

Vibrational Dynamics and Heat Capacity of Poly (ethylene glycol)

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Abstract-Using the Urey-Bradley force field and Wilson's GF matrix method as modified by Higgs, normal modes of vibration and their dispersions in poly (ethylene glycol) have been obtained. It provides a detailed interpretation of I.R. and Raman spectra. Characteristic features of the dispersion curves, such as regions of high density-of-states, repulsion and character mixing of dispersive modes are discussed. Predictive values of the heat capacity as a function of temperature have been calculated.

Keywords-Poly (ethylene glycol); Infrared; Raman spectroscopy; Phonon dispersion; Density-of-states; Heat capacity

1. INTRODUCTION

Poly (ethylene glycol) (PEG)/Poly (ethylene oxide) (PEO) is a crystalline, non-ionic homopolymer of ethylene oxide. PEG has varied uses in the medical field, including drug delivery (e.g.; treatment of hepatitis C), cell immobilization, (as adhesion promoters), biosensor materials, and encapsulation of islets of langerhans for treatment of diabetes. It is also used as carrier material for encapsulated cells for tissue engineering purposes. Thus PEG, with its biocompatibility, flexibility and stealth properties is an ideal material for use in pharmaceutical applications [1-5].

The conductivity values for PEO complexes increased continuously and reached a maximum of 10^{-3} S cm^{-1} when doped with carbon nano tubes [6]. The PEO chains adopt a helical conformation with four monomers per turn, which is very similar to the 7_2 helix of the pure polymer [7, 8]. Vibrational spectroscopy plays a very important role in elucidating polymer structure and normal mode analysis. It provides a better identification of various vibrational modes and interpretation of IR and Raman spectra. Several authors have reported the infrared and Raman spectra of PEO [8-11].

Infrared absorption, Raman spectra, and inelastic neutron scattering from polymeric systems are very complex and cannot be unraveled without the full knowledge of their dispersion curves. Dispersion curves and dispersion profiles also provide information about the extent of coupling along the polymeric chain or between the chains. These curves also facilitate correlation of the microscopic behavior of a crystal with its macroscopic properties such as specific heat, enthalpy and free energy. The frequency of a given mode depends upon the sequence length of ordered conformation. Thus, the study of phonon dispersion in polymeric systems continues to be of topical importance. In the present work, we report a complete normal mode

analysis of PEO using the Urey-Bradley force field, including calculation of the phonon dispersion and heat capacity obtained via the density-of-states derived from the dispersion curves. The experimental data of IR and Raman spectroscopic studies reported by previous authors [8-11] have been used for comparison.

2. THEORITICAL APPROACH

2.1 Normal Mode Calculation:

The calculation of normal mode frequencies was carried out according to the well-known Wilson's GF matrix method [12], as modified by Higgs [13]. The method consists of writing the inverse kinetic energy matrix G, and the potential energy matrix F, in terms of internal coordinates. In the case of an infinite isolated helical polymer, there are an infinite number of internal coordinates that lead to G and F matrices of infinite order. The presence of screw symmetry in the polymer enables that a transformation similar to that given by Born and Von Karman can be performed that reduces the infinite problem to finite dimensions [14]. The vibrational secular equation gives normal mode frequencies and their dispersion as a function of phase angle and has the form:

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

The vibrational frequencies $\nu(\delta)$ (in cm^{-1}) are related to the eigen values $\lambda(\delta)$ by the following relation:

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

2.2 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, $g(\nu)$, or the frequency distribution function, expresses the way the energy is distributed among various branches of normal modes in the crystal. It can be calculated from the relation:

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

$$\text{with} \quad \int g(\nu_j) \delta \nu_j = 1$$

The sum is over all branches j, where j is the index for dispersion curves. 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 using Debye's relation.

$$C_v = \sum_j g(v_j) kN_A (h v_j / kT)^2 \frac{\exp(h v_j / kT)}{[\exp(h v_j / kT) - 1]^2} \dots\dots\dots (4)$$

The constant volume heat capacity, C_v , given by the above equation is converted into constant pressure heat capacity, C_p , using the Nernst-Lindemann approximation [15, 16].

$$C_p - C_v = 3R A_o (C_p^2 T / C_v T_m^0) \dots\dots\dots (5)$$

Where A_o is a constant, often of a universal value [3.9×10^{-9} (Kmol/J)], and T_m^0 is the equilibrium melting temperature.

3. RESULTS AND DISCUSSION

Using molecular modeling technique, the minimum energy structure as a function of dihedral angles of PEO was determined by us as helical structure. It also agrees with the helical structure reported by others [7, 8]. The number of atoms per residue in PEO is nine and, hence, there would be $(9 \times 3) - 4 = 23$ normal modes of vibration. The vibrational frequencies have been calculated for each of the values of δ varying from 0 to π in steps of 0.05π . The optically active modes are those for which $\delta = 0, \phi$ and 2ϕ . The four zone center zero-frequencies correspond to acoustic modes; three representing translations along the three axes and one rotation around the chain axis. The assignments have been made on the basis of potential energy distribution (PED), band intensity, band profile and absorption/scattering in similar molecules having groups placed in similar environments. The Urey-Bradley force constants have been initially transferred from the earlier work on molecules having similar groups and have been further refined by using the least-square deviation method [17]. All vibrational modes along with their potential energy distribution are given in Table 1 at $\delta = 0.0$.

3.1. Dispersion Curves:

The dispersion curves below 1400 cm^{-1} are shown in Fig. 1(a). The modes above 1400 cm^{-1} have been either non-dispersive or their dispersion was less than 5 cm^{-1} . A very interesting feature of the dispersion curves is the convergence of various modes. The modes that are separated by a large wave number at the zone center ($\delta = 0.0$) come very close at the zone boundary ($\delta = 1.0$). This convergence arises mainly because of phonon-phonon coupling and consequent sharing of potential energy in different measures by the coupled modes. The extent of sharing depends on the strength of coupling. For example, the two zone center modes calculated at 1162 and 1055 cm^{-1} are separated by 107 wave numbers but at the zone boundary they are separated by only 5 wave numbers. Similar features have been observed in the pair of modes, which appear at the zone center at 873 and 834 cm^{-1} , and 583 and 545 cm^{-1} etc..

Another specific feature of some of the dispersion curves was the exchange of character that occurs at repulsion points. For instance, the modes calculated at 545 and 343

cm^{-1} at the zone center showed repulsion at $\delta = 0.60$. These two modes have been separated by 202 wave numbers at $\delta = 0.0$, but at $\delta = 0.60$, they come close to each other, separated by only 9 wave numbers but again they repel to each other and separated by 178 wave numbers at $\delta = 1.0$.

3.2. Heat Capacity:

The dispersion curves obtained for PEO have been used to calculate the density-of-states and heat capacity as a function of temperature. The density-of-states are shown in Fig. 1(b). Heat capacity of PEO has been calculated in the temperature range 0–300 K, as shown in Fig. 2.

4. CONCLUSION

The vibrational dynamics of PEO have been satisfactorily interpreted from the dispersion curves and dispersion profiles of the normal modes of PEO as obtained by Higg's method for infinite systems. Some of the internal symmetry-dependent features, such as attraction and exchange of characters, have been predicted. Heat capacity behavior of PEO with temperature was nearly linear in nature. REFERENCES

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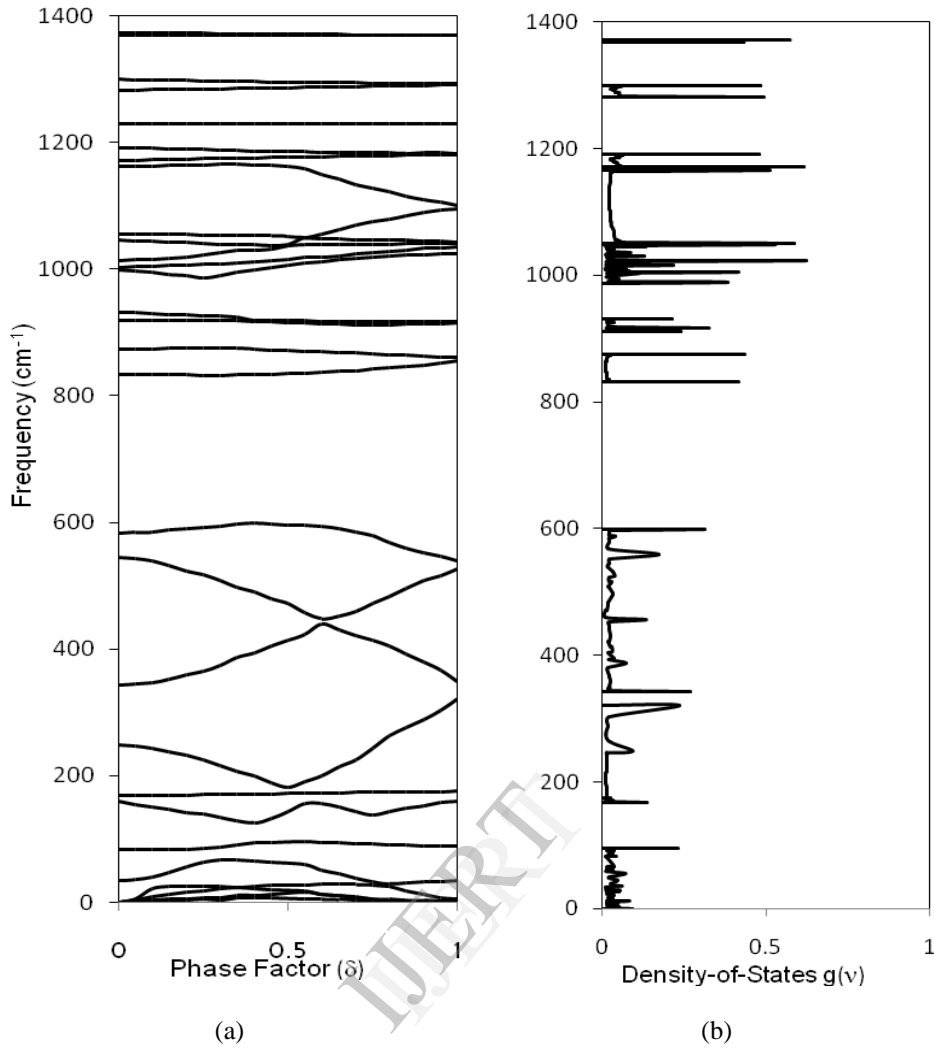


Figure 1(a): Dispersion curves of PEO (0-1400 cm^{-1}) (b) Density-of-states of PEO (0-1400 cm^{-1})

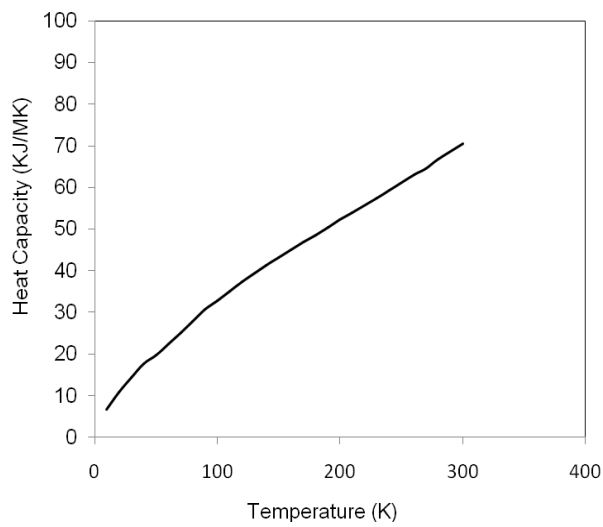


Figure 2: Variation of heat capacity with temperature of PEO

Table 1: Vibrational modes at $\delta = 0.0$

Calculated	Observed		% Potential Energy Distribution
	IR	Raman	
2890	2879		$\nu(\text{C-H})(100)$
2890	2879		$\nu(\text{C-H})(100)$
2883	2879		$\nu(\text{C-H})(99)$
2882	2879		$\nu(\text{C-H})(99)$
2811	2808		$\nu(\text{C-H})(100)$
2811	2808		$\nu(\text{C-H})(100)$
2809	2808		$\nu(\text{C-H})(99)$
2808	2808		$\nu(\text{C-H})(99)$
1477	1470	1487	$\phi(\text{H-C-H})(72)+\phi(\text{H-C-C})(24)$
1474	1470	1471	$\phi(\text{H-C-H})(67)+\phi(\text{H-C-C})(22)$
1458	1464	1445	$\phi(\text{H-C-H})(67)+\phi(\text{H-C-C})(13)$
1452	1451	1445	$\phi(\text{H-C-H})(69)+\phi(\text{H-C-C})(13)$
1372	1362	1397	$\phi(\text{H-C-C})(39)+\phi(\text{O-C-H})(30)+\nu(\text{C-O})(22)$
1368	1362	1363	$\phi(\text{H-C-C})(41)+\phi(\text{O-C-H})(29)+\nu(\text{C-O})(18)$
1300	1306		$\phi(\text{O-C-H})(43)+\phi(\text{H-C-C})(30)+\nu(\text{C-O})(23)$
1282	1279	1283	$\phi(\text{O-C-H})(55)+\phi(\text{H-C-C})(35)$
1229	1231	1234	$\phi(\text{H-C-C})(82)+\nu(\text{C-C})(15)$
1228	1231	1234	$\phi(\text{H-C-C})(85)+\phi(\text{O-C-H})(11)$
1191	1183		$\phi(\text{O-C-H})(53)+\phi(\text{H-C-C})(47)$
1171	1171		$\phi(\text{H-C-C})(54)+\phi(\text{O-C-H})(46)$
1162	1171	1143	$\phi(\text{O-C-C})(32)+\nu(\text{C-O})(29)+\phi(\text{O-C-H})(17)$
1055	1062	1065	$\nu(\text{C-O})(81)+\phi(\text{O-C-H})(18)$
1045	1033	1065	$\phi(\text{O-C-H})(78)+\omega(\text{C-H})(16)$
1012	1010		$\nu(\text{C-O})(70)+\phi(\text{O-C-H})(24)$
1002	1010		$\phi(\text{O-C-H})(81)+\omega(\text{C-H})(15)$
998	1010		$\nu(\text{C-O})(84)+\phi(\text{O-C-H})(12)$
931	932	936	$\nu(\text{C-C})(62)+\phi(\text{O-C-C})(28)$
919	917		$\nu(\text{C-C})(67)+\nu(\text{C-O})(19)$
873	884	862	$\phi(\text{H-C-C})(44)+\phi(\text{O-C-H})(35)+\omega(\text{C-H})(23)$
834	843	844	$\phi(\text{O-C-H})(43)+\phi(\text{H-C-C})(37)+\omega(\text{C-H})(19)$
583			$\phi(\text{O-C-C})(56)+\nu(\text{C-C})(30)$
545			$\phi(\text{C-O-C})(46)+\tau(\text{O-C})(39)$

343	$\phi(\text{O-C-C})(87)+\tau(\text{C-C})(15)$
248	$\phi(\text{C-O-C})(64) + \phi(\text{O-C-C})(25)$
168	$\tau(\text{C-C})(29)+\tau(\text{C-C})(26)+\tau(\text{C-O})(21)+\tau(\text{C-O})(18)$
159	$\tau(\text{O-C})(54)+ \omega(\text{C-H})(31)+\tau(\text{C-O})(14)$
82	$\tau(\text{C-O})(63)+ \omega(\text{C-H})(19)+\tau(\text{O-C})(15)$
34	$\tau(\text{C-C})(52)+ \omega(\text{C-H})(28)+\tau(\text{C-O})(22)$
2	$\tau(\text{C-C})(36)+\tau(\text{C-O})(21)+\omega(\text{C-H})(17)$
1	$\tau(\text{C-O})(32)+\tau(\text{O-C})(28)+\omega(\text{C-H})(22)$

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

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