Normal Modes, Their Dispersions and Heat Capacity of Isotactic Poly(Vinyl Alcohol)

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Abstract

The normal modes of vibration and their dispersion in isotactic poly(vinyl alcohol) based on the Urey-Bradley force field is reported. It provides a detailed interpretation of infrared and Raman spectra. Characteristic features 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.

1. Introduction

Poly(vinyl alcohol) (PVA) is a synthetic water-soluble hydrophilic polymer. The basic properties of PVA are dependent on the degree of polymerization or on the degree of hydrolysis [1]. It has been widely used in adhesives, emulsificants, in the textile and paper industry application and in the attainment of amphiphilic membranes for enzyme immobilization [2]. Most recently, PVA has been used in pharmaceutical and biomedical applications for controlled drug release tests due to its degradable and non-toxic properties [3]. Chemical cosslinking is highly versatile method to create and modify polymers, where properties can be improved, such as mechanical, thermal and chemical stability [2, 4].

Due to large number of hydroxyl groups in PVA, hydrogen bonding has a pronounced effect on the bulk properties of PVA materials. Because of the presence of hydrogen bonding, PVA has a high melting temperature [5]. The X – ray diffraction data [6, 7] suggest that all the –OH groups which are located in the same side of the plane i.e. isotactic PVA shows the planar zigzag configuration. Murahashi et al. showed that isotactic PVA has a planar zigzag configuration [8]. In the gel form, isotactic PVA is much softer as compared with atatic and syndiotactic PVA due to intermolecular hydrogen bond [9]. In earlier works [10, 11], several authors have reported IR and Raman spectra of isotactic PVA. Wunderlich et al. reviewed experimental measurements of heat capacity of PVA [12].

In general, IR absorption, Raman spectra, and inelastic neutron scattering from polymeric systems are very complex and cannot be unraveled without the full knowledge of dispersion curves. Without this, one cannot appreciate the origin of both symmetry dependent and symmetry independent features. Further, the presences of regions of high density-of-states, which appear in all these techniques and play an important role in the thermodynamical behavior, are also dependent on the profile of dispersion curves. Dispersion curve also provide information on the extent of coupling along the chain together with an under standing of the dependence of the frequency of a given mode upon the sequence length of ordered conformation. Thus, the study of phonon dispersion in polymeric system continues to be of topical importance.

A study of normal modes and their dispersion in polymeric system is essential to understand the dynamical and thermodynamical behavior of polymers. In the present work, we have reported a complete normal mode analysis included non-bonded interactions using Urey-Bradley force field, phonon dispersion and heat capacity via density-of-states derived from dispersion curves for isotactic PVA.

2. Theoretical Approach

2.1 Normal Mode Calculation

The calculation of normal mode frequencies has been carried out according to the well-known Wilson's

GF [13] matrix method as modified by Higgs [14]. It 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 coordinate that lead to G and F matrices of infinite order. Due to the screw symmetry of the polymer, a transformation similar to that given by Born and Von Karman can be performed that reduces the infinite problem to finite dimensions [15]. The vibrational secular equation, which gives normal mode frequencies and their dispersion as a function of phase angle, has the form:

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

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

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

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 or the frequency distribution function expresses the way energy is distributed among various branches of normal modes in the crystal, is calculated from the relation:

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

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

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

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

The constant volume heat capacity C_v, given by equation is converted into constant pressure heat capacity C_p using the Nernst-Lindemann approximation [16, 17].

$$C_p - C_v = 3RA_o (C_p^2 T / C_v T_m^o) \quad ....(5)$$

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

3. Result and Discussion

The structure of the isotactic poly(vinyl alcohol) has been determined by using the molecular modeling technique. Software used for this purpose is CS-Chemdraw. The planar zigzag conformation for isotactic poly(vinyl alcohol) has been reported by Shunsuke Murahashi et al. [8]. On the basis of this study and molecular modeling we have taken a planar zigzag geometry.

3.1 Vibrational Modes

The number of atoms per residue in isotactic PVA is seven and hence there would be (7x3)-4 = 17 normal modes of vibration. The vibrational frequencies have been calculated for values of delta δ varying from 0 to π in steps of 0.05π. The optically active modes are those for which $\delta = 0$, π, 2π. The four zero frequencies correspond to the acoustic modes three representing translations along three axes and the fourth one is rotation around the chain axis. $\delta = 0$ refers to the zone centre where $\delta = \pi$ is the zone boundary. The assignments were made on the basis of potential energy distribution, band position band shape, band intensity and absorption/scattering from molecules having similar group placed in similar environment the Urey-Bradley force constants were initially transferred from the earlier work on molecule having similar groups and were further refined by using the least square method as described earlier [18]. The final set of force constants for isotactic PVA is given in table 1. Except for a couple of frequencies, most of them are fitted with in better than 1%. As we mentioned earlier the modes correspond to the $\delta = 0.0$ are both Raman and IR active. Therefore, the calculated frequencies are first fitted to observed frequencies for this phase value. All vibrational modes along with their potential energy distribution (PED) are given in table 2 at δ = 0.0. ….............. (5)

Int.coord. Stretches	Force constant value	Int.coord. in-plane bending	Force constant value		Int.coord. out-of-plane bend	Force constant value
			Bonded	Nonbonded		
ν(C-C)	2.45	ϕ(H-C-C)	0.360	0.245	ω(CH)$_2$	0.15
ν(C-H)$_2$	4.32	ϕ(C-C-C)	0.150	0.239	ω(HC)	0.18
ν(C-H)	4.05	ϕ(H-C-H)	0.425	0.231	τ(-C-C-)	0.06
ν(C-O)	3.15	ϕ(C-N-H)	0.400	0.255	τ(-C-O-)	0.05
ν(O-H)	6.10	ϕ(C-C-O)	0.500	0.252	τ(-C-N-)	0.023
		ϕ(H-C-O)	0.300	0.248		
		ϕ(C-O-H)	0.135	0.223		

Note: ν, ϕ, ω and τ represent stretches, angle bends, wags and torsions respectively.

Table 1. Internal coordinates and Force constants (mdA^{-1})

Cal.	Obs.	% of PED at δ=0.0
3343	3340[+]	ν (O-H)(100)
2939	2942[+]	ν (C-H)$_2$(100)
2910	2910[+]	ν (C-H)$_2$(100)
2839	2840[+]	ν (C-H)(100)
1448	1450[+]	ϕ (H-C-H)(75)+ ϕ(H-C-C)(31)+w(HC)(5)
1321	1326[+]	ϕ (H-C-O)(42)+ ϕ (H-C-C)(25)+ ν(C-O)(10)+w(CH)(8)+ν(C-C)(7)
1260	1250[*]	ϕ (H-C-C)(52)+)+ ν (C-C)(37)
1131	1125[+]	ϕ (H-C-C)(93)
1083	1083[*]	ϕ (H-C-C)(98)
1033	1040[+]	ν (C-O)(36)+ ϕ (H-C-C)(22)+ϕ(H-C-O)(15)+ϕ(C-O-H)(9)+ϕ(C-C-O)(6))
979	980[*]	ϕ (C-O-H)(37)+ ν (C-C)(27)+ ϕ (H-C-C)(24)
933	922[*]	ν (C-C)(51)+ ϕ (H-C-C)(21)+ ϕ (C-O-H)(9)+ ϕ(C-C-C)(7)+ ν (C-O)(5)
880	890[*]	ϕ (C-O-H)(38)+ ϕ (H-C-C)(19)+ ν (C-C)(17)+ ν(C-O)(8)+w (HC)(8)
713		ν (C-O)(35)+ ν (C-C)(26)+ ϕ (H-C-C)(16)+ ϕ (C-C-C)(12)+w (HC)(6)
369	375[*]	ϕ (C-C-O)(48)+ ϕ (H-C-C)(25)+ ϕ (H-C-O)(11)+w (HC)(7)
283		ϕ (C-C-O)(88)+t (C-O)(8)
209	200[*]	t (C-O)(8)+ ϕ (C-C-O)(7)
12		ϕ (C-C-C)(51)+ν (C-C)(29)+ ϕ (H-C-C)(13)
2		t (C-C)(99)
0.044		ϕ (C-C-C)(30)+w (HC)(22) + ϕ (H-C-C)(20) +w (HC)(12)+ ϕ (H-C-H)(5)
0.000		ϕ (H-C-C)(48)+ ϕ (C-C-C)(37)+ ϕ (H-C-H)(8)

Note: *All frequencies are in cm^{-1}.*
Frequencies marked by '' are taken from Raman spectra.*
Frequencies marked by '+' are taken from Infrared spectra.

Table 2. Vibrational modes of isotactic poly(vinyl alcohol)

3.2 Dispersion Curve

The dispersion curves below 1400 cm^{-1} are shown in figure 1(a). The modes above 1400 cm^{-1} are either non dispersive or their dispersion is less than 5 cm^{-1}. A very interesting feature of the dispersion curve is the convergence of various modes, i.e. they are far separated at the zone centre but move closer at the zone boundary. For example, the two modes calculated at the 1260 cm^{-1} and 1130 cm^{-1} are separated by 130 wave numbers at the zone centre, but at the zone boundary, they are separated by 83 wave numbers only. The convergence arises mainly because of the close sharing of the potential energy. Similar features are observed in the pair of modes 880 and 713 cm^{-1} in which they are separated by 167 wave number at the zone centre but at the zone boundary they are separated by only 7 wave numbers.

Another specific feature of the dispersion curve is repulsion and mixing of character of various pairs of modes. The modes calculated at 1033 and 979 cm^{-1} show the repulsion and exchange of character at δ = 0.40, these two modes are separated by 54 wave numbers at δ = 00 but at δ = 0.40, they are separated by 22 wave numbers. Beyond this they repel each other and at the zone boundary they are again separated by 32 wave numbers. Similar feature is shown by the modes calculated at the zone boundary at 369 and 283 cm^{-1}. Detailed PED of these modes at different δ values are shown in the table 3.

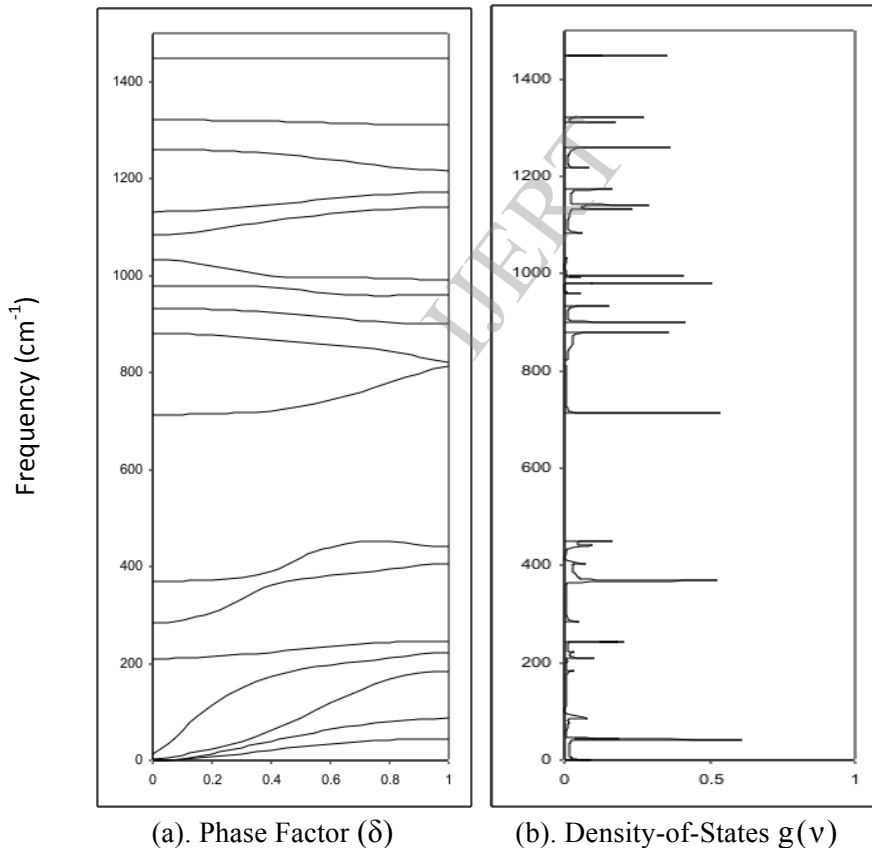(a). Phase Factor (δ)   (b). Density-of-States g(ν)

Figure 1. (a) Dispersion curves of isotactic poly(vinyl alcohol) (0 - 1400 cm^{-1}).

(b) Density-of-states of isotactic poly(vinyl alcohol) (0 - 1400 cm^{-1}).

BEFORE EXCHANGE							AFTER EXCHANGE			
Freq. $\delta=0.00$	δ/π	Freq	PED	δ/π	Freq	PED	δ/π	Freq	PED	
1033	0.35	1003	$\phi(H\text{-}C\text{-}C)_{31}+$ $\nu(C\text{-}O)_{29}$	0.55	966	$\phi(H\text{-}C\text{-}C)_{28}+$ $\nu(C\text{-}C)_{26}$	1	991	$\nu(C\text{-}C)_{40}+$ $\phi(C\text{-}O\text{-}H)_{39}$	
979		978	$\varphi(C\text{-}O\text{-}H)_{36}+$ $\nu(C\text{-}C)_{23}+$ $\varphi(H\text{-}C\text{-}C)_{23}$		970	$\varphi(C\text{-}O\text{-}H)_{33}+$ $\nu(C\text{-}O)_{25}$		961	$\nu(C\text{-}C)_{36}+$ $\nu(C\text{-}O)_{34}$	
369	0.30	377	$\varphi(C\text{-}C\text{-}O)_{55}$	0.4	390	$\varphi(C\text{-}C\text{-}O)_{63}$	1	441	$\varphi(C\text{-}C\text{-}O)_{53}+$ $\varphi(C\text{-}C\text{-}C)_{26}$	
283		333	$\varphi(C\text{-}C\text{-}O)_{56}$		361	$\varphi(C\text{-}C\text{-}O)_{35}+$ $\varphi(H\text{-}C\text{-}C)_{25}$		405	$\varphi(H\text{-}C\text{-}C)_{31}+$ $\varphi(C\text{-}C\text{-}O)_{20}$	

Table 3. Pair of modes showing specific features of dispersion curves

3.3 Heat Capacity

The dispersion curves obtained for isotactic PVA have been used to calculate the density-of-states and heat capacity as a function of temperature. The density-of-states are shown in the figure 1(b). The predicted variation of heat capacity as a function of temperature is shown in figure 2.
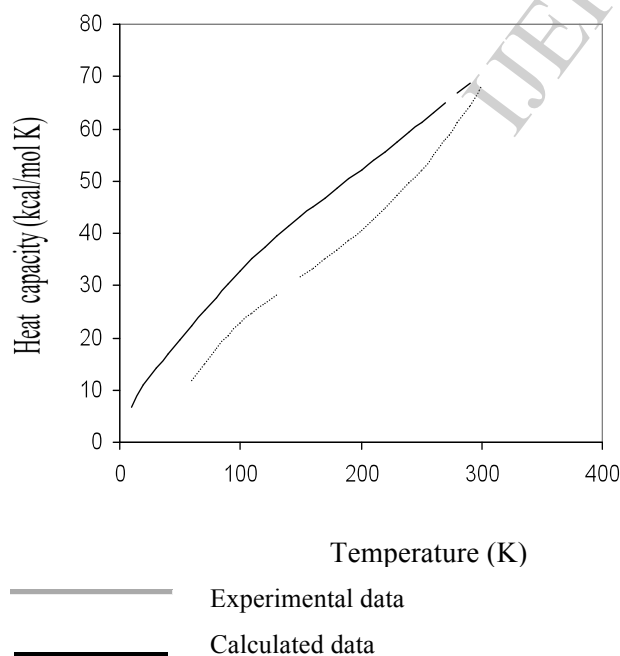

Figure 2. Variation of heat capacity with temperature of isotactic poly(vinyl alcohol)

4. Conclusion

Dispersion curves obtained for isotactic PVA using Urey-Bradley force field provide a good interpretation of the infrared and Raman spectra. Some of the symmetry dependent features such as regions of high density-of-states, repulsion and exchange of characters and intersection of dispersion curves are also explained.

5. References

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