

Vibrational Dynamics of Gamma Form of Nylon 6 (γ NY6)

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ABSTRACT: Normal mode analyses including phonon dispersion have been performed, to understand completely the spectra (Infrared/Raman) of (γ NY6), using Wilson GF matrix method and Urey-Bradley force field. Characteristic features of the dispersion curves such as repulsion and region of high density-of-states have been explained. Heat

capacity measurements have been interpreted and the limitation of this work discussed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3202–3211, 2010

Key words: γ NY6; phonon dispersion; density-of-states; heat capacity

INTRODUCTION

Nylon-6 $[-(\text{CH}_2)_5-\text{NHCO}-]_n$, a real star of the polymer industry has applications ranging from broom-stick and spacecraft to beautiful apparels. Its high specific strength, low density, and stiffness (modulus/density) makes it promising as metal replacement material. One can change properties like melting point, low temperature impact strength, and moduli, etc. by modifying the density of amide linkages. These linkages provide hydrogen bonding between the polymer chains.

Nylon-6 is known to exist in two crystalline forms α and γ . In α form, the plane of amide groups and that of CH_2 groups are parallel and it is thermodynamically most stable form. When α form is treated with a solution of iodine in aqueous potassium iodide, the polymer absorbs iodine and swells. On removing the iodine by treatment with aqueous sodium thiosulphate, the polymer is still found to be oriented, but gives an x-ray diffraction pattern different from that of original α material and thus a new helical shaped γ form of Nylon-6 (γ NY6) comes into existence.^{1–6} The dichroism of the N–H stretching and C=O stretching bands showed that these bands now had a preferred orientation perpendicular to the plane of rolled sheet. The principal structural difference between α and γ form is that the amide-to-methylene dihedrals are near trans (164–168°) in the α and nearly perpendicular to the peptide plane (120°) in γ form. With axial tension the γ form can be

converted into α form.^{7–9} The transformation between α and γ form can't be a direct single step process because it requires breaking a number of H-bonds, making new H-bonds, changing conformation.

Vibrational spectroscopy plays an important role in polypeptide characterization, conformation, intra & inter molecular hydrogen bonding, fold structure of polymers, Composition, and sequence distribution in copolymers. In the past decade a lot of studies have been made on polypeptides and synthetic polymers using infrared (IR) and Raman spectra.^{10–13} In general, the IR absorption, Raman spectra, and inelastic neutron scattering (INS) from polymeric systems are very complex and can not be unraveled without the full knowledge of dispersion curves. Normal mode analysis helps in precise assignment and identification of spectral features. Further the presence of regions of high density-of-states that appears in all these techniques and play an important role in thermodynamical behavior is also dependent on the profile of dispersion curves. The evaluation of the normal modes of a polymeric system is in general an order of magnitude more difficult than molecular system. However, the advent of lasers and fast computers has eased these problems. The lack of this information in many polymeric systems has been responsible for the incomplete understanding of polymeric spectra.

In this article, we present here a complete normal mode analysis of γ NY6 with phonon dispersion in the first Brillouin Zone using Urey-Bradley force field (UBFF).^{14,15} Schmidt et al.¹⁶ reported the IR and Raman spectra of γ NY6 within the range (3298–407 cm^{-1}). The assignments made by them are qualitative in nature. Whereas Jakes and Krimm¹⁷ have used simple valence force field in their normal mode calculations considering methylene group as a point mass. It is a serious approximation because it hides

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all the modes coupled with the dynamics of methylene group and thus their contribution to thermodynamic behavior.

In our calculations, we have used 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 vander Waals force¹⁸ 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 an isolated polymeric chain was carried out using Wilson's GF matrix¹⁹ method as modified by Higgs²⁰ for an infinite polymeric chain. The vibrational secular equation to be solved is:

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

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

$$\lambda_i(\delta) = 4\pi^2 c^2 \nu_i^2(\delta). \quad (2)$$

A plot of $\nu_i(\delta)$ 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.²¹ In this work, we used the UBFF, as it is more comprehensive than the valence force field. In the UBFF (1) relatively fewer parameters are required to express the potential energy, (2) no quadratic terms cross terms are included, the interaction between non-bonded atoms in *gem* and tetra-configuration can be included, and (3) the arbitrariness in choosing the force constant is reduced. Qian et al.¹⁸ have tried to minimize this arbitrariness by using spectroscopically effective molecular mechanics model and intra and inter molecular interactions consisting of charges, atomic dipoles, and Vander Waals interactions. This approach has been used only for small molecules but not for infinite polymers. The UBFF is not limited by these considerations.

Calculation of heat capacity

Dispersion curves can be used to calculate the specific heat of a polymeric system. For a one-dimensional system, the density-of-states function or the frequency distribution function expresses the way energy is distributed among the various branches of normal modes in the crystal and is calculated from the relation:

$$g(\nu) = \sum (\partial \nu_j / \partial \delta)^{-1} \Big|_{\nu_j(\delta) = \nu_j} \quad (3)$$

The sum is over all the dispersion 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 Debey's relation:

$$C_v = \sum g(\nu_j) K N_A (h\nu_j / KT)^2 [\exp(h\nu_j / KT) / \{\exp(h\nu_j / KT) - 1\}^2] \quad (4)$$

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

The constant volume heat capacity C_v , given by equation 4, can be converted into constant-pressure heat capacity C_p using the Nernst-Lindemann approximation.²²

$$C_p - C_v = 3RA_0(C_p^2 T / C_v T_m^0) \quad (5)$$

where A_0 is a constant often of a universal value [3.90×10^{-3} (K mol)/J] and T_m^0 is the estimated equilibrium melting temperature.

RESULT AND DISCUSSION

γ NY6 has 19 atoms per residue unit (Fig. 1), which gives rise to 57 dispersion curves. The geometry of the chain was obtained by molecular modeling techniques and minimization of conformational energy. Just as in case of polyglycine II²³ the γ form of Nylon6 also we have parallel chains connected together by hydrogen bonds and this parallel arrangement of chains forces the isolated chain into a three-fold helix where as in antiparallel chain arrangement, the chains have a planer zig-zag structure both in case of polyglycine I and α form of Nylon6. The dihedral angles for the γ NY6 are χ_1 [(NH)-(CO)-(CH₂)] = 120°, χ_2 [(OC)-(NH)-(CH₂)-(CH₂)] = 120°. ²⁴ These can be approximated to a three-fold helix with a CH₂ planes running at the right angles to the amide plane. The vibrational frequencies have been calculated for the values of δ ranging from 0 to π in steps of 0.05π . The modes corresponding to $\delta = 0$ and $\delta = \varphi$ are both Raman and IR active while the modes corresponding to $\delta = 2\varphi$ are only Raman active. The helix angle φ is the angle of rotation about the helix

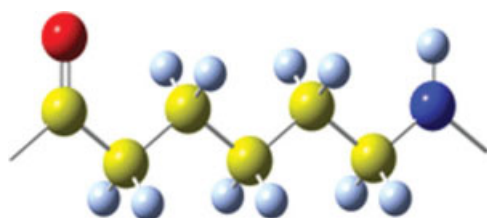


Figure 1 One Chemical repeat unit of γ form of Nylon-6 (γ NY6). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

axis, which separates the adjacent units in the chain. For the helical form of γ Nylon6, helix angle is $2\pi/3$. Initially the force constants are transferred from α NY6²⁵ and calculated frequencies at $\delta = 0$ and $\delta = 2\pi/3$ are compared with the observed ones. The best-fitted force constants are given in Table I.

For the low frequency region we have used INS spectra reported by Papanek et al.²⁶ The modes above 500 cm^{-1} are either nondispersive or show very little dispersion so they are not shown. The dispersion curves below this region are shown in Figure 3(a), and corresponding density-of-states are plotted in Figure 3(b). The dispersion curves shown in Figure 3(a) have four zero frequencies, two at $\delta = 0$, corresponding to translational mode along chain axis and rotational mode about helix axis, the other two degenerate zero modes at $\delta = 0.66\pi$ (helix angle) belong to translations perpendicular to the helix axis. The observed and calculated frequencies along

with potential energy distribution (PED) are shown in Table II at both $\delta = 0$ and $\delta = 0.66\pi$. For sake of discussion modes are separated under amide modes and methylene modes.

Amide modes

The amide groups of polyamides are strongly chromatophoric in I.R. absorption and give rise to strong characteristic bands (amide A, I-VI). The observed and calculated frequencies of amide modes along with the PEDs at the zone center and zone boundary are shown in Table III. A comparison of the amide modes of γ NY6 with α NY6 is given in Table IV.

The amide A band, due to N—H stretching vibration is calculated at 3298 cm^{-1} and assigned to the observed peak¹⁶ at the same value. It is highly sensitive to the strength of N—H...O=C hydrogen bond.

Amide I is usually the strongest band in the spectrum of an amide. It involves the stretching of both C=O and C—N bonds. Here it is calculated at 1644 cm^{-1} matched well with the observed peak at 1644 cm^{-1} in IR, Raman spectra.¹⁶ While in the monoclinic planner α form of nylon6 (α NY6) this band is calculated at 1648 cm^{-1} . The total PED of $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{N})$ for both the forms are same (81%) but their corresponding force constants are changed. In the γ NY6 the separation of $\nu(0,0)$ and $\nu(\pi,0)$ depends upon the separation between neighboring amide groups, which is very small because the interacting

TABLE I
Internal Coordinates and Force Constants for γ NY6 (mydn/Å)

Internal coordinates	Force constants	Internal coordinates	Force constants
$\nu(\text{C}=\text{O})$	7.78	$\varphi(\text{C}_4-\text{C}_5-\text{C}_6)$	0.650 (0.600)
$\nu(\text{C}_1-\text{C}_2)$	2.18	$\varphi(\text{H}-\text{C}_5-\text{C}_6)$	0.440 (0.220)
$\nu(\text{C}_2-\text{H})$	4.18	$\varphi(\text{C}_5-\text{C}_6-\text{N})$	0.180 (0.600)
$\nu(\text{C}_2-\text{C}_3)$	3.35	$\varphi(\text{C}_5-\text{C}_6-\text{H})$	0.390 (0.220)
$\nu(\text{C}-\text{H})$	4.18	$\varphi(\text{H}-\text{C}_6-\text{H})$	0.354 (0.360)
$\nu(\text{C}-\text{C})$	2.87	$\varphi(\text{H}-\text{C}-\text{N})$	0.270 (0.780)
$\nu(\text{C}_5-\text{C}_6)$	3.10	$\varphi(\text{C}_6-\text{N}-\text{H})$	0.285 (0.520)
$\nu(\text{C}_6-\text{H})$	3.91	$\varphi(\text{C}-\text{N}-\text{C})$	0.440 (0.540)
$\nu(\text{C}_6-\text{N})$	2.47	$\varphi(\text{H}-\text{N}-\text{C}_1)$	0.453 (0.520)
$\nu(\text{N}-\text{H})$	5.37	$\varphi(\text{N}-\text{C}=\text{O})$	0.990 (0.900)
$\nu(\text{N}-\text{C}_1)$	5.72	$\varphi(\text{N}-\text{C}_1-\text{C}_2)$	0.480 (0.600)
$\varphi(\text{O}=\text{C}_1-\text{C}_2)$	0.110 (0.900)	$\omega(\text{N}-\text{H})$	0.205
$\varphi(\text{C}_1-\text{C}_2-\text{H})$	0.406 (0.215)	$\omega(\text{C}=\text{O})$	0.510
$\varphi(\text{H}-\text{C}_2-\text{H})$	0.394 (0.340)	$\tau(\text{C}_1-\text{C}_2)$	0.010
$\varphi(\text{H}-\text{C}_2-\text{C}_3)$	0.455 (0.215)	$\tau(\text{C}_2-\text{C}_3)$	0.011
$\varphi(\text{C}_1-\text{C}_2-\text{C}_3)$	0.750 (0.500)	$\tau(\text{C}_3-\text{C}_4)$	0.009
$\varphi(\text{C}_2-\text{C}_3-\text{H})$	0.408 (0.230)	$\tau(\text{C}_4-\text{C}_5)$	0.017
$\varphi(\text{H}-\text{C}-\text{C})$	0.440 (0.230)	$\tau(\text{C}_5-\text{C}_6)$	0.030
$\varphi(\text{C}_2-\text{C}_3-\text{C}_4)$	0.580 (0.500)	$\tau(\text{C}_6-\text{N})$	0.011
$\varphi(\text{H}-\text{C}-\text{H})$	0.382 (0.340)	$\tau(\text{N}-\text{C}_1)$	0.030
$\varphi(\text{C}_3-\text{C}_4-\text{C}_5)$	0.520 (0.600)		

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

TABLE II
Calculated and Observed Modes of γ NY6

Cal. freq	Obs. freq.		Assignment ($\delta = 0$) PED (%)	Cal. freq	Obs. freq.		Assignment ($\delta = 0.66\pi$) PED (%)
	IR	Raman			IR	Raman	
2936	2927	2928	$\nu(\text{C}_6\text{--H})(58)\nu(\text{C--H})(41)$	2936	2927	2928	$\nu(\text{C}_6\text{--H})(58)\nu(\text{C--H})(41)$
2933	2927	2928	$\nu(\text{C--H})(67)\nu(\text{C}_6\text{--H})(26)\nu(\text{C}_2\text{--H})(6)$	2933	2927	2928	$\nu(\text{C--H})(67)\nu(\text{C}_6\text{--H})(26)\nu(\text{C}_2\text{--H})(7)$
2928	2927	2928	$\nu(\text{C--H})(68)\nu(\text{C}_2\text{--H})(21)\nu(\text{C}_6\text{--H})(10)$	2928	2927	2928	$\nu(\text{C--H})(68)\nu(\text{C}_2\text{--H})(21)\nu(\text{C}_6\text{--H})(10)$
2927	2927	2928	$\nu(\text{C--H})(55)\nu(\text{C}_2\text{--H})(40)$	2923	2927	2928	$\nu(\text{C--H})(55)\nu(\text{C}_2\text{--H})(40)$
2922	2927	2928	$\nu(\text{C--H})(67)\nu(\text{C}_2\text{--H})(31)$	2922	2927	2928	$\nu(\text{C--H})(67)\nu(\text{C}_2\text{--H})(31)$
2863	2857	2855	$\nu(\text{C--H})(96)$	2863	2857	2855	$\nu(\text{C--H})(96)$
2860	2857	2855	$\nu(\text{C--H})(83)\nu(\text{C}_2\text{--H})(14)$	2860	2857	2855	$\nu(\text{C--H})(83)\nu(\text{C}_2\text{--H})(14)$
2857	2857	2855	$\nu(\text{C--H})(70)\nu(\text{C}_2\text{--H})(22)\nu(\text{C}_6\text{--H})(8)$	2857	2857	2855	$\nu(\text{C--H})(70)\nu(\text{C}_2\text{--H})(22)\nu(\text{C}_6\text{--H})(7)$
2855	2857	2855	$\nu(\text{C}_2\text{--H})(59)\nu(\text{C--H})(38)$	2855	2857	2855	$\nu(\text{C}_2\text{--H})(59)\nu(\text{C--H})(38)$
2852	2857	2855	$\nu(\text{C}_6\text{--H})(87)\nu(\text{C--H})(12)$	2852	2857	2855	$\nu(\text{C}_6\text{--H})(87)\nu(\text{C--H})(12)$
1470	1462	-	$\phi(\text{H--C}_2\text{--H})(67)\phi(\text{H--C}_2\text{--C}_3)(11)\phi(\text{H--C--H})(10)$	1470	1462	-	$\phi(\text{H--C}_2\text{--H})(67)\phi(\text{H--C}_2\text{--C}_3)(11)\phi(\text{H--C--H})(10)$
1466	1462	-	$\phi(\text{H--C--H})(70)\phi(\text{H--C--C})(9)\phi(\text{C}_2\text{--C}_3\text{--H})(6)\phi(\text{H--C}_2\text{--H})(5)$	1466	1462	-	$\phi(\text{H--C--H})(70)\phi(\text{H--C--C})(9)\phi(\text{C}_2\text{--C}_3\text{--H})(6)\phi(\text{H--C}_2\text{--H})(5)$
1456	1462	-	$\phi(\text{H--C--H})(70)\phi(\text{H--C--C})(9)$	1456	1462	-	$\phi(\text{H--C--H})(69)\phi(\text{H--C--C})(9)$
1449	1462	-	$\phi(\text{H--C--H})(72)\phi(\text{H--C--C})(7)\phi(\text{C}_2\text{--C}_3\text{--H})(6)$	1449	1462	-	$\phi(\text{H--C--H})(73)\phi(\text{H--C--C})(7)\phi(\text{C}_2\text{--C}_3\text{--H})(6)$
1441	1441	1439	$\phi(\text{H--C}_6\text{--H})(62)\phi(\text{H--C--N})(20)\phi(\text{H--C--H})(7)$	1441	1441	1439	$\phi(\text{H--C}_6\text{--H})(62)\phi(\text{H--C--N})(21)\phi(\text{H--C--H})(7)$
1377	1368	1372	$\nu(\text{C}_3\text{--C}_4)(27)\phi(\text{H--C--C})(26)\phi(\text{C}_2\text{--C}_3\text{--H})(20)\nu(\text{C}_2\text{--C}_3)(8)\phi(\text{H--C}_5\text{--C}_6)(6)$	1377	1368	1372	$\nu(\text{C}_3\text{--C}_4)(27)\phi(\text{H--C--C})(26)\phi(\text{C}_2\text{--C}_3\text{--H})(20)\nu(\text{C}_2\text{--C}_3)(8)\phi(\text{H--C}_5\text{--C}_6)(5)$
1354	1368	1372	$\phi(\text{H--C--C})(19)\nu(\text{C}_5\text{--C}_6)(12)\nu(\text{C}_2\text{--C}_3)(12)\phi(\text{H--C}_5\text{--C}_6)(11)\phi(\text{C}_2\text{--C}_3\text{--H})(8)\phi(\text{C}_1\text{--C}_2\text{--H})(7)\nu(\text{C}_3\text{--C}_4)(7)\phi(\text{H--C}_2\text{--C}_3)(6)$	1357	1368	1372	$\phi(\text{H--C--C})(18)\nu(\text{C}_5\text{--C}_6)(12)\nu(\text{C}_2\text{--C}_3)(11)\phi(\text{H--C}_5\text{--C}_6)(10)\phi(\text{C}_1\text{--C}_2\text{--H})(7)\phi(\text{C}_2\text{--C}_3\text{--H})(7)\nu(\text{C}_3\text{--C}_4)(7)\phi(\text{H--C}_2\text{--C}_3)(6)\nu(\text{C}_1\text{--C}_2)(5)$
1315	1304	1297	$\nu(\text{C}_1\text{--C}_2)(16)\phi(\text{H--C--N})(8)\phi(\text{C}_5\text{--C}_6\text{--H})(8)\phi(\text{C}_1\text{--C}_2\text{--H})(7)\phi(\text{H--C--C})(6)\phi(\text{C}_2\text{--C}_3\text{--H})(6)\phi(\text{C}_6\text{--N--H})(6)\phi(\text{H--C}_2\text{--C}_3)(6)\nu(\text{C}_5\text{--C}_6)(6)\nu(\text{C=O})(6)\phi(\text{N--C=O})(5)\nu(\text{N--C}_1)$	1306	1304	1297	$\nu(\text{C}_1\text{--C}_2)(15)\phi(\text{H--C--C})(8)\phi(\text{C}_5\text{--C}_6\text{--H})(8)\phi(\text{H--C--N})(7)\phi(\text{C}_1\text{--C}_2\text{--H})(6)\nu(\text{C=O})(6)\phi(\text{C}_2\text{--C}_3\text{--H})(6)\phi(\text{H--C}_2\text{--C}_3)(6)\nu(\text{C}_5\text{--C}_6)(6)\nu(\text{N--C}_1)(5)$
1258	1268	1266	$\phi(\text{H--C--C})(19)\phi(\text{H--C--N})(18)\phi(\text{C}_5\text{--C}_6\text{--H})(16)\phi(\text{H--C}_5\text{--C}_6)(14)\phi(\text{C}_1\text{--C}_2\text{--H})(9)\phi(\text{H--C}_2\text{--C}_3)(8)\phi(\text{C}_2\text{--C}_3\text{--H})(5)$	1258	1268	1266	$\phi(\text{H--C--N})(24)\phi(\text{H--C--C})(16)\phi(\text{C}_5\text{--C}_6\text{--H})(15)\phi(\text{H--C}_5\text{--C}_6)(11)\phi(\text{C}_1\text{--C}_2\text{--H})(8)\phi(\text{H--C}_2\text{--C}_3)(7)$
1233	1235	1231	$\phi(\text{H--C--N})(56)\phi(\text{C}_5\text{--C}_6\text{--H})(14)\phi(\text{H--C--C})(10)$	1230	1235	1231	$\phi(\text{H--C--N})(52)\phi(\text{C}_5\text{--C}_6\text{--H})(14)\phi(\text{H--C--C})(11)\phi(\text{H--C}_5\text{--C}_6)(5)$
1212	1213	-	$\phi(\text{H--C--C})(32)\phi(\text{C}_2\text{--C}_3\text{--H})(26)\phi(\text{C}_1\text{--C}_2\text{--H})(14)\phi(\text{H--C}_2\text{--C}_3)(11)\phi(\text{H--C}_5\text{--C}_6)(5)$	1213	1213	-	$\phi(\text{H--C--C})(32)\phi(\text{C}_2\text{--C}_3\text{--H})(27)\phi(\text{C}_1\text{--C}_2\text{--H})(14)\phi(\text{H--C}_2\text{--C}_3)(11)\phi(\text{H--C}_5\text{--C}_6)(5)$
1170	1170	1168	$\phi(\text{C}_2\text{--C}_3\text{--H})(34)\phi(\text{H--C--C})(33)\phi(\text{H--C}_5\text{--C}_6)(15)\phi(\text{H--C}_2\text{--C}_3)(7)$	1171	1170	1168	$((\text{H--C--C})(34)/(\text{C}_2\text{--C}_3\text{--H})(31))((\text{H--C}_5\text{--C}_6)(17)/(\text{H--C}_2\text{--C}_3)(7))\phi(\text{H--C--C})(54)\phi(\text{C}_2\text{--C}_3\text{--H})(30)$
1155	-	-	$\phi(\text{H--C--C})(52)\phi(\text{C}_2\text{--C}_3\text{--H})(25)\phi(\text{H--C}_5\text{--C}_6)(8)\phi(\text{H--C--N})(5)$	1155	-	-	
1137	-	-	$\phi(\text{H--C--C})(36)\phi(\text{H--C}_5\text{--C}_6)(17)\phi(\text{C}_1\text{--C}_2\text{--H})(14)\phi(\text{C}_2\text{--C}_3\text{--H})(14)\phi(\text{H--C}_2\text{--C}_3)(12)$	1134	-	-	$\phi(\text{H--C--C})(34)\phi(\text{H--C}_5\text{--C}_6)(19)\phi(\text{C}_1\text{--C}_2\text{--H})(13)\phi(\text{H--C}_2\text{--C}_3)(13)\phi(\text{C}_2\text{--C}_3\text{--H})(11)$
1120	1122	1119	$\phi(\text{H--C}_2\text{--C}_3)(36)\phi(\text{H--C--C})(21)\phi(\text{C}_2\text{--C}_3\text{--H})(19)\phi(\text{C}_1\text{--C}_2\text{--H})(17)$	1122	1122	1119	$\phi(\text{H--C}_2\text{--C}_3)(35)\phi(\text{H--C--C})(21)\phi(\text{C}_2\text{--C}_3\text{--H})(20)\phi(\text{C}_1\text{--C}_2\text{--H})(17)$
1072	1080	1079	$\nu(\text{C}_6\text{--N})(38)\nu(\text{C}_3\text{--C}_4)(13)\nu(\text{C}_2\text{--C}_3)(9)\phi(\text{C}_4\text{--C}_5\text{--C}_6)(7)$	1066	1080	1079	$\nu(\text{C}_6\text{--N})(40)\nu(\text{C}_3\text{--C}_4)(12)\nu(\text{C}_2\text{--C}_3)(7)\phi(\text{C}_4\text{--C}_5\text{--C}_6)(7)$
1034	1030	-	$\nu(\text{C}_6\text{--N})(33)\nu(\text{C}_3\text{--C}_4)(15)\nu(\text{C}_2\text{--C}_3)(13)\nu(\text{C}_5\text{--C}_6)(7)\phi(\text{C}_2\text{--C}_3\text{--C}_4)(6)$	1042	1030	-	$\nu(\text{C}_6\text{--N})(28)\nu(\text{C}_2\text{--C}_3)(16)\nu(\text{C}_3\text{--C}_4)(15)\phi(\text{C}_2\text{--C}_5\text{--C}_4)(6)\nu(\text{C}_3\text{--C}_4\text{--C}_5)(5)$
1000	1000	-	$\nu(\text{C}_3\text{--C}_4)(32)\nu(\text{C}_2\text{--C}_3)(30)\nu(\text{C}_5\text{--C}_6)(10)\phi(\text{C}_4\text{--C}_5\text{--C}_6)(8)$	1000	1000	-	$\nu(\text{C}_3\text{--C}_4)(35)\nu(\text{C}_2\text{--C}_3)(24)\nu(\text{C}_5\text{--C}_6)(12)\phi(\text{C}_4\text{--C}_5\text{--C}_6)(5)$
982	976	-	$\nu(\text{C}_3\text{--C}_4)(15)\phi(\text{C}_5\text{--C}_6\text{--H})(15)\phi(\text{H--C--C})(13)\phi(\text{C}_2\text{--C}_3\text{--H})(12)\nu(\text{C}_5\text{--C}_6)(10)\phi(\text{H--C}_5\text{--C}_6)(8)$	980	976	-	$\nu(\text{C}_5\text{--C}_6)(27)\nu(\text{C}_3\text{--C}_4)(19)\phi(\text{C}_5\text{--C}_6\text{--H})(10)\phi(\text{H--C--C})(10)\phi(\text{C}_2\text{--C}_3\text{--H})(7)\phi(\text{H--C}_5\text{--C}_6)(6)$

TABLE II. Continued

Cal. freq	Obs. freq.		Assignment ($\delta = 0$) PED (%)	Cal. freq	Obs. freq.		Assignment ($\delta = 0.66\pi$) PED (%)
	IR	Raman			IR	Raman	
975	976	-	$\nu(\text{C}_5\text{-C}_6)(25)\nu(\text{C}_3\text{-C}_4)(14)\phi$ (H-C-C)(13) $\phi(\text{C}_2\text{-C}_3\text{-H})(10)$ $\phi(\text{C}_5\text{-C}_6\text{-H})(8)\phi(\text{H-C}_5\text{-C}_6)$ (7)	968	976	-	$\phi(\text{H-C-C})(16)\phi(\text{C}_2\text{-C}_3\text{-H})(15)\phi$ ($\text{C}_5\text{-C}_6\text{-H})(12)\phi(\text{H-C}_5\text{-C}_6)(10)$ $\nu(\text{C}_5\text{-C}_6)(8)$ $\nu(\text{C}_3\text{-C}_4)(8)$ $\nu(\text{C}_6\text{-N})(6)$
952	-	964	$\nu(\text{C}_3\text{-C}_4)(42)\nu(\text{C}_5\text{-C}_6)(19)\phi$ (H-C-C)(12) $\phi(\text{C}_2\text{-C}_3\text{-H})(8)$ $\nu(\text{C}_2\text{-C}_3)(6)\phi(\text{H-C}_5\text{-C}_6)(5)$	952	-	964	$\nu(\text{C}_3\text{-C}_4)(44)\nu(\text{C}_5\text{-C}_6)(18)\phi$ (H-C-C)(13) $\phi(\text{C}_2\text{-C}_3\text{-H})(9)\nu(\text{C}_2\text{-C}_3)(5)$
915	917	921	$\nu(\text{C}_1\text{-C}_2)(25)\phi(\text{H-C-C})(12)\phi$ ($\text{C}_2\text{-C}_3\text{-H}$) (10) $\nu(\text{C}=\text{O})(10)\phi(\text{C}_1\text{-C}_2\text{-H})$ (8) $\phi(\text{N-C}=\text{O})$ (6)	926	917	921	$\phi(\text{H-C-C})(16)\nu(\text{C}_1\text{-C}_2)(14)$ $\phi(\text{C}_2\text{-C}_3\text{-H})$ (12) $\phi(\text{C}_1\text{-C}_2\text{-H})(11)\nu(\text{N-C}_1)(10)$ $\nu(\text{C}=\text{O})$ (5)
872	-	-	$\phi(\text{H-C-C})(26)\phi(\text{C}_1\text{-C}_2\text{-H})(19)\phi(\text{H-C}_2\text{-C}_3)$ (8) $\phi(\text{H-C-N})(8)\phi(\text{C}_5\text{-C}_6\text{-H})$ (8) $\phi(\text{H-C}_5\text{-C}_6)$ (8) $\phi(\text{C}_2\text{-C}_3\text{-H})(8)$	876	-	-	$\phi(\text{H-C-C})(19)\phi(\text{C}_1\text{-C}_2)(17)$ $\phi(\text{C}_1\text{-C}_2\text{-H})$ (17) $\phi(\text{C}_5\text{-C}_6\text{-H})(7)\phi(\text{H-C}_2\text{-C}_3)(7)$ $\phi(\text{H-C-N})$ (6) $\phi(\text{H-C}_5\text{-C}_6)(5)$
816	-	-	$\phi(\text{C}_5\text{-C}_6\text{-H})(26)\phi(\text{C}_2\text{-C}_3\text{-H})(14)\phi$ (H-C-C) (11) $\phi(\text{H-C}_2\text{-C}_3)$ (10) $\phi(\text{C}_1\text{-C}_2\text{-H})$ (9) $\nu(\text{C}_1\text{-C}_2)$ (7) $\phi(\text{H-C-N})(6)\phi(\text{H-C}_5\text{-C}_6)(6)$	808	-	-	$\phi(\text{C}_5\text{-C}_6\text{-H})(27)\phi(\text{C}_2\text{-C}_3\text{-H})(10)\phi$ (H-C-C) (8) $\phi(\text{H-C}_2\text{-C}_3)(8)\phi$ (H-C ₅ -C ₆)(8) $\phi(\text{H-C-N})$ (8) $\phi(\text{C}_1\text{-C}_2\text{-H})(7)$
796	-	-	$\omega(\text{N-H})(38)\omega(\text{C}=\text{O})(12)\phi$ (H-C-C)(8) $\phi(\text{H-C}_5\text{-C}_6)(7)\phi(\text{C}_5\text{-C}_6\text{-H})(6)$	796	-	-	$\omega(\text{N-H})(38)\omega(\text{C}=\text{O})(12)\phi$ (H-C-C)(7) $\phi(\text{H-C}_5\text{-C}_6)(5)$
787	777	-	$\phi(\text{H-C-C})(21)\phi(\text{H-C}_5\text{-C}_6)(13)$ $\omega(\text{N-H})$ (13) $\tau(\text{C}_5\text{-C}_6)(8)\phi$ ($\text{C}_5\text{-C}_6\text{-H}$)(7) $\phi(\text{C}_2\text{-C}_3\text{-H})(6)$	788	777	-	$\phi(\text{H-C-C})(27)\phi(\text{H-C}_5\text{-C}_6)(13)$ $\phi(\text{C}_2\text{-C}_3\text{-H})$ (10) $\omega(\text{N-H})(7)$ $\tau(\text{C}_5\text{-C}_6)(7)\phi(\text{C}_5\text{-C}_6\text{-H})(6)$
730	730	-	$\phi(\text{C}_2\text{-C}_3\text{-H})(38)\phi(\text{H-C-C})$ (30) $\phi(\text{H-C}_2\text{-C}_3)(8)\tau(\text{C}_2\text{-C}_3)$ (8) $\tau(\text{C}_3\text{-C}_4)(5)$	732	730	-	$\phi(\text{C}_2\text{-C}_3\text{-H})(38)\phi(\text{H-C-C})(29)$ $\tau(\text{C}_2\text{-C}_3)$ (7) $\phi(\text{H-C}_2\text{-C}_3)$ (7) $\tau(\text{C}_3\text{-C}_4)(5)$
515	519	-	$\phi(\text{C}_4\text{-C}_5\text{-C}_6)(21)\phi(\text{N-C}_1\text{-C}_2)(17)\phi(-\text{O}=\text{C}_1\text{-C}_2)$ (15) $\phi(\text{C-N-C})(6)\phi(\text{C}_3\text{-C}_4\text{-C}_5)(5)$	516	519	-	$\phi(\text{O}=\text{C}_1\text{-C}_2)(21)\phi(\text{N-C}_1\text{-C}_2)(17)\phi$ ($\text{C}_4\text{-C}_5\text{-C}_6$) (16) $\phi(\text{C}_5\text{-C}_6\text{-N})$ (9) $\phi(\text{C}_2\text{-C}_3\text{-C}_4)(8)$
445	440	-	$\phi(\text{C}_2\text{-C}_3\text{-C}_4)(24)\phi(\text{C}_5\text{-C}_6\text{-N})$ (20) $\phi(\text{C}_3\text{-C}_4\text{-C}_5)(17)$ $\phi(\text{C}_4\text{-C}_5\text{-C}_6)(11)$ $\phi(\text{H-C-C})(5)$	427	440	-	$\phi(\text{C}_3\text{-C}_4\text{-C}_5)(34)\phi(\text{C}_5\text{-C}_6\text{-N})(11)\phi(-\text{C}_4\text{-C}_5\text{-C}_6)$ (10) $\phi(\text{C}_1\text{-C}_2\text{-C}_3)(7)$
405	407	-	$\phi(\text{C}_3\text{-C}_4\text{-C}_5)(14)\phi(\text{C}_5\text{-C}_6\text{-N})$ (12) $\phi(\text{N-C}_1\text{-C}_2)(10)\phi(\text{O}=\text{C}_1\text{-C}_2)$ (9) $\phi(\text{C}_1\text{-C}_2\text{-C}_3)(9)$	361	407	-	$\phi(\text{C}_2\text{-C}_3\text{-C}_4)(16)\phi(\text{C}_5\text{-C}_6\text{-N})(11)\phi(-\text{N-C}_1\text{-C}_2)$ (10) $\phi(\text{C}_4\text{-C}_5\text{-C}_6)(9)\phi(\text{O}=\text{C}_1\text{-C}_2)$ (8) $\nu(\text{C}_6\text{-N})$ (6) $\nu(\text{C}_1\text{-C}_2)(6)$
298	294 ^a	-	$\phi(\text{C-N-C})(29)\phi(\text{N-C}=\text{O})(14)\tau$ ($\text{C}_5\text{-C}_6$) (12) $\phi(\text{C}_1\text{-C}_2\text{-C}_3)(7)$ $\phi(\text{H-N-C}_1)(5)$	288 ^a	294 ^a	-	$\phi(\text{C-N-C})(22)\tau(\text{C}_5\text{-C}_6)(10)\phi(\text{C}_1\text{-C}_2\text{-C}_3)$ (9) $\phi(\text{C}_5\text{-C}_6\text{-N})(8)\phi(\text{N-C}=\text{O})(7)$
215	-	-	$\phi(\text{C}_5\text{-C}_6\text{-N})(19)\tau(\text{C}_5\text{-C}_6)(18)\phi$ ($\text{C}_1\text{-C}_2\text{-C}_3$) (13) $\phi(\text{C}_4\text{-C}_5\text{-C}_6)$ (9) $\omega(\text{C}=\text{O})(5)$	252	-	-	$\phi(\text{C}_5\text{-C}_6\text{-N})(16)\tau(\text{C}_5\text{-C}_6)(13)\phi(\text{C}_1\text{-C}_2\text{-C}_3)$ (8) $\tau(\text{N-C}_1)(7)\phi(\text{C-N-C})(6)\phi(\text{C}_3\text{-C}_4\text{-C}_5)(6)$ $\phi(\text{N-C}_1\text{-C}_2)(5)$
173	177 ^a	-	$\tau(\text{C}_4\text{-C}_5)(34)\tau(\text{C}_6\text{-N})(19)$ $\tau(\text{C}_3\text{-C}_4)(8)\tau(\text{C}_2\text{-C}_3)(6)$ $\phi(\text{C}_3\text{-C}_4\text{-C}_5)(5)$	213	177 ^a	-	$\phi(\text{C}_4\text{-C}_5\text{-C}_6)(15)\phi(\text{C}_1\text{-C}_2\text{-C}_3)$ (13) $\phi(\text{C}_2\text{-C}_3\text{-C}_4)(12)\nu(\text{C}_3\text{-C}_4)$ (10) $\nu(\text{C}_1\text{-C}_2)(6)$
142	145 ^a	-	$\tau(\text{C}_1\text{-C}_2)(21)\tau(\text{C}_3\text{-C}_4)(18)\tau$ (N-C_1)(13) $\phi(\text{C}_3\text{-C}_4\text{-C}_5)$ (10) $\phi(\text{C}_1\text{-C}_2\text{-C}_3)(7)$ $\tau(\text{C}_4\text{-C}_5)(7)$ $\phi(\text{C}_2\text{-C}_3\text{-C}_4)(6)$	170	145 ^a	-	$\tau(\text{C}_4\text{-C}_5)(33)\tau(\text{C}_3\text{-C}_4)(16)$ $\tau(\text{C}_6\text{-N})(12)\tau(\text{C}_1\text{-C}_2)(10)$ $\tau(\text{C}_5\text{-C}_6)(8)\tau(\text{C}_2\text{-C}_3)(7)$
137	-	-	$\tau(\text{C}_5\text{-C}_6)(16)\tau(\text{C}_2\text{-C}_3)$ (14) $\phi(\text{C}_5\text{-C}_6\text{-N})$ (11) $\phi(\text{C}_2\text{-C}_3\text{-C}_4)$ (10) $\nu(\text{C}_3\text{-C}_4)(6)$	156	-	-	$\tau(\text{C}_2\text{-C}_3)(18)\tau(\text{C}_5\text{-C}_6)$ (18) $\tau(\text{C}_4\text{-C}_5)(12)\phi$ (C-N-C)(10) $\tau(\text{C}_3\text{-C}_4)(7)$
124	-	-	$\tau(\text{C}_2\text{-C}_3)(19)$ $\tau(\text{C}_3\text{-C}_4)(14)\phi(\text{C-N-C})$	104	-	-	$\tau(\text{C}_1\text{-C}_2)$ (18) $\tau(\text{C}_3\text{-C}_4)(16)$

TABLE II. Continued

Cal. freq	Obs. freq.		Assignment ($\delta = 0$) PED (%)	Cal. freq	Obs. freq.		Assignment ($\delta = 0.66\pi$) PED (%)
	IR	Raman			IR	Raman	
			(13) $\tau(\text{C}_5\text{--C}_6)$ (12) $\tau(\text{C}_6\text{--N})$ (6) $\tau(\text{C}_4\text{--C}_5)$ (6)				$\tau(\text{N--C}_1)$ (10) $\phi(\text{C}_3\text{--C}_4\text{--C}_5)$ (10) $\phi(\text{C}_2\text{--C}_3\text{--C}_4)$ (7) $\phi(\text{C}_1\text{--C}_2\text{--C}_3)$ (7)
99	-	-	$\tau(\text{C}_1\text{--C}_2)$ (28) $\tau(\text{C}_6\text{--N})$ (19) $\tau(\text{N--C}_1)$ (10) $\tau(\text{C}_3\text{--C}_4)$ (9) $\tau(\text{C}_4\text{--C}_5)$ (8)	88	-	-	$\tau(\text{C}_6\text{--N})$ (22) $\tau(\text{C}_1\text{--C}_2)$ (20) $\tau(\text{C}_2\text{--C}_3)$ (13) $\phi(\text{C}_3\text{--C}_4\text{--C}_5)$ (8)
58	64 ^a	-	$\tau(\text{C}_2\text{--C}_3)$ (19) $\phi(\text{C}_2\text{--C}_3\text{--C}_4)$ (14) τ ($\text{C}_5\text{--C}_6$) (10) $\phi(\text{C}_4\text{--C}_5\text{--C}_6)$ (13)	61	64 ^a	-	$\tau(\text{C}_6\text{--N})$ (23) $\tau(\text{C}_1\text{--C}_2)$ (18) $\tau(\text{N--C}_1)$ (8) $\tau(\text{C}_5\text{--C}_6)$ (6)
27	26 ^a	-	$\tau(\text{C}_3\text{--C}_4)$ (23) $\tau(\text{C}_4\text{--C}_5)$ (20) $\tau(\text{C}_2\text{--C}_3)$ (17) $\tau(\text{C}_6\text{--N})$ (15) $\tau(\text{C}_5\text{--C}_6)$ (10)	37	26 ^a	-	$\tau(\text{C}_3\text{--C}_4)$ (19) $\tau(\text{C}_4\text{--C}_5)$ (13) $\tau(\text{N--C}_1)$ (10) $\tau(\text{C}_6\text{--N})$ (8) $\tau(\text{C}_2\text{--C}_3)$ (5)

All frequencies are in cm^{-1} .

^a INS spectra.²⁵

amide groups are separated by five methylene groups.

In the Amide II mode most of the motion is in plane deformation of N—H bond, but there is also a considerable stretching of C—N bond, this mode is calculated at 1559 cm^{-1} and assigned to the peak appearing at same value of IR.¹⁶ In αNY6 it has been calculated at 1554 cm^{-1} .

Amide III band is a mixture of N—H bending, C—N stretch and C=O stretch. It has been calculated at 1276 cm^{-1} and assigned to the observed IR¹⁶ frequency at 1272 cm^{-1} at $\delta = 0$. The phase relation between N—H bending and C—N stretch are reversed in Amide III as compared with Amide II. It is usually considerably weaker than Amide II.

The Amide V band is due to out-of-plane deformation of the N—H group and it is calculated at 710 cm^{-1} corresponding to the observed band at 711 cm^{-1} in IR¹⁶ at $\delta = 0$. At the helix angle ($\delta = 0.66\pi$) this mode is calculated at 718 cm^{-1} , in αNY6 it was calculated at 698 cm^{-1} . The Amide VI band is believed to be due to out-of-plane bending mode of the C=O group, it is calculated at 622 cm^{-1} and assigned to the same value of IR¹⁶ peak.

Methylene modes

The skeletal structure of γNY6 consists of the five methylene groups, which are flanked by amide group at both the ends. Because of such anchoring, a

TABLE III
Amide Modes of γNY6

Mode	Freq (calc.)	Obs. freq.			Potential energy distribution at $\delta = 0$	Freq (calc.)	Obs. freq.			Potential energy distribution at $\delta = 0.66\pi$
		IR	Raman	INS			IR	Raman	INS	
Amide A	3298	3298	3298	-	$\nu(\text{N--H})$ (99)	3298	3298	3298	-	$\nu(\text{N--H})$ (99)
Amide I	1644	1644	1644	-	$\nu(\text{C=O})$ (55) $\nu(\text{N--C}_1)$ (26)	1648	1646	1635	-	$\nu(\text{C=O})$ (55) $\nu(\text{N--C}_1)$ (26)
Amide II	1559	1559	1559	-	$\phi(\text{H--N--C}_1)$ (37) $\phi(\text{C}_6\text{--N--H})$ (27) $\nu(\text{N--C}_1)$ (18)	1559	1559	1559	-	$\phi(\text{H--N--C}_1)$ (37) $\phi(\text{C}_6\text{--N--H})$ (27) $\nu(\text{N--C}_1)$ (18)
Amide III	1276	1272	1272	-	$\nu(\text{N--C}_1)$ (12) $\phi(\text{C}_5\text{--C}_6\text{--H})$ (11) $\phi(\text{H--C--N})$ (11) $\nu(\text{C=O})$ (10) $\phi(\text{H--C--C})$ (7) $\phi(\text{C}_2\text{--C}_3\text{--H})$ (7) $\phi(\text{N--C=O})$ (6) $\nu(\text{C}_1\text{--C}_2)$ (5) $\phi(\text{C}_6\text{--N--H})$ (5)	1282	1272	1272	-	$\phi(\text{H--C--N})$ (13) $\phi(\text{C}_5\text{--C}_6\text{--H})$ (12) $\nu(\text{N--C}_1)$ (10) $\phi(\text{H--C--C})$ (9) $\phi(\text{C}_2\text{--C}_3\text{--H})$ (8) $\nu(\text{C=O})$ (7) $\phi(\text{N--C=O})$ (6) $\phi(\text{C}_6\text{--N--H})$ (6)
Amide V	710	711	-	725	$\omega(\text{N--H})$ (18) $\phi(\text{N--C=O})$ (12) $\phi(\text{O=C}_1\text{--C}_2)$ (10) $\phi(\text{C}_1\text{--C}_2\text{--C}_3)$ (10) $\nu(\text{C}_1\text{--C}_2)$ (9)	718	711	-	725	$\omega(\text{N--H})$ (17) $\phi(\text{N--C=O})$ (12) $\phi(\text{C}_1\text{--C}_2\text{--C}_3)$ (10) $\nu(\text{C}_1\text{--C}_2)$ (9) $\phi(\text{O=C}_1\text{--C}_2)$ (8)
Amide VI	622	622	-	701	$\omega(\text{C=O})$ (40) $\omega(\text{N--H})$ (12) $\tau(\text{N--C}_1)$ (10) $\tau(\text{C}_1\text{--C}_2)$ (6) $\phi(\text{N--C=O})$ (5)	618	622	-	701	$\omega(\text{C=O})$ (43) $\omega(\text{N--H})$ (11) $\tau(\text{C}_1\text{--C}_2)$ (41) $\tau(\text{N--C}_1)$ (6) $\nu(\text{C}_1\text{--C}_2)$ (6) $\phi(\text{N--C=O})$ (5)

All frequencies are in cm^{-1} .

TABLE IV
Comparison of Amide Modes of γ NY6 with Other α NY6

Modes	γ NY6		α NY6	
	$\delta = 0$	$\delta = 0.66\pi$	$\delta = 0$	$\delta = \pi$
Amide A	3298	3298	3301	3301
Amide I	1644	1644	1648	1648
Amide II	1559	1559	1554	1554
Amide III	1276	1282	1286	1299
Amide IV	–	–	722	729
Amide V	711	718	698	699
Amide VI	622	618	584	584

All frequencies are in cm^{-1}

comparison of the wave numbers obtained from the dispersion curves of PE, corresponding to phase values given by eq. (6) 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 $\phi(\text{C}-\text{C}-\text{C})$ and $\tau(\text{C}-\text{C})$ and are spread over the entire chain.

$$\delta = k\pi/(m + 1) \quad (6)$$

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)²⁷ in this case. The wave numbers thus obtained are given in Table V. The calculated CH_2 group frequencies of γ NY6 are in good agreement with those calculated from the dispersion curves of PE (Fig. 2). Small

TABLE V
Comparison of CH_2 Modes of γ NY6 with α NY6

Modes	Calculated by selection rule from PE dispersion curves.	Frequency of γ NY6 (cm^{-1})		Cal. freq. of α NY6 (cm^{-1})
		Calculated	Observed	
CH_2 asymmetric stretch	2919 ^a	2928	2927	2933
CH_2 symmetric stretch	2848 ^a	2860	2857	2857
CH_2 scissoring	1473	1466	1462	1473
	1440	1456	1441	1464
		1449		1459
		1441		1451
		1390	1377	1368
CH_2 wag	1360	1354	1368	1364
	1310	1315	1315	1346
	1260	1258	1268	1259
	1210	1212	1213	1210
CH_2 twist	1300	1233	1235	1287
	1280	1170	–	1236
	1247	1155	–	1191
	1195	1137	–	1171,1153
	–	1120	1122	1114
CH_2 rock	1005	975	976	987
	935	915	914	897
	835	872	–	837
	770	787	777	806
	740	730	730	749
C–C stretch	1069	1072	1080	1071
	1040	1034	1030	1027
	1040	1000	1000	1002
	1010	982	976	981
	995	952	962	950
C–C–C bend	490	515	519	531
	420	445	440	431
	290	405	407	357
	240	298	294	290
	60	58	64	57
C–C torsion	178	173	177	175
	165	142	145	148
	110	137	–	107
	90	99	–	30
	30	27	26	22

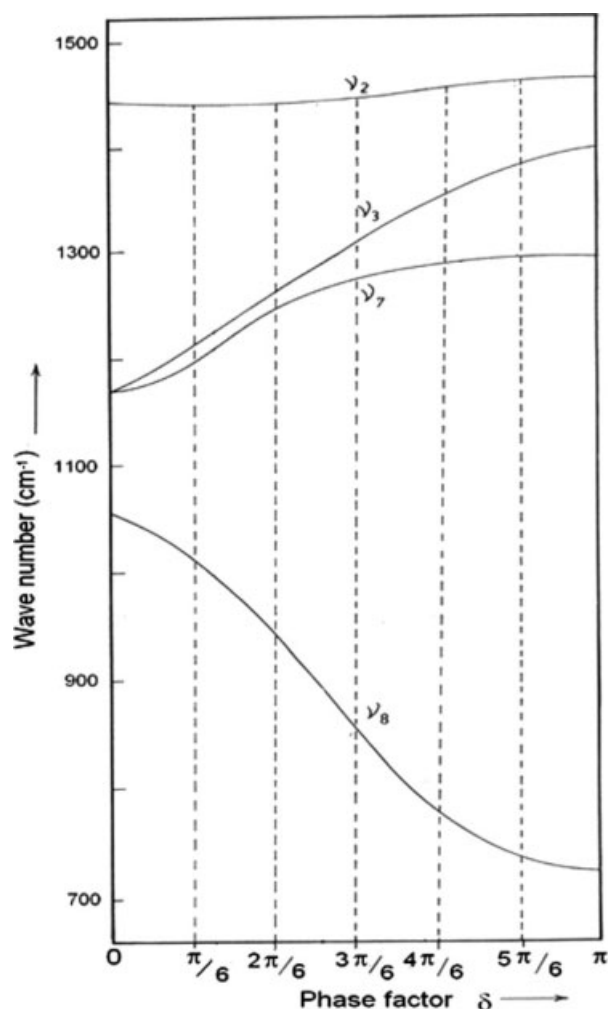


Figure 2 Dispersion curves of the scissoring (ν_2), wagging (ν_3), twisting (ν_7), and rocking (ν_8) modes of polyethylene. - - -, indicates the allowed phase value (δ).

deviations arise because of the intra and inter chain interactions of CH_2 group with the amide group in γNY6 .

In PE, these modes are acoustical in nature whereas in γNY6 , 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 αNY6 . 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). The CH_2 group modes are in order and in agreement with the modes CH_2 groups of αNY6 (Table V). Because of more or less identical situations, the agreement of the CH_2 segmental and others modes with αNY6 is almost total.

Dispersion curves

Dispersion curves of γNY6 are shown in Figure 3(a). Characteristic feature of dispersion curves like repul-

sion and exchange of character between various pairs of modes are observed. Such feature is observed for pair of modes 142 & 137 cm^{-1} at $\delta = 0.117\pi$. Calculations show that these modes approach each other and PEDs of the two modes start mixing. At a particular value of δ they exchange their character and then diverge. Such repulsions occur for modes belonging to same symmetry species. The regions of density-of-states, where $d\omega/dK \rightarrow 0$ are akin to critical points and are known as von Hove type singularities in lattice dynamics. A knowledge of these is more important in obtaining several thermodynamic properties, such as heat capacity, enthalpy changes, etc. They are more conveniently observable in inelastic incoherent neutron scattering.

The mode calculated at 405 cm^{-1} observed in IR¹⁶ at 407 cm^{-1} at $\delta = 0$ disperses by 44 wave numbers and thus it is calculated at 361 cm^{-1} at the helix angle $\delta = 0.66\pi$. This mode has prominent contributions from angle bends [$\varphi(\text{C}_3-\text{C}_4-\text{C}_5)(14)\%$ + $\varphi(\text{C}_5-\text{C}_6-\text{N})(12)\%$ + $\varphi(\text{N}-\text{C}_1-\text{C}_2)(10)\%$ + $\varphi(\text{O}=\text{C}_1-\text{C}_2)(9)\%$ + $\varphi(\text{C}_1-\text{C}_2-\text{C}_3)(9)\%$] but beyond $\delta = 0.65\pi$, the contribution of $\varphi(\text{C}_2-\text{C}_3-\text{C}_4)$ dominates. The mode calculated at 215 cm^{-1} at zone center disperses by 37 wave number at $\delta = 0.66\pi$. This mode involves mainly $(\text{C}_5-\text{C}_6-\text{N})$ bending, $(\text{C}-\text{N}-\text{C})$ bending and $(\text{C}=\text{O})$ in plane bending. As the value of δ increases, the contribution of $(\text{C}=\text{O})$ in plane bending decreases and torsion of $(\text{N}-\text{C}_1)$ increases, at the zone boundary this mode appears at 252 cm^{-1} [$\varphi(\text{C}_5-\text{C}_6-\text{N})(16)\%$ +

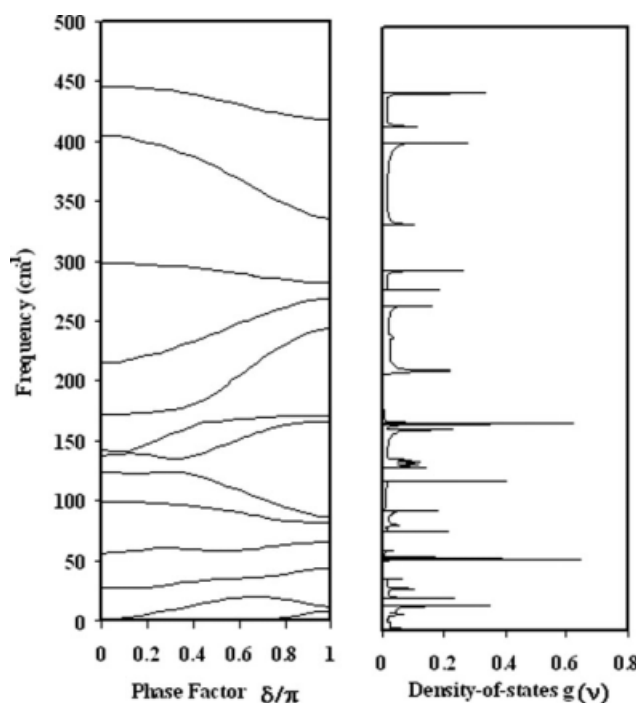


Figure 3 (a) Dispersion curves (below 500 cm^{-1}) (b) Density-of-states (below 500 cm^{-1}).

$\tau(\text{C}_5\text{--C}_6)(13)\% + \varphi(\text{C}_1\text{--C}_2\text{--C}_3)(8)\% + \tau(\text{N--C}_1)(7)\% + \varphi(\text{C--N--C})(6)\% + \varphi(\text{C}_3\text{--C}_4\text{--C}_5)(6)\% + \varphi(\text{N--C}_1\text{--C}_2)(5)$]. The modes calculated at 142 and 137 cm^{-1} are pure torsional mode at $\delta = 0$ these modes disperse by 28 & 19 wave numbers, respectively, at the zone boundary. At $\delta = 0.117\pi$ these modes exchange their PED. This interesting phenomenon of exchange of character may be viewed as the collision of the two phonons approaching each other and exchanging their energy and then moving apart. The vibrational mode calculated at 124 cm^{-1} at $\delta = 0$ is also a torsional mode beyond $\delta = 0.45\pi$ this mode decreases by 20 wave number and at helix angle the PED contains a mixture of torsion and (C–C–C) angle bend.

The pair of modes at 58 and 27 cm^{-1} (at $\delta = 0$) shows parallelism and they disperse by nearly the same amount in same phase. This parallelism indicates that the speed of the two optical phonons is the same.

The lower frequency modes, especially the acoustic modes, are the characteristic of three-fold helical chain symmetry. The two acoustic branches in the dispersion curves are similar in shape to the dispersion curves of these branches in other three-fold helical polymers like polyglycine II. Agreement with the experimental values for frequencies at $\delta = 0$ and $\delta = 0.66\pi$ shows that basically the profile of dispersion curves is correct

Dispersion curves provide knowledge of the degree of coupling and information concerning the dependence of the frequency of a given mode on the sequence length of ordered conformations. In addition, the evaluation of the dispersion curves for a three dimensional systems (3D) is somewhat difficult both in terms of dimensions and large number of interactions involved, it is not easy to solve it with out first solving the problem for a linear isolated chain. This alone can provide the best starting point. It has been generally observed that, the intramolecular interactions (covalent, bonded) are generally stronger than the intermolecular interactions (hydrogen bonding and non-bonded). There are four possible phase relationship between intra and intermolecular interactions as given later.

$$\nu(0, 0) = \text{infrared inactive} \quad (7)$$

$$\nu(0, \pi) = \nu_0 + D_1 - D_1' \quad (8)$$

$$\nu(\pi, 0) = \nu_0 + D_1 + D_1' \quad (9)$$

$$\nu(\pi, \pi) = \nu_0 - D_1 - D_1' \text{ infrared inactive for fully extended chain} \quad (10)$$

Where ν_0 is the unperturbed peptide group frequency, D_1 is the interaction between neighboring peptide groups in the same chain and D_1' is the interaction between peptide groups of neighboring chains. The values of these constants are obtained

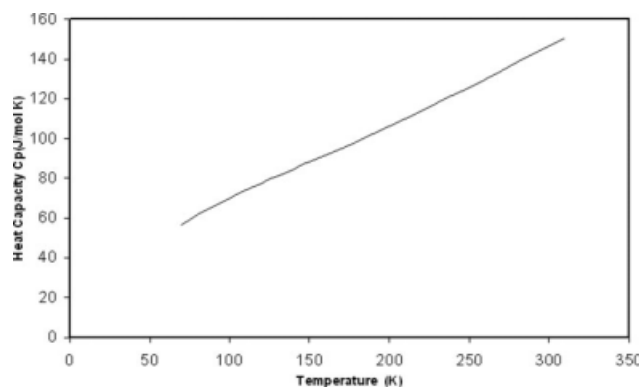


Figure 4 Variation of heat capacity of γ NY6 as function of temperature.

from the homologous series of polyamides having numbers with odd number of CH_2 groups such as Nylon 2, 4, 6 (α and γ), 8, 10. These polymers differ only in length of hydrocarbon chain between the amide groups γ NY6. It is therefore obvious that the interaction constant D_1' will be same for all whereas as D_1 will diminish rapidly with increasing distance between the successive amide groups in one chain. In the γ NY6 the separation of $\nu(0, 0)$ and $\nu(\pi, 0)$ according to equation number 8 & 9 depends upon the separation between neighboring amide groups (D_1), which is very small because the interacting amide groups are separated by five methylene groups therefore Amide I band of γ NY6 appears single in consequence. Therefore, one does not expect large crystal field splitting and the evaluation for an isolated chain provides a good starting point for a three dimensional system.

Frequency distribution function and heat capacity

The state density distribution function, which expresses the way in which energy is distributed among various branches of normal modes, is obtained from the dispersion curves for isolated chain of γ NY6 and is shown in Figure 3(b). The peaks in the frequency distribution curves corresponding to the regions of high density-of-states compare well with the observed frequencies. The frequency distribution function can also be used to calculate the thermodynamical properties, such as heat capacity, enthalpy changes, etc. We have calculated the heat capacity of γ NY6 in the temperature range 70–310 K (Fig. 4). As no experimental data is available at present, only predictive values are shown here. It is expected that this predictive values will stimulate experimental work on heat capacity.

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