi(\text{C}_1\text{-C}_2\text{-C}_3)(5)$
57	0.452	0.45	134	$\varphi(\text{C}_2\text{-C}_3\text{-C}_4)(13) + \varphi(\text{C}_5\text{-C}_6\text{-N})(12) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(12) + \nu(\text{C}_3\text{-C}_4)(9) + \nu(\text{C}_6\text{-N})(7) + \nu(\text{C}_1\text{-C}_2)(6) + \varphi(\text{N-C}_1\text{-C}_2)(5) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(5)$	0.50	132	$\tau(\text{C}_3\text{-C}_4)(27) + \tau(\text{C}_1\text{-C}_2)(22) + \tau(\text{N-C}_1)(15) + \tau(\text{C}_2\text{-C}_3)(11) + \tau(\text{C}_5\text{-C}_6)(8)$
107	0.426	0.40	102	$\tau(\text{C}_6\text{-N})(35) + \tau(\text{C}_2\text{-C}_3)(29) + \tau(\text{C}_1\text{-C}_2)(16) + \tau(\text{N-C}_1)(14)$	0.45	104	$\varphi(\text{C}_1\text{-C}_2\text{-C}_3)(17) + \varphi(\text{C}_3\text{-C}_4\text{-C}_5)(13) + \varphi(\text{C-N-C})(13) + \varphi(\text{C}_5\text{-C}_6\text{-N})(12) + \varphi(\text{C}_2\text{-C}_3\text{-C}_4)(10) + \varphi(\text{C}_4\text{-C}_5\text{-C}_6)(8)$

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freq. $\delta = 0$	δ^a/π	δ^b/π	freq.	P.E.D before crossing	δ^b/π	freq.	P.E.D after crossing
50	0.426	0.40	98	$\varphi(C_1-C_2-C_3)(17) + \varphi(C_3-C_4-C_5)(14) + \varphi(C-N-C)(13) + \varphi(C_5-C_6-N)(12) + \varphi(C_2-C_3-C_4)(10) + \varphi(C_4-C_5-C_6)(8)$	0.45	100	$\tau(C_6-N)(35) + \tau(C_2-C_3)(29) + \tau(C_1-C_2)(16) + \tau(N-C_1)(14)$
107	0.341	0.30	103	$\tau(C_6-N)(35) + \tau(C_2-C_3)(29) + \tau(C_1-C_2)(17) + \tau(N-C_1)(14)$	0.35	106	$\varphi(C_2-C_3-C_4)(17) + \varphi(C_4-C_5-C_6)(13) + \varphi(C_5-C_6-N)(12) + \nu(C_3-C_4)(8) + \nu(C_6-N)(7) + \varphi(N-C_1-C_2)(6) + \nu(C_1-C_2)(6)$
57	0.341	0.30	101	$\varphi(C_2-C_3-C_4)(18) + \varphi(C_4-C_5-C_6)(13) + \varphi(C_5-C_6-N)(12) + \nu(C_3-C_4)(8) + \nu(C_6-N)(7) + \varphi(N-C_1-C_2)(7) + \nu(C_1-C_2)(6)$	0.35	103	$\tau(C_6-N)(35) + \tau(C_2-C_3)(29) + \tau(C_1-C_2)(17) + \tau(N-C_1)(14)$
23	0.335	0.30	24	$\tau(C_2-C_3)(26) + \tau(C_6-N)(19) + \tau(C_4-C_5)(16) + \tau(N-C_1)(13) + \tau(C_1-C_2)(10) + \tau(C_3-C_4)(8)$	0.35	23	$\varphi(C_5-C_6-N)(17) + \varphi(C_2-C_3-C_4)(12) + \varphi(C_3-C_4-C_5)(11) + \varphi(C_4-C_5-C_6)(11) + \varphi(C-N-C)(11) + \varphi(C_1-C_2-C_3)(11) + \varphi(N-C_1-C_2)(6)$
0	0.335	0.30	24	$\varphi(C_5-C_6-N)(17) + \varphi(C_2-C_3-C_4)(12) + \varphi(C_3-C_4-C_5)(11) + \varphi(C_4-C_5-C_6)(11) + \varphi(C-N-C)(11) + \varphi(C_1-C_2-C_3)(11) + \varphi(N-C_1-C_2)(6)$	0.035	25	$\tau(C_2-C_3)(26) + \tau(C_6-N)(19) + \tau(C_4-C_5)(16) + \tau(N-C_1)(13) + \tau(C_1-C_2)(11) + \tau(C_3-C_4)(8)$
30	0.176	0.15	38	$\varphi(C_5-C_6-N)(25) + \varphi(C_3-C_4-C_5)(12) + \varphi(C_2-C_3-C_4)(11) + \varphi(N-C_1-C_2)(8) + \varphi(C_1-C_2-C_3)(7) + \varphi(C_4-C_5-C_6)(7) + \varphi(C-N-C)(7)$	0.20	38	$\tau(C_3-C_4)(23) + \tau(N-C_1)(11) + \tau(C_4-C_5)(9) + \tau(C_6-N)(8) + \tau(C_2-C_3)(8) + \tau(C_1-C_2)(8) + \tau(C_5-C_6)(7) + \omega(N-H)(6) + \varphi(H-C-C)(5)$
0	0.176	0.15	35	$\tau(C_3-C_4)(23) + \tau(C_4-C_5)(10) + \tau(N-C_1)(10) + \tau(C_6-N)(9) + \tau(C_2-C_3)(8) + \tau(C_5-C_6)(8) + \tau(C_1-C_2)(7) + \omega(N-H)(6) + \varphi(H-C-C)(6)$	0.20	35	$\varphi(C_5-C_6-N)(25) + \varphi(C_3-C_4-C_5)(12) + \varphi(C_2-C_3-C_4)(11) + \varphi(N-C_1-C_2)(8) + \varphi(C_1-C_2-C_3)(7) + \varphi(C_4-C_5-C_6)(7) + \varphi(C-N-C)(7)$
30	0.113	0.10	33	$\tau(C_3-C_4)(23) + \tau(C_4-C_5)(12) + \tau(C_6-N)(11) + \tau(C_2-C_3)(8) + \tau(C_5-C_6)(8) + \tau(N-C_1)(8) + \varphi(H-C-C)(6) + \omega(N-H)(5)$	0.15	38	$\varphi(C_5-C_6-N)(25) + \varphi(C_3-C_4-C_5)(12) + \varphi(C_2-C_3-C_4)(11) + \varphi(N-C_1-C_2)(8) + \varphi(C_1-C_2-C_3)(7) + \varphi(C_4-C_5-C_6)(7) + \varphi(C-N-C)(7)$
0	0.113	0.10	29	$\varphi(C_5-C_6-N)(18) + \varphi(C_3-C_4-C_5)(11) + \nu(C_3-C_4)(8) + \varphi(C_1-C_2-C_3)(8) + \varphi(C_2-C_3-C_4)(7) + \nu(C_1-C_2)(6) + \nu(C_6-N)(6)$	0.15	35	$\tau(C_3-C_4)(23) + \tau(C_4-C_5)(10) + \tau(N-C_1)(10) + \tau(C_6-N)(9) + \tau(C_2-C_3)(8) + \tau(C_5-C_6)(8) + \tau(C_1-C_2)(7) + \omega(N-H)(6) + \varphi(H-C-C)(6)$
23	0.072	0.05	22	$\tau(N-C_1)(20) + \tau(C_1-C_2)(18) + \tau(C_2-C_3)(16) + \omega(C=O)(10) + \omega(N-H)(9) + \tau(C_6-N)(7)$	0.10	29	$\varphi(C_5-C_6-N)(18) + \varphi(C_3-C_4-C_5)(11) + \nu(C_3-C_4)(8) + \varphi(C_1-C_2-C_3)(8) + \varphi(C_2-C_3-C_4)(7) + \nu(C_1-C_2)(6) + \nu(C_6-N)(6)$
0	0.072	0.05	15	$\varphi(C_5-C_6-N)(15) + \varphi(C_3-C_4-C_5)(10) + \varphi(C_1-C_2-C_3)(9) + \nu(C_3-C_4)(9) + \varphi(C_2-C_3-C_4)(7) + \nu(C_1-C_2)(6) + \nu(C_6-N)(6) + \varphi(C_4-C_5-C_6)(6)$	0.10	21	$\tau(N-C_1)(18) + \tau(C_2-C_3)(17) + \tau(C_1-C_2)(14) + \tau(C_6-N)(9) + \omega(N-H)(9) + \omega(C=O)(8) + \tau(C_3-C_4)(6) + \tau(C_4-C_5)(5)$

Note: 1. ^a marked δ corresponds to crossing point.
2. ^b marked δ corresponds to points before/after crossing.

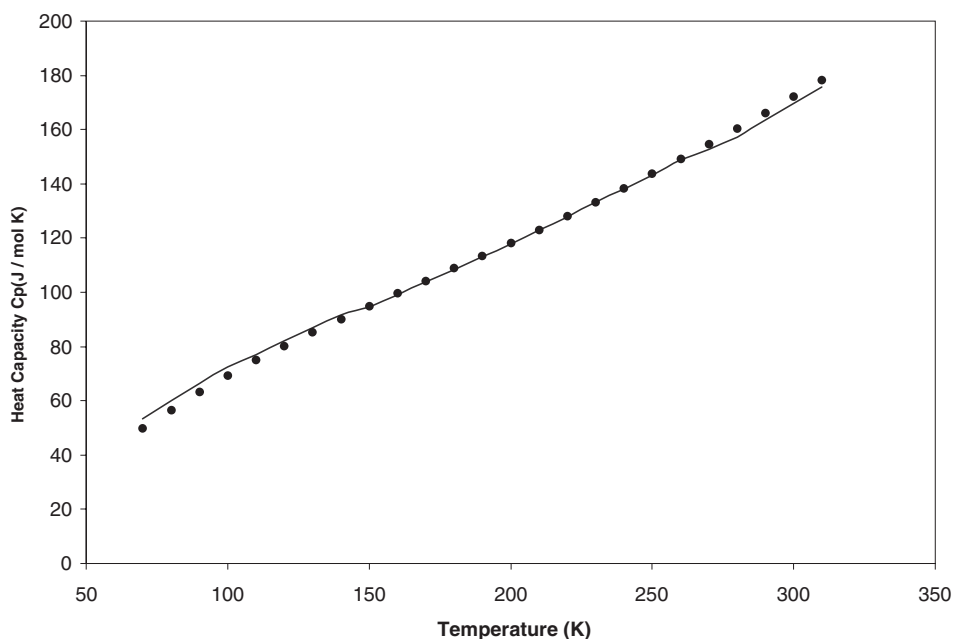


Figure 3. Variation of heat capacity of α NY6 as a function of temperature. [Theoretical values (—) and experimental data (●)]

neighbouring amide groups. This can be treated on the basis of perturbation theory using the ‘intramolecular interactions’²⁸ between the adjacent peptide groups in the same chain and similar interchain peptide interactions in the neighbouring chains. As a consequence of these interactions the separation of $\nu(0, \pi)$ and $\nu(\pi, 0)$ modes is not very large. It is approximately 20–25 wave numbers. These crystal field splittings do not have significant change on dispersion profiles. Intermolecular interactions are important in another way. They give rise to low frequency lattice modes which have to be considered in the evaluation of heat capacity. This would involve calculation of the dispersion curves for a three-dimensional unit cell. The 3D system can be treated in an analogous manner. Even for this the calculation for an isolated chain are very important. Apart from lattice modes, the heat capacity is also very sensitive to skeletal and torsional modes which have been considered in the present work. Consideration of 3D problem would increase the dimensionality of the problem manifold and would also render the visualization of the force field very difficult. In spite of the above unavoidable limitations, the present work using the isolated chain provides a good deal of information on the vibrational dynamics of α NY6. These studies may also prove useful for study of other Nylon derivatives.

CONCLUSION

All the characteristic features of the dispersion curves such as region of high density of states, crossing between the various pairs of modes have been well interpreted from the vibrational dynamics of Nylon-6 (α NY6). In addition the heat capacity as a function of temperature in the region 70 to 310 K is in good agreement with the experimental data.

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