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RESEARCH ARTICLE

Poly (chlorotrifluoroethylene): Normal Modes, Phonon Dispersion and Heat Capacity

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Abstract

Normal modes of vibration and their dispersions in poly(chlorotrifluoroethylene) (PCTFE) have been obtained by using Urey-Bradley force field and Wilson's GF matrix method as modified by Higgs. 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 dispersion modes are discussed. Predictive values of heat capacity as a function of temperature between 50-400 K have been evaluated.

Introduction

Poly(chlorotrifluoroethylene) (PCTFE) is a thermoplastic chlorofluoro polymer with molecular formula $(CF2CClF)_n$. In 1953, PCTFE was commercialized by M.W. Kellog Company under the trade mark Kel-F. It is prepared by the free radical polymerization of chlorotrifluoroethylene (CTFE) and can be carried out by solution, bulk, suspension and emulsion polymerization [1]. PCTFE is a crystalline polymer with melting point 218^0C and density of 2.13 g/cm^3. At room temperature, the polymer is inert to most reactive chemicals. PCTFE has wide applications in fittings, flexible tubings, membranes, printed networks, insulating foils, pharmaceutical packaging, electrical components etc. [2-4].

The crystal structure of PCTFE was studied by Mencik [5]. In this study, the polymer chain is found to be helical with on the average 16.8 monomer units in one turn of the helix. The result of the x-ray diffraction study agrees best with the assumption that the polymer is atactic with random position of the chlorine substituent. The crystallization of PCTFE from dilute solution and from the melt of dispersion powder at atmospheric pressure and from the melt of the bulk material under high pressure have been carried out revealing a 17 monomer in one turn helix configuration of PCTFE [6]. The infrared and Raman spectra of PCTFE were reported by many authors [7, 8]. Different investigations [9-11] have been reported in the literatures which deal with the heat capacity of PCTFE at different temperatures. In all these studies, to the best of our knowledge no one has reported vibrational dynamics of PCTFE.

In general the IR 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 (line shape, if optically active) also provide information about the extent of coupling along the polymeric chain or between the chains. 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 PCTFE 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 spectra reported by previous authors [7, 8] used for comparison. The calculated value of heat capacity is in fairly good agreement with experimental data [9-11].

2. Theoretical Approach

2.1. Calculation of normal mode frequencies

Normal modes calculation for a polymeric chain was carried out using Wilson's GF matrix method [12] as modified by Higgs [13] for an infinite polymeric chain. The vibration secular equation to be solved is

$$\left| G(\delta)F(\delta) - \lambda(\delta)I \right| = 0, \qquad 0 \leq \delta \leq \pi \qquad \text{.............(1)}$$

Where δ is the phase difference between the modes of adjacent repeat units, $G(\delta)$ is the inverse kinetic energy matrix and $F(\delta)$ is the force field matrix for a certain phase value.

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

$$\lambda(\delta) = 4\pi^2 c^2 \nu^2(\delta) \qquad \text{............. (2)}$$

A plot of $v_i(\delta)$ versus δ gives the dispersion curve for the ith mode.

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

$$g(\nu) = \sum (\partial\nu_j/\partial\delta)^{-1}]_{\nu j(\delta)=\nu j} \qquad \text{.............(3)}$$

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

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

$$\text{with } \int g(\nu_i)d\nu_i = 1$$

The constant volume heat capacity C_v, given by above equation, can be converted into constant-pressure heat capacity C_p using the Nernst-Lindemann approximation [14, 15];

$$C_p - C_v = 3RA_0 (C_p^2 T/ C_v T_m^0) \qquad \text{............ (5)}$$

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

3. Results and Discussion

The structure of PCTFE has been determined by using molecular modeling technique. For this purpose CS-Chemdraw has been used to minimize the energy of the complete polymer in a given conformation at once. The helical structure of PCTFE has been reported [5]. On the basis of these studies and molecular modeling, we have accepted helical geometry for analysis.

The number of atoms per residue in PCTFE is six and, hence, there would be (6 x 3) - 4 = 14, normal modes of vibration. The vibrational frequencies were 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 $\delta = 0$, ϕ and 2ϕ, where ϕ is the helix angle. The four zone center zero-frequencies correspond to acoustic modes; three representing translations along the three axes and one rotation around the chain axis.

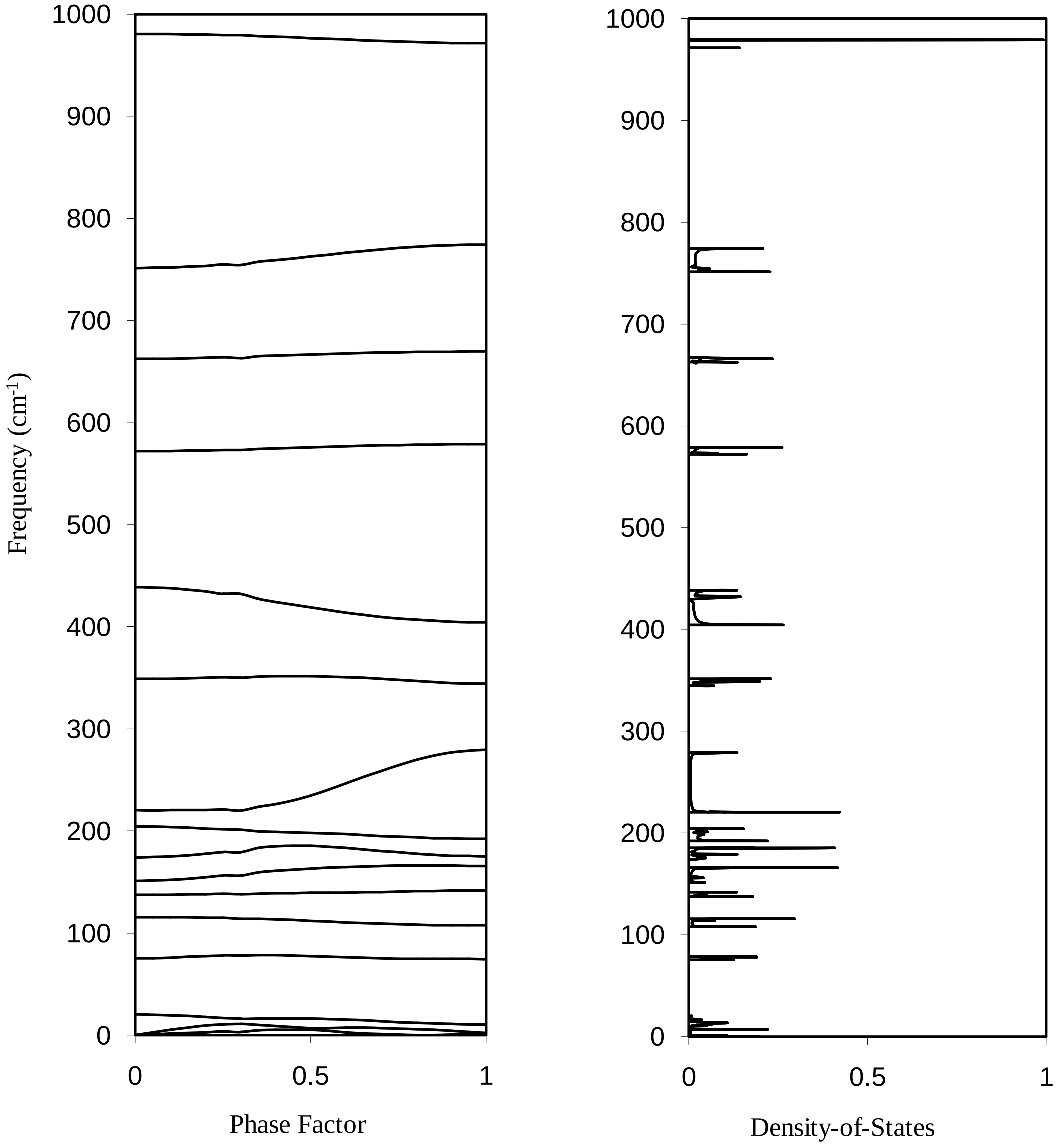
The assignments were made on the basis of potential energy distribution (P.E.D.), band position, band shape, band intensity, and absorption / scattering in similar molecules having groups placed in similar environments. The Urey-Bradley force constants were initially transferred from earlier work on molecules having similar groups and were further refined by using the least-square method as described earlier [16]. Except for a couple of frequencies, most of the frequencies were fitted within less than 1%. The modes corresponding to $\delta = 0.0$ are both Raman and IR active. All vibrational modes along with their PEDs' are given in Table 1 Table 2 at $\delta = 0.0$ and $\delta = 1.0$, respectively.

In the present case 16.8 residues are contained in one turn hence the helix angle is 360/16.8 = 21.43. Helix frequencies which are IR active are on the intercept vertical line at phase angle 21.43. The approximate helical structure refers to helix angle 21.43 which give the zone boundary point on the wave vector axis at 0.119π. This 0.119π within flat region of almost all the dispersion curves. As the result of it the assignments and energy of modes remain the same at the zone centre for planar zig-zag structure.

3.1 Dispersion Curves

The dispersion curves below 1000 cm^{-1}, are shown in Fig. 1a. The modes above 1000 cm^{-1} are either non-dispersive or their dispersion less than 5 cm^{-1}.

A very interesting feature of dispersion curves is convergance of various modes i.e. the modes separated by a large wave number at the zone center come very close at the zone boundary. The convergence arises mainly because of the close sharing of potential energy in different measures by various modes. For example, the 754 and 663 cm^{-1} modes remain constant at the $\delta = 0.3$ but on increasing the value of δ the 754 cm^{-1} mode slightly moves up or repel towards higher frequency mode. At the same time it is also observed that the 661 and 571 cm^{-1} mode remain constant from the zone center to the zone boundary. We see for the 438 and 348 cm^{-1} modes, as the value of δ increases from $\delta = 0.0$ to $\delta = 1.00$ both come closer to each other and shows little convergence between these two modes mainly at $\delta = 0.65$, this can be explained as that both the modes are separated by 90 wave numbers on the zone center and separated by only 60 wave numbers on the zone boundary.



(a) (b)

Fig. 1 (a): Dispersion curves of PCTFE (0-1000 cm^{-1})
(b): Density-of-Stats of PCTFE (0-1000 cm^{-1})

Table 1: Vibrational modes of PCTFE at $\delta = 0.00$

Calculated	Observed		% PED (Potential Energy Distribution) at $\delta = 0.00$
	I.R.	Raman	
1298	1290	1293	ν(C-F)(81)+ν(C-C)(11)
1183	1198	1201	ν(C-F)(67)+ν(C-Cl)(22)
980	972	969	ν(C-C)(53)+ν(C-F)(21)+φ(F-C-F)(10)+ν(C-Cl)(7)+φ(F-C-C)(5)
751	744		ν(C-F)(51)+ν(C-Cl)(20)+ν(C-C)(10)+φ(F-C-C)(8)
662	660	667	ν(C-C)(61)+ν(C-F)(17)+φ(F-C-C)(15)
571	582	556	ν(C-F)(27)+φ(F-C-F)(22)+ν(C-Cl)(20)+ν(C-C)(16)+φ(F-C-C)(11)
438	440	439	φ(F-C-C)(24)+ν(C-Cl)(17)+φ(C-C-Cl)(15)+φ(F-C-F)(14)+ν(C-F)(11)
348		339	φ(F-C-C)(37)+φ(C-C-Cl)(22)+φ(C-C-C)(9)+ν(C-Cl)(7)
220		205	φ(F-C-C)(29)+φ(F-C-F)(24)+φ(F-C-Cl)(18)+ν(C-C)(8)
204		198	φ(F-C-C)(65)+φ(C-C-Cl)(15)+ω(Cl-C)(6)
174		180	φ(F-C-C)(41)+φ(C-C-Cl)(22)+ω(Cl-C)(10)
151			φ(F-C-C)(59)+φ(C-C-Cl)(17)+φ(F-C-Cl)(13)+ω(Cl-C)(6)
137		120	φ(F-C-C)(80)+ν(C-C)(10)
115		116	φ(F-C-C)(49)+φ(C-C-Cl)(33)+φ(C-C-C)(8)+ω(F-C)(5)
75			φ(F-C-C)(68)+φ(C-C-C)(63)+φ(C-C-Cl)(19)
20			τ(C-C)(90)+τ(C-C)(8)

Table 2: Vibrational modes of PCTFE at $\delta = 1.00$

Calculated	Observed		% PED (Potential Energy Distribution) at $\delta = 1.00$
	I.R.	Raman	
1314	1290	1293	ν(C-F)(86)+φ(F-C-C)(7)+ν(C-C)(5)
1198	1198	1201	ν(C-F)(58)+ ν(C-Cl)(24)+ν(C-C)(8)
971	972	969	ν(C-C)(51)+ ν(C-F)(22)+φ(F-C-C)(11)+φ(F-C-F)(11)
774			ν(C-F)(30)+ ν(C-C)(28)+ν(C-Cl)(23)
669	666	667	ν(C-C)(54)+ν(C-F)(29)+φ(F-C-C)(12)
578	582	556	ν(C-F)(37)+ν(C-Cl)(24)+ φ(F-C-F)(15)+ ν(C-C)(10)+φ(F-C-C)(9)
404			φ(F-C-F)(25)+ν(C-Cl)(23)+φ(F-C-C)(14)+ φ(F-C-Cl)(9)+φ(C-C-Cl)(7)+ν(C-F)(6)
344		339	φ(F-C-C)(51)+φ(C-C-Cl)(28)+φ(C-C-C)(14)+ω(Cl-C)(11)
279		287	φ(F-C-C)(43)+ φ(F-C-F)(16)+ ν(C-C)(13)+φ(C-C-Cl)(12)+φ(C-C-C)(10)+ν(C-F)(8)
192		196	φ(F-C-Cl)(45)+φ(C-C-Cl)(11)+φ(F-C-F)(7)+ φ(F-C-C)(7)+ν(C-C)(7)
175		180	φ(F-C-C)(87)+ω(Cl-C)(6)
165			φ(F-C-C)(77)+φ(C-C-Cl)(9)
141			φ(F-C-C)(67)+φ(C-C-Cl)(10)+ν(C-C)(8)
107		116	φ(C-C-Cl)(67)+φ(F-C-C)(14)
74			φ(F-C-C)(81)+φ(C-C-C)(52)+ω(F-C)(6)
10			ω(F-C)(34)+τ(C-C)(28)+φ(F-C-C)(14)+τ(C-C)(12)+ω(Cl-C)(11)

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

Another interesting feature shown by the lower frequency modes 220, 204 and 174 cm^{-1} modes at $\delta = 0.0$ show that these three modes remain constant from the zone center to $\delta = 0.3$ but on increasing the value of δ the upper mode at 220 cm^{-1} curves shows great divergence, it diverges more at $\delta = 0.8$ to the zone boundary. It is also shown that the middle frequency mode that is of 204 cm^{-1} mode remains constant but the mode at 174 cm^{-1} shows convergence when the value of δ increases.

3.2 Density-of-States and Heat capacity

The dispersion curves obtained for PCTFE 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. 1b. Heat capacity of PCTFE has been calculated in the temperature range 50–400 K (Fig. 2), which is in fairly good agreement with the experimental data [9-11].

It should be noted here that the contribution from the lattice modes is bound to make a difference to the heat capacity because of its sensitivity to low frequency modes. However, so far we have predicted the values only for an isolated chain. Calculation of dispersion curves for a three-dimensional system would be extremely difficult. Inter-chain modes involving hindered translatory and rotatory motion will appear and the total number of modes will depend on the contents of the unit cell. For each additional atom in the unit cell there is a 3-fold increase in the number of internal coordinates and it rapidly makes dimensionality of the problem prohibitive. The force field also simultaneously brings in an enormous number of interactions that are difficult to visualize and quantify. Thus the problem will become intractable. The inter-chain interactions will contribute primarily to lower frequencies. They are generally of the same order of magnitude as the weak intra-chain interactions. Their introduction will, at best, bring about crystal field splitting at the zone center and zone boundary depending on the symmetry-dependent selection rules. However, the intra-chain assignments will remain by and large undisturbed. Thus, in spite of several limitations involved in the calculation of specific heat, we believe the present work provides a good starting point for further basic studies on the dynamic and thermodynamic behavior of polymers like PCTFE. Complete 3-D studies have been reported only on polyethylene [17] and polyglycine, [18, 19] where the unit cell is small. Other calculations with approximate inter-chain interactions, as in a β sheet of polypeptides, have been confined to calculations of only zone center and zone boundary frequencies, by considering short segments and nearest neighbor interactions only [20]. The present work calculates the dispersion curves within the entire zone which is the only method to locate regions of high density-of-states which are important for thermodynamic behavior.

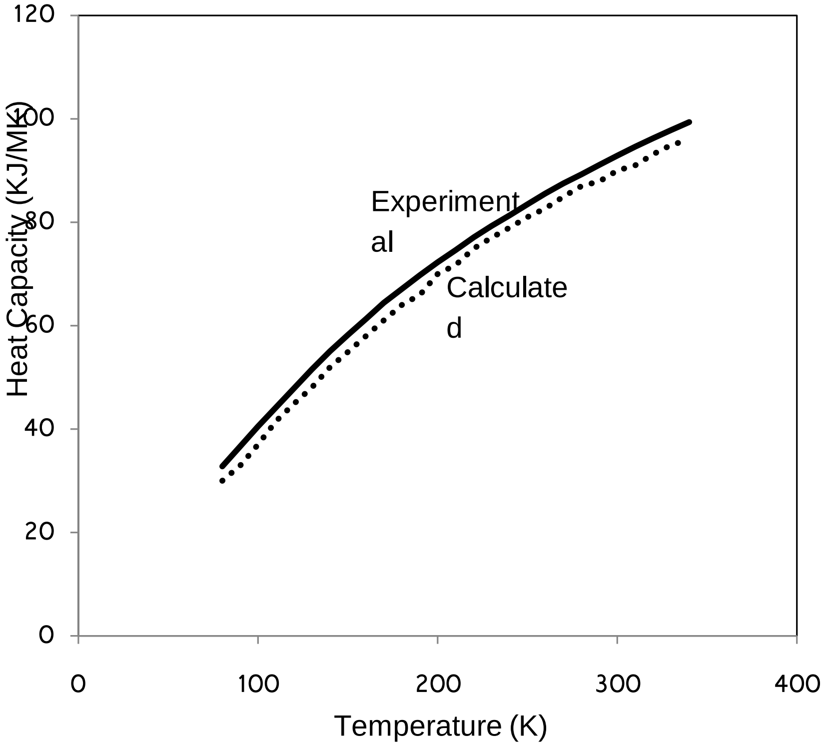


Fig. 2: Variation of heat capacity with temperature of PCTFE

4. Conclusion

Raman and IR spectral data on PCTFE can be well interpreted by solving the secular equation based on Wilson's GF matrix method as modified by Higgs and using Urey-Bradley force field. Some of the characteristic features such as repulsion are observed. These give rise to higher density-of-states. Heat capacity behavior with temperature is linear in nature.

References

[1] H. Teng, Applied Sciences, 496-512, 2012.
[2] W. Martienssen, H. Warlimont, Springer Handbook of Condensed Matter and Materials Data, 496, 2005.
[3] J.G. Drobny, Technology of Fluoropolymers, 73-75, 2001.
[4] M. Chandra, S.K. Roy, Industrial Polymers, Specialty Polymers, and Their Applications, 28, 2007.
[5] Z. Mencik, J. Polym. Sci. Polym.:Polym. Phys.Ed., 11 (8), 1585–1599,1973.
[6] Y. Miyamoto, C. Nakafuku, T. Takemura, Polymer Journal, 3, 122-128, 1972.
[7] C.Y. Liang, S. Krimm, Journal of Chemical Physics, 25(3), 561-571, 1956.
[8] Y. Kawano, S.C. Araujo, J. Braz. Chem. Soc., 7(6), 491-496, 1996.
[9] W.K. Lee, P.C. Lau, C.L. Choy, Polymer, 15(8), 487-490, 1974.
[10] S.S. Chang, J.J. Weeks, J. Res. Natl. Inst. Stand. Technol. 97(3), 341-363, 1992.
[11] U. Gaur, B.B. Wunderlich, B. Wunderlich, J. Phys. Chem. Ref. Data, 12(1), 31-62, 1983.
[12] E. B. Wilson, J. C. Decuis, P. C. Cross, and Molecular Vibrations: The theory of infrared and Raman vibrational spectra, Dover Publication, New York, 1980.
[13] P. W. Higgs, Proc. Roy. Soc, London 220, 472-480, 1953.
[14] R. Pan, M.N. Verma, B. Wunderlich, J. Therm. Annal. 35, 955-961,1989.
[15] K.A. Roles, A. Xenopoulos, B. Wunderlich, Biopolymers 33, 753-755, 1993.
[16] P. Ali, S. Srivastava, S.U. Ansari, V.D. Gupta, Spectochim. Acta-A 111, 86-90, 2013.
[17] S. Krimm, C.Y. Liang, G.B.B.M. Sutherland, G.B.B.M., J.Chem.Phys. 25, 1956, 549-563.
[18] Y. Abe, S. Krimm, Biopolymers 11, 1817-1839, 1972.
[19] V.D. Gupta, S. Trevino, H. Boutin, J.Chem. Phys. 48, 3008-3015, 1968.
[20] S. Krimm, "Vibrational Spectroscopy of Polypeptides" in Modern Polymer Spectroscopy" ed. G. Zerbi, Wiley-VCH, Weinheim, Chap. 5, 239-285, 1999.