

# Phonon Dispersion and Heat Capacity in Poly N-Isopropylacrylamide

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**Abstract**—A study of the normal modes of vibration and their dispersion in Poly N-Isopropylacrylamide (PNIPAm) based on the Urey–Bradley force field is reported. It provides a detailed interpretation of IR and Raman spectra. Characteristic feature of dispersion curves such as regions of high density-of-states, repulsion and character mixing of dispersive modes are discussed. Predictive values of heat capacity as a function of temperature are calculated.

**Keywords**—Dispersion curves, Density-Of-States, Heat Capacity, Normal Modes, Phonon Dispersion, Poly N-Isopropylacrylamide, Vibrational Dynamics.

## 1 INTRODUCTION

Poly N-Isopropylacrylamide is a temperature-sensitive polymer. It exhibits a sharp phase transition close to 32° C. When heated in water above this temperature it undergoes a reversible phase transition from a swollen hydrated, coil conformation to a sunken dehydrated, globule transition [1]. Since PNIPAm expels it's liquid content at a temperature near that of the human body, it has a great potential for application in tissue engineering [2],[3], drug delivery [4],[5],[6], switches [7].

Sami Makharza, et al [8] have reported the FT-IR spectra of PNIPAm in water. A large number of studies like FTIR spectra [9],[10], Raman spectra [11], electronic spectra [12], synthesis [13],[14], have been made. None of the spectroscopic studies contain dispersion curves. In general the IR absorption, Raman spectra & Inelastic Neutron Scattering from polymeric systems are very complex and cannot be unraveled without the full knowledge of dispersion curves. Dispersion curves also give information on the extent of coupling along the chain and dependence of the frequency of a given mode upon the sequence length of ordered conformation. Thus the study of phonon dispersion in polymeric systems constitutes to be of topical importance.

In the present work we report a complete normal mode analysis of PNIPAm (Fig.1a) using Urey-Bradley force field which in addition to valence force field accounts for the intra-unit nonbonded and tension terms. The FT-IR spectra reported by Sami Makharza, et al [8] have been used. The density of states obtained from the dispersion curves is used to calculate the heat capacity of PNIPAm in the temperature range 50-500 K.

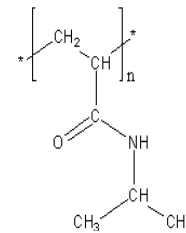


Fig 1a Chemical repeat unit of PNIPAm.

## 2 METHOD

### 2.1 Normal mode calculation

The calculation of normal mode frequencies has been carried out according to well known Wilson's GF matrix [15] method as modified by Higg's [16]. It consists of writing the inverse kinetic energy matrix G and the potential energy matrix F in terms of internal co-ordinates which are infinite in number. However due to screw symmetry of the polymer, a transformation similar to that given by Born and Von Karman can be performed. It reduces the infinite problem to finite dimensions [17]. The vibrational secular equation, which gives normal mode frequencies and their dispersion as a function of phase angle, has the form:

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

The vibrational frequencies  $\nu(\delta)$ (in cm<sup>-1</sup>) are related to the eigen values  $\lambda(\delta)$  by the following relation:

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

A plot of  $\nu_i(\delta)$  verses  $\delta_i$  gives the dispersion curve of  $i^{\text{th}}$  mode. The frequencies obtained from this expression are in wave numbers.

### 2.2 Calculation of Specific heat

Dispersion curves can be used to calculate the specific heat of polymeric system. For a one-dimensional system the density-of-state function or the frequency distribution function expresses the way energy is distributed among the

various branches of normal modes of the crystal and it can be calculated from the relation:

$$g(\nu) = \sum_j \left( \frac{\partial \nu_j}{\partial \delta} \right)^{-1} \quad \left| \quad \nu_j(\delta) = \nu \right. \quad (3)$$

$$\text{With } \int g(\nu) d\nu_j = 1$$

The sum is over all branches  $j$ . Considering a solid as an assembly of harmonic oscillators, the frequency distribution  $g(\nu)$  is equivalent to a partition function. The constant volume heat capacity  $C_v$  can be calculated from the Debye's relation:

$$C_v = \sum_j g(\nu_j) k N_A \left( \frac{h\nu_j}{kT} \right)^2 \frac{\exp(h\nu_j/kT)}{[\exp(h\nu_j/kT) - 1]^2} \quad (4)$$

The constant volume heat capacity  $C_v$ , given by the equation is converted into constant pressure heat capacity  $C_p$  using the Nerst-Lindemann approximation [18],[19].

$$C_p - C_v = 3RA_0 \left( \frac{C_p^2 T}{C_v T_m^0} \right) \quad (5)$$

Where  $A_0$  is a constant often of a universal value [ $3.9 \times 10^{-3}$  (kmol/J)] and  $T_m^0$  is the equilibrium melting temperature.

### 3 RESULT AND DISCUSSION

Molecular modeling technique (CS-Chemdraw) has been used to determine the structure of PNIPAm (Fig. 1b). It calculates the interatomic distances of atoms over all ranges of dihedral angles which are of interest. After this one selects a set of contact distance for the various kinds of atoms which are fully allowed and another which are considered minimal. The fully allowed contact distances result in fully allowed regions of conformational space. In other words, the minimal contact distances result in limiting the region of conformational space. Thus all unfavorable steric overlaps are excluded from consideration.

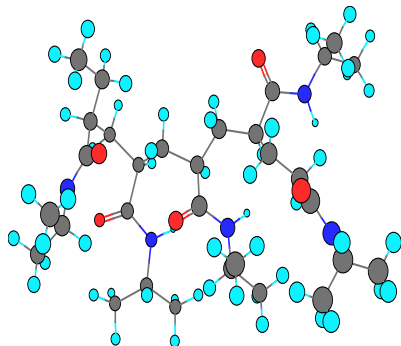


Fig 1b Energy minimized structure of PNIPAm.

#### 3.1 Vibrational modes

A chemical repeat unit of PNIPAm (Fig. 1a), has 19 atoms per residue and hence there would be  $19 \times 3 - 4 = 53$  normal modes of vibrations. The vibrational frequencies have been calculated for the value of  $\delta$  varying from 0 to  $\pi$  in the steps of  $0.05\pi$ . The optically active modes are those for which  $\delta = 0, \pi$ . The four zero frequencies at  $\delta=0$  correspond to acoustic modes, three representing translation along the three axes and the fourth one is rotation around the chain axis.

The assignments have been made on the basis of potential energy distribution, band position, band shape, band intensity. The Urey-Bradley force field, takes into account interactions in both bonded and non-bonded atoms, is used for the calculations of vibrational frequencies. A satisfactory match of the calculated frequencies with the observed peaks in the FTIR spectra [8] has been obtained by varying the force constants. The force constants giving "best fit" at  $\delta=0$  to the experimental data, are given in Table 1. All vibrational modes along with their potential energy distribution are given in Table 2 at  $\delta = 0.0$  and Table 3 at  $\delta = 1.0$  respectively.

The (N-H) stretching vibration has been calculated at  $3295 \text{ cm}^{-1}$  showing good agreement with the observed band also at  $3296 \text{ cm}^{-1}$ . The frequencies calculated at  $1649 \text{ cm}^{-1}$  are mainly due to (C=O) in combination with the contribution from (C-C) stretching and (C-N-H) angle bend. Again these are in agreement with the calculated value at  $1648 \text{ cm}^{-1}$ . The angle bend for (H-C-H) have been calculated at  $1461 \text{ cm}^{-1}$  and the observed value is also  $1461 \text{ cm}^{-1}$ .

TABLE 1  
INTERNAL COORDINATES AND FORCE CONSTANTS

Internal Coordinates- Stretches	Force Constant Values (mdA <sup>-1</sup> )	Internal Coordinates- In Plane Bending	Force Constant Values (mdA <sup>-1</sup> )		Internal Coordinates- Out of Plane Bends	Force Constant Values (mdA <sup>-1</sup> )
			Bonded	Non Bonded		
$\nu(\text{C-H})$	4.435	$\phi(\text{H-C-H})$	0.385	0.25	$\omega(\text{C-H})$	0.10
$\nu(\text{C-C})$	2.7	$\phi(\text{H-C-C})$	0.280	0.22	$\omega(\text{C=O})$	0.56
$\nu(\text{C=O})$	8.8	$\phi(\text{C-C-C})$	0.50	0.18	$\omega(\text{N-H})$	0.11
$\nu(\text{C-N})$	4.1	$\phi(\text{C-C-N})$	0.50	0.50	$\tau(\text{C-C})$	0.005
$\nu(\text{N-H})$	5.725	$\phi(\text{C-C-O})$	0.30	0.60	$\tau(\text{C-N})$	0.01
$\nu(\text{C-N})_1$	4.0	$\phi(\text{O=C-N})$	0.72	0.80		
$\nu(\text{C-H})_M$	4.675	$\phi(\text{C-N-H})$	0.47	0.25		
		$\phi(\text{C-N-C})$	0.60	0.35		
		$\phi(\text{H-C-N})$	0.24	0.80		
		$\phi(\text{H-C-C})_M$	0.455	0.21		

		$\phi(H-C-H)_M$	0.44	0.24	

		$\phi(H-C-C)_1$	0.31	0.20	

TABLE 2  
 VIBRATIONAL MODES OF PNIPAm AT  $\delta = 0.0$

Cal	Obs.	% of Potential Energy Distribution at $\delta = 0.0$	Cal	Obs.	% of Potential Energy Distribution at $\delta = 0.0$
3295	3296	$\nu(N-H)(100)$	891	890	$\phi(H-C-C)(135) + \phi(H-C-C)(16) + \nu(C-N)(11) + \nu(C-C)(7) + \nu(C=O)(5)$
3057	3062	$\nu(C-H)(99)$	819	820	$\phi(H-C-C)(35) + \omega(C=O)(18) + \omega(C-H)(6) + \nu(C-C)(56)$
3056	3062	$\nu(C-H)(99)$	772	782	$\nu(C-C)(69) + \phi(H-C-C)(11)$
3030		$\nu(C-H)(99)$	720	726	$\omega(C=O)(21) + \phi(O=C-N)(14) + \phi(C-C-C)(9) + \phi(C-N-C)(9) + \nu(C-C)(8) + \phi(C-C-N)(6) + \phi(H-C-C)(5) + \phi(H-C-C)(5) + \omega(N-H)(5)$
3028		$\nu(C-H)(99)$	687	695	$\phi(H-C-C)(26) + \nu(C-C)(23) + \omega(C=O)(20) + \omega(N-H)(9) + \omega(C-H)(5)$
3027		$\nu(C-H)(100)$	661	656	$\nu(C-C)(42) + \phi(C-C-C)(24) + \phi(H-C-C)(9) + \omega(C=O)(6) + \omega(N-H)(6)$
3014		$\nu(C-H)(96)$	565	555	$\phi(H-C-C)(36) + \phi(H-C-H)(15) + \phi(C-C-C)(14) + \phi(H-C-C)(114)$
2966	2976	$\nu(C-H)(99)$	509	516	$\omega(N-H)(43) + \omega(C=O)(27) + \phi(C-C-N)(17)$
2950	2968	$\nu(C-H)(99)$	440	445	$\phi(C-C-N)(23) + \phi(C-C-O)(16) + \phi(O=C-N)(15) + \phi(H-C-C)(14) + \nu(C-N)(6) + \phi(C-N-C)(5)$
2892	2875	$\nu(C-H)(99)$	424	414	$\phi(C-C-C)(34) + \phi(C-C-N)(19) + \phi(H-C-C)(11) + \nu(C-C)(7) + \phi(H-C-C)(15)$
1649	1648	$\nu(C-O)(70) + \phi(C-N-H)(8) + \nu(C-C)(5)$	351		$\phi(C-C-N)(66) + \omega(N-H)(28)$
1549	1539	$\phi(C-N-H)(62) + \nu(C-N)(18) + \nu(C-N)(20)$	331		$\phi(C-C-C)(69) + \phi(C-C-N)(14) + \phi(H-C-C)(6)$
1465	1461	$\phi(H-C-H)(93) + \phi(H-C-C)(5)$	247		$\phi(C-C-C)(38) + \phi(C-C-O)(16) + \nu(C-C)(9) + \phi(C-C-N)(8) + \phi(O=C-N)(8) + \phi(H-C-C)(8)$
1463	1461	$\phi(H-C-H)(95)$	202		$\phi(H-C-C)(37) + \phi(C-C-C)(27) + \omega(C-H)(17) + \tau(C-C)(6)$
1461	1461	$\phi(H-C-H)(95)$	141		$\phi(C-C-N)(28) + \phi(C-C-C)(23) + \nu(C-C)(14) + \phi(O=C-N)(9) + \phi(H-C-C)(6)$
1461	1461	$\phi(H-C-H)(95)$	128		$\phi(C-N-C)(34) + \phi(C-C-N)(19) + \phi(C-N-H)(11) + \phi(H-C-C)(11) + \phi(C-C-C)(8) + \nu(C-C)(7)$
1453	1454	$\phi(H-C-H)(62) + \phi(H-C-C)(19) + \phi(H-C-C)(114)$	51		$\tau(C-C)(97)$
1384	1391	$\phi(H-C-C)(47) + \phi(H-C-H)(42) + \nu(C-C)(10)$	50		$\tau(C-C)(99)$
1382	1391	$\phi(H-C-C)(46) + \phi(H-C-H)(42) + \nu(C-C)(11)$	33		$\tau(C-N)(86) + \tau(C-C)(10)$
1305	1305	$\phi(H-C-C)(57) + \nu(C-C)(30)$	22		$\tau(C-C)(45) + \tau(C-N)(31) + \phi(C-C-C)(15)$
1290	1281	$\phi(H-C-N)(32) + \nu(C-N)(130) + \phi(H-C-C)(9) + \phi(H-C-C)(8) + \nu(C-C)(8)$	10		$\tau(C-N)(64) + \tau(C-C)(22) + \phi(C-C-C)(8)$
1235	1242	$\nu(C-C)(37) + \nu(C-N)(12) + \phi(H-C-C)(12) + \phi(H-C-N)(12) + \phi(C-N-H)(11)$	8		$\tau(C-C)(86) + \tau(C-N)(13)$
1206	1219	$\nu(C-C)(30) + \phi(H-C-C)(22) + \nu(C-N)(110) + \phi(H-C-N)(9) + \phi(C-N-H)(6) + \phi(H-C-C)(15)$	1		$\phi(C-C-N)(23) + \phi(C-C-O)(21) + \phi(H-C-C)(17) + \phi(O=C-N)(11) + \omega(C-H)(9) + \phi(H-C-N)(8)$
1168	1172	$\nu(C-C)(36) + \phi(H-C-C)(34) + \phi(H-C-C)(11) + \phi(C-C-N)(7)$	0		$\phi(H-C-H)(51) + \phi(H-C-C)(47)$
1138	1133	$\nu(C-C)(29) + \phi(H-C-C)(25) + \phi(H-C-N)(9) + \nu(C-N)(8) + \nu(C-N)(17) + \phi(H-C-C)(5)$			
1046		$\phi(H-C-C)(34) + \phi(H-C-C)(124) + \nu(C-C)(15) + \phi(H-C-C)(7) + \nu(C-N)(6)$			
1018	1023	$\phi(H-C-C)(72) + \nu(C-C)(8) + \phi(H-C-C)(7)$			
976	969	$\phi(H-C-C)(40) + \phi(H-C-C)(34) + \nu(C-C)(15)$			
960	969	$\phi(H-C-C)(21) + \nu(C-C)(20) + \phi(H-C-C)(119) + \phi(H-C-C)(11) + \nu(C-N)(11)$			
917	929	$\phi(H-C-C)(75) + \phi(H-C-C)(14)$			
911	906	$\phi(H-C-C)(43) + \phi(H-C-C)(118) + \nu(C-N)(115) + \phi(H-C-C)(6) + \nu(C-N)(5)$			
900	906	$\phi(H-C-C)(63) + \nu(C-C)(29)$			

TABLE 3  
 VIBRATIONAL MODES OF PNIPAm AT  $\delta = 1.0$

Cal	Obs.	% of Potential Energy Distribution at $\delta = 1.0$	Cal	Obs.	% of Potential Energy Distribution at $\delta = 1.0$
3295	3296	$\nu(N-H)(100)$	917	906	$\phi(H-C-C)(77) + \phi(H-C-C)(13)$
3057	3062	$\nu(C-H)(99)$	901	906	$\phi(H-C-C)(57) + \nu(C-C)(27) + \phi(H-C-C)(6)$
3056	3062	$\nu(C-H)(99)$	897	882	$\phi(H-C-C)(29) + \phi(H-C-C)(28) + \nu(C-C)(10) + \nu(C-N)(9) + \nu(C-N)(8) + \phi(H-C-C)(6)$
3030		$\nu(C-H)(99)$	824	820	$\phi(H-C-C)(28) + \omega(C-H)(11) + \omega(C=O)(10) + \nu(C-C)(9) + \phi(O=C-N)(8) + \phi(C-N-C)(6) + \phi(H-C-C)(5)$
3028		$\nu(C-H)(99)$	782	782	$\nu(C-C)(29) + \phi(H-C-C)(16) + \phi(O=C-N)(11) + \omega(C=O)(8) + \phi(C-N-C)(7) + \omega(C-H)(5)$
3027		$\nu(C-H)(98)$	768		$\nu(C-C)(68) + \phi(H-C-C)(11) + \nu(C-N)(7) + \phi(H-C-C)(5)$
3027		$\nu(C-H)(100)$	708	711	$\omega(C=O)(44) + \phi(H-C-C)(20) + \omega(N-H)(15) + \nu(C-C)(9)$
3014		$\nu(C-H)(96)$	619	609	$\nu(C-C)(33) + \phi(H-C-C)(18) + \omega(N-H)(8) + \phi(C-C-C)(8) + \phi(C-C-N)(5)$
2957	2968	$\nu(C-H)(99)$	534	531	$\phi(H-C-C)(24) + \nu(C-C)(20) + \phi(C-C-N)(10) + \phi(H-C-H)(78) + \phi(C-C-C)(7) + \omega(N-H)(6) + \phi(C-N-C)(5)$
2951	2968	$\nu(C-H)(99)$	515	516	$\omega(N-H)(26) + \omega(C=O)(15) + \phi(H-C-C)(13) + \phi(C-C-C)(11) + \phi(C-C-N)(11) + \phi(H-C-C)(10)$
2892	2875	$\nu(C-H)(99)$	475	476	$\phi(C-C-C)(34) + \omega(C=O)(13) + \phi(C-C-N)(13) + \omega(N-H)(10) + \phi(C-C-O)(8) + \phi(H-C-C)(7)$
1650	1648	$\nu(C=O)(70) + \phi(C-N-H)(6) + \nu(C-C)(5)$	414	414	$\phi(O=C-N)(23) + \phi(H-C-C)(15) + \phi(C-C-N)(15) + \phi(C-C-O)(9) + \phi(C-C-C)(9)$
1549	1539	$\phi(C-N-H)(62) + \nu(C-N)(18) + \nu(C-N)(10)$	351		$\phi(C-C-N)(65) + \omega(N-H)(28)$
1465	1453	$\phi(H-C-H)(93) + \phi(H-C-C)(5)$	336		$\phi(C-C-C)(62) + \phi(C-C-N)(14) + \phi(H-C-C)(7) + \nu(C-C)(6)$
1463	1453	$\phi(H-C-H)(95)$	310		$\phi(C-C-C)(50) + \phi(H-C-C)(10) + \nu(C-C)(8) + \phi(C-C-O)(7) + \phi(H-C-C)(7) + \phi(H-C-H)(6)$
1461	1453	$\phi(H-C-H)(78) + \phi(H-C-H)(10)$	248		$\phi(C-C-N)(32) + \phi(C-C-C)(24) + \nu(C-C)(15) + \phi(H-C-C)(7) + \phi(C-C-O)(6)$
1461	1453	$\phi(H-C-H)(49) + \phi(H-C-C)(18) + \phi(H-C-H)(16) + \phi(H-C-C)(11)$	164		$\phi(C-N-C)(31) + \phi(C-C-N)(18) + \nu(C-C-C)(15) + \phi(C-N-H)(10) + \phi(H-C-C)(9)$
1461	1453	$\phi(H-C-H)(95)$	54		$\tau(C-C)(32) + \phi(C-C-C)(28) + \phi(H-C-C)(12) + \tau(C-N)(8) + \phi(C-C-N)(8)$
1384	1375	$\phi(H-C-C)(47) + \phi(H-C-H)(42) + \nu(C-C)(10)$	51		$\tau(C-C)(97)$
1382	1375	$\phi(H-C-C)(46) + \phi(H-C-H)(42) + \nu(C-C)(11)$	49		$\tau(C-C)(71) + \phi(C-C-C)(10) + \phi(H-C-C)(5)$
1293	1281	$\phi(H-C-C)(34) + \nu(C-C)(21) + \nu(C-N)(11) + \phi(H-C-N)(11)$	34		$\tau(C-N)(54) + \phi(C-C-C)(20) + \tau(C-C)(7) + \phi(C-C-N)(5)$
1288	1281	$\phi(H-C-C)(26) + \phi(H-C-N)(23) + \nu(C-N)(20) + \nu(C-C)(13) + \phi(H-C-C)(6)$	27		$\tau(C-N)(36) + \phi(C-C-C)(24) + \omega(C-H)(11) + \phi(H-C-C)(10) + \tau(C-C)(9)$
1224		$\phi(H-C-N)(22) + \phi(C-N-H)(19) + \nu(C-N)(17) + \phi(H-C-C)(12) + \nu(C-N)(11) + \nu(C-C)(8)$	10		$\tau(C-N)(82) + \tau(C-C)(5)$
1168	1172	$\nu(C-C)(37) + \phi(H-C-C)(33) + \phi(H-C-C)(11) + \phi(C-C-N)(7)$	8		$\tau(C-C)(86) + \tau(C-N)(13)$
1138	1133	$\nu(C-C)(34) + \phi(H-C-C)(19) + \phi(H-C-N)(9) + \nu(C-N)(8) + \nu(C-N)(8) + \phi(H-C-C)(6)$	0.8		$\phi(C-C-N)(23) + \phi(C-C-O)(21) + \phi(H-C-C)(16) + \phi(O=C-N)(12) + \omega(C-H)(10) + \phi(H-C-N)(8)$
1118	1117	$\nu(C-C)(48) + \phi(H-C-C)(20) + \phi(H-C-C)(17) + \phi(C-C-C)(9)$			
1097		$\phi(H-C-C)(37) + \nu(C-C)(26) + \phi(H-C-C)(15) + \phi(H-C-H)(8) + \phi(C-C-C)(5)$			
1018	1023	$\phi(H-C-C)(75) + \nu(C-C)(7) + \phi(H-C-C)(6)$			
988		$\phi(H-C-C)(25) + \nu(C-N)(18) + \phi(H-C-C)(15) + \nu(C-C)(13) + \phi(C-C-C)(9)$			
976	969	$\phi(H-C-C)(39) + \phi(H-C-C)(35) + \nu(C-C)(15)$			
924	929	$\phi(H-C-C)(34) + \phi(H-C-C)(31) + \nu(C-N)(11) + \phi(H-C-C)(9)$			

### 3.2 Dispersion Curves

Dispersion curves provide information on the extent and degree of coupling. They also help in the understanding of both symmetry-dependent and symmetry independent features. In general the IR absorption spectra and Raman scattering from polymeric systems are complex

and cannot be unraveled without the full knowledge of the dispersion curves. The regions of high density of state, which are observable in the IR and Raman spectra under suitable conditions, depend on the profile of the dispersion curves which play an important role in thermodynamical behavior of the system.

The dispersion curves below 1600 cm<sup>-1</sup> are shown in Fig. 2(a) and 3(a). The modes above 1600 cm<sup>-1</sup> are either non dispersive or their dispersion is less than 5 cm<sup>-1</sup>. A very interesting feature of the dispersion curve is convergence of various modes, i.e, the modes that are separated by a large wave number at the zone center come very close at the zone boundary. This convergence arises mainly because of the close sharing of potential energy in different measures by the various modes. For example, the two zone center wave modes calculated at 772 and 720 cm<sup>-1</sup> are separated by 52 wave numbers at zone center, but at the zone boundary they are separated by only 14 wave numbers. Different PED'S of both modes at different  $\delta$  values are shown in Table 4. Similar features are observed in pairs of modes, which appear at zone center at 1138 and 1046 cm<sup>-1</sup>. These are separated by 92 wave numbers at zone center but are separated by 21 wave numbers at the zone boundary. Similar is the case for zone center modes at 1305 and 1289 cm<sup>-1</sup>.

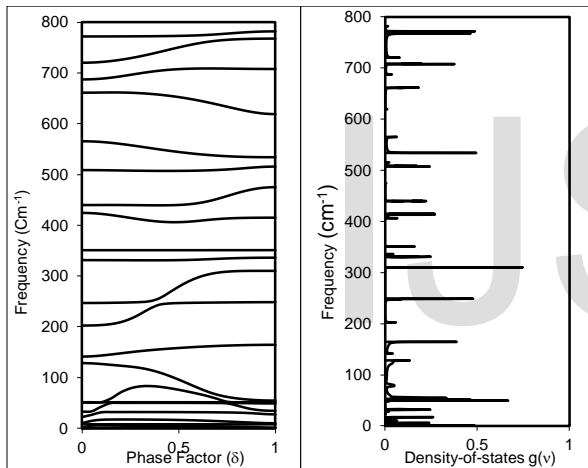


Fig 2a Dispersion curves of PNIPAm (0 – 800 cm<sup>-1</sup>) and (b) density-of-states of PNIPAm (0 – 800 cm<sup>-1</sup>).

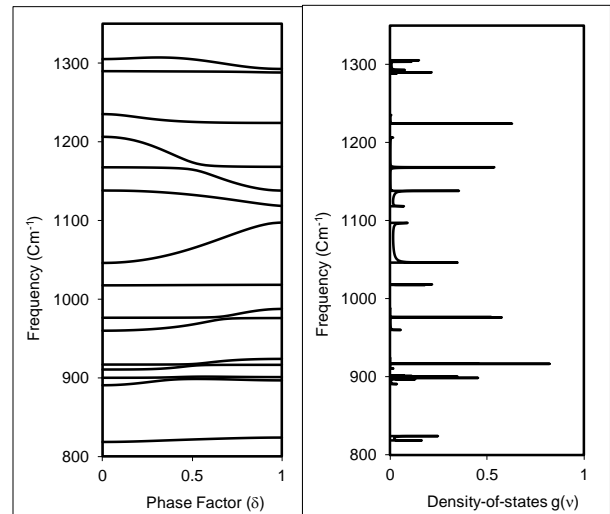


Fig 2b Dispersion curves of PNIPAm ( 800-1600 cm<sup>-1</sup>) and (b) density-of-states of PNIPAm (800-1600 cm<sup>-1</sup>).

TABLE 4  
 PAIR OF MODES SHOWING FEATURES OF DISPERSION CURVES

Before Exchange						After Exchange								
$\delta/\pi$	Freq	PED	$\delta/\pi$	Freq	PED	$\delta/\pi$	Freq	PED	$\delta/\pi$	Freq	PED			
0.0	1206	v(C-C)(30)+ $\phi$ (H-C-C)(21)+ v(C-N)1(10)	0.25	1197	v(C-C)(39)+ $\phi$ (H-C-C)(25)	0.5	1174	v(C-C)(41)+ $\phi$ (H-C-C)(29)	0.75	1168	v(C-C)(36)+ $\phi$ (H-C-C)(32)+ $\phi$ (H-C-C)M(11)	1.0	1168	v(C-C)(37)+ $\phi$ (H-C-C)(33)+ $\phi$ (H-C-C)M(11)
0.0	1168	v(C-C)(36)+ $\phi$ (H-C-C)(34)+ $\phi$ (H-C-C)M(11)	0.25	1167	v(C-C)(36)+ $\phi$ (H-C-C)(34)+ $\phi$ (H-C-C)M(10)	0.5	1165	v(C-C)(38)+ $\phi$ (H-C-C)(33)	0.75	1147	v(C-C)(37)+ $\phi$ (H-C-C)(26)	1.0	1138	v(C-C)(34)+ $\phi$ (H-C-C)(19)
0.0	976	$\phi$ (H-C-C)M(40)+ $\phi$ (H-C-C)(34)+ v(C-C)(15)	0.25	976	$\phi$ (H-C-C)M(40)+ $\phi$ (H-C-C)(34)+ v(C-C)(15)	0.5	976	$\phi$ (H-C-C)M(40)+ $\phi$ (H-C-C)(33)+ v(C-C)(15)	0.75	981	$\phi$ (H-C-C)M(19)+ $\phi$ (H-C-C)(22)+ v(C-C)(15)+ v(C-N)(16)	1.0	987	$\phi$ (H-C-C)M(14)+ $\phi$ (H-C-C)(24)+ v(C-C)(12)+ v(C-N)(18)
0.0	960	$\phi$ (H-C-C)M(21)+ $\phi$ (H-C-C)1(19)+ $\phi$ (H-C-C)(11)+ v(C-C)(20)+ v(C-N)(11)	0.25	961	$\phi$ (H-C-C)M(22)+ $\phi$ (H-C-C)1(15)+ $\phi$ (H-C-C)(12)+ v(C-C)(20)+ v(C-N)(12)	0.5	967	$\phi$ (H-C-C)M(21)+ $\phi$ (H-C-C)(16)+ v(C-C)(19)+ v(C-N)(14)	0.75	975	$\phi$ (H-C-C)M(36)+ $\phi$ (H-C-C)(34)+ v(C-C)(16)	1.0	976	$\phi$ (H-C-C)M(39)+ $\phi$ (H-C-C)(35)+ v(C-C)(14)

0.0	917	$\phi(\text{H-C-C})\text{M}(74)+$ $\phi(\text{H-C-C})(13)$	0.25	917	$\phi(\text{H-C-C})\text{M}(74)+$ $\phi(\text{H-C-C})(13)$	0.5	922	$\phi(\text{H-C-C})\text{M}(56)+$ $\phi(\text{H-C-C})(14)+$ $\phi(\text{H-C-C})1(10)$	0.75	922	$\phi(\text{H-C-C})\text{M}(30)+$ $\phi(\text{H-C-C})(11)+$ $\phi(\text{H-C-C})1(32)$	1.0	924	$\phi(\text{H-C-C})\text{M}(33)+$ $\phi(\text{H-C-C})1(30)+$ $v(\text{C-N})1(10)$
0.0	911	$\phi(\text{H-C-C})\text{M}(43)+$ $\phi(\text{H-C-C})1(18)+$ $v(\text{C-N})1(15)$	0.25	911	$\phi(\text{H-C-C})\text{M}(40)+$ $\phi(\text{H-C-C})1(20)+$ $\phi(\text{C-N})1(13)$	0.5	915	$\phi(\text{H-C-C})\text{M}(45)$ $\phi(\text{H-C-C})1(22)+$ $\phi(\text{H-C-C})(12)$	0.75	916	$\phi(\text{H-C-C})\text{M}(75)+$ $\phi(\text{H-C-C})(12)$	1.0	916	$\phi(\text{H-C-C})\text{M}(76)+$ $\phi(\text{H-C-C})(12)$
0.0	900	$\phi(\text{H-C-C})\text{M}(63)+$ $v(\text{C-C})(29)$	0.25	900	$\phi(\text{H-C-C})(62)+$ $v(\text{C-C})(29)$	0.5	901	$\phi(\text{H-C-C})\text{M}(45)+$ $v(\text{C-C})(20)+$ $\phi(\text{H-C-C})1(15)$	0.75	901	$\phi(\text{H-C-C})\text{M}(52)+$ $v(\text{C-C})(23)$	1.0	901	$\phi(\text{H-C-C})\text{M}(57)+$ $v(\text{C-C})(26)$
0.0	891	$\phi(\text{H-C-C})1(35)+$ $\phi(\text{H-C-C})(16)+$ $v(\text{C-N})(11)$	0.25	894	$\phi(\text{H-C-C})1(34)+$ $\phi(\text{H-C-C})(15)+$ $v(\text{C-N})(10)$	0.5	898	$\phi(\text{H-C-C})\text{M}(39)+$ $\phi(\text{H-C-C})1(17)+$ $v(\text{C-C})(15)$	0.75	897	$\phi(\text{H-C-C})\text{M}(34)+$ $\phi(\text{H-C-C})1(23)+$ $v(\text{C-C})(12)$	1.0	896	$\phi(\text{H-C-C})\text{M}(28)+$ $\phi(\text{H-C-C})1(29)$
0.0	772	$v(\text{C-C})(69)+$ $\phi(\text{H-C-C})\text{M}(10)$	0.25	772	$v(\text{C-C})(68)+$ $\phi(\text{H-C-C})\text{M}(10)$	0.5	772	$v(\text{C-C})(62)$	0.75	777	$v(\text{C-C})(38)+$ $\phi(\text{H-C-C})(11)$	1.0	781	$v(\text{C-C})(29)+$ $\phi(\text{H-C-C})(16)+$ $\phi(\text{O=C-N})(11)$
0.0	720	$\omega(\text{C=O})(21)+$ $\phi(\text{O=C-N})(14)$	0.25	729	$\omega(\text{C=O})(18)+$ $\phi(\text{O=C-N})(12)+$ $v(\text{C-C})(14)$	0.5	750	$\omega(\text{C=O})(10)+$ $\phi(\text{H-C-C})(12)+$ $v(\text{C-C})(30)$	0.75	765	$v(\text{C-C})(58)$	1.0	767	$v(\text{C-C})(68)+$ $\phi(\text{H-C-C})\text{M}(11)$
0.0	247	$\phi(\text{C-C-C})(37)+$ $\phi(\text{C-C-O})(16)$	0.25	247	$\phi(\text{C-C-C})(35)+$ $\phi(\text{C-C-O})(14)+$ $\phi(\text{C-C-N})(11)$	0.5	278	$\phi(\text{C-C-C})(60)+$ $\phi(\text{H-C-C})(15)$	0.75	308	$\phi(\text{C-C-C})(54)+$ $\phi(\text{H-C-C})(10)$	1.0	310	$\phi(\text{C-C-C})(49)+$ $\phi(\text{H-C-C})(10)$
0.0	202	$\phi(\text{C-C-C})(27)+$ $\phi(\text{H-C-C})(36)+$ $\omega(\text{C-H})(17)$	0.25	215	$\phi(\text{C-C-C})(35)+$ $\phi(\text{H-C-C})(26)+$ $\phi(\text{C-C-N})(18)$	0.5	246	$\phi(\text{C-C-C})(29)+$ $\phi(\text{C-C-O})(10)+$ $v(\text{C-C})(14)$	0.75	247	$\phi(\text{C-C-C})(25)+$ $\phi(\text{C-C-N})(28)+$ $v(\text{C-C})(14)$	1.0	248	$\phi(\text{C-C-C})(23)+$ $\phi(\text{C-C-ON})(32)+$ $v(\text{C-C})(14)$

Another specific feature of the dispersion curves is the repulsion and mixing of the character of various pairs of modes. Greater dispersion implies that the mode is strongly coupled to others as given in Table 4. The modes calculated at 247 and 202  $\text{cm}^{-1}$  at  $\delta = 0.4$ . These two modes are separated by 45 wave number at  $\delta = 0.0$ , but at  $\delta = 0.4$  they are separated by 12 wave numbers. After this they repel each other and exchange potential energy at the zone boundary where they are separated by 62 wave numbers. Similar behavior is observed by the modes 900 and 890  $\text{cm}^{-1}$  at zone boundary. At zone center they are separated by 10 wave numbers, whereas at  $\delta = 0.4$  they are separated by 3 wave numbers only, again at zone boundary they are separated by 4 wave numbers only. Similar features are observed in the modes 917 and 911  $\text{cm}^{-1}$ , 1206 and 1168  $\text{cm}^{-1}$ .

### 3.3 Heat Capacity

As explained in theory, the inverse of the slope of the dispersion curves leads to density-of-states which indicate how the energy is partitioned in various normal modes. These are shown in Fig. 2(b) and 3(b) respectively. The peaks in the frequency distribution curves 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. It has been used to obtain the heat capacity as a function of temperature. The predictive values of heat capacity have been calculated and plotted within temperature range 50-500 K (Fig. 4)

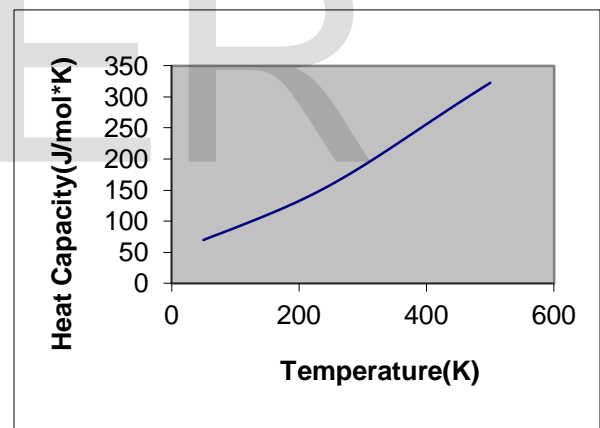


Fig. 4 Variation of heat Capacity with temperature of PNIPAm.

It may be added here that the contribution from the lattice models is bound to make a difference to the heat capacity because of its sensitivity to low frequency modes. However we have solved the problem only for an isolated chain. The calculation of dispersion curves for a three dimensional system is extremely difficult. Inter-chain modes involving hindered translator and rotatory motion will appear and the total number of modes will depend on the contents of the unit cell. It would not only make the dimensionality of the problem prohibitive but also bring in an enormous number of interactions which are difficult to visualize and quantify. Thus it makes the problem somewhat intractable. The inter-chain interactions will contribute to lower

frequencies. They are generally of the same order and magnitude as in the weak inter-chain interactions. Their introduction would, at best bring about crystal field splitting at the zone center and zone boundary depending on the symmetry dependent selection rules. However, the inter-chain assignments will remain by and large undisturbed. Thus in spite of several limitations involved in the calculation of specific heat, the present work does provide a good starting point for further basic studies on the dynamic and thermodynamic behavior of conducting polymers which go into well defined conformations. The present work goes beyond it and calculates the dispersion curves within the entire zone.

#### 4 CONCLUSION

The vibrational dynamics of PNIPAm can be satisfactorily interpreted from the dispersion curve and dispersion profile of the normal modes of PNIPAm as obtained by Higg's method for infinite system. Some of the internal symmetry dependent features such as attraction and exchange of character are also well understood.

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