Chapter One

Introduction
1.1 Introduction:

The present thesis comprises a detailed study of normal modes of vibrations, dispersion curves, heat capacity and complete vibrational dynamics of some vinyl polymers such as isotactic poly (vinyl alcohol), syndiotactic poly (vinyl alcohol) and poly (vinyl butyral). This chapter provides the necessary introduction to the next three chapters, which contain the work on the aforesaid systems. The last chapter deals with the merits and shortcomings of the present work.

1.2 Polymers, Classification, Properties and Their Applications:

A polymer is a chemical compound or mixture of compounds consisting of repeating structural units formed through a process of polymerization. The term polymer derived from the Greek word (polus, meaning "many, much") and (meros, meaning "parts"), and refers to a molecule whose structure is composed of multiple chemical repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. The units composing polymers derive, actually or conceptually, from molecules of low relative molecular mass. The term polymer was coined by Johns Jacob Berzelius in 1833.

Polymerization is the process of combining many small molecules known as monomers into a covalently bonded chain or network. During the polymerization process, some chemical groups may be lost from each monomer. This is the case, for example, in the polymerization of PET polyester. The monomers are terephthalic acid (HOOC-C₆H₄-COOH) and ethylene glycol (HO-CH₂-CH₂-OH) but the repeating unit is -OC-C₆H₄-COO-CH₂-CH₂-O-, which corresponds to the combination of the two monomers with the loss of two water molecules.
1.2.1 Classification of Polymers:

On the basis of different chemical structures, physical properties, mechanical behavior, thermal characteristics, stereochemistry, polymers can be classified into following ways:

Depending on their origin, polymers may be grouped as:
Natural e.g., cotton, silk, wool and rubber, cellulose rayon, leather etc.
Synthetic e.g., polyethylene, PVC, nylon and terylene etc.

Depending on how they are linked or joined (chemical bonds or intermolecular forces) and on the arrangement of the different chains that forms the polymer, the resulting polymeric materials can be classified as:
Thermoplastics e.g., Polyethylene, PVC, nylon and sealing wax
Elastomers e.g., natural rubber, synthetic rubber, silicone rubber.

Depending on the chemical composition, polymers can be inorganic such as glass, or they can be organic, such as adhesives of epoxy resin.
On the basis of the configurations, (stereochemistry) polymers can be classified into three categories viz., atactic, isotactic (cis-arrangement) and syndiotactic (trans-arrangement).

1.2.2 Properties of Polymers:

Among the properties that define the properties of polymers, the most important are:

1.2.2.1 Glass transition temperature of the polymer
1.2.2.2 Average molecular weight of the polymer molecule

The glass transition temperature of polymers determines the temperature at which the polymer mechanical properties of polymers change dramatically, when the glass transition temperature is slightly below room temperature the polymer behaves like an elastic material (elastomer), when the temperature is higher than the glass transition temperature the polymer behaves as a rigid material (thermoset).
The average molecular weight directly determines both the size of the polymer and its chemical and mechanical properties of the polymer (viscosity, wet, creep resistance, abrasion resistance), for example polymers with high average molecular weight materials are very viscous.

1.2.3 Characteristics and typical applications of few plastic materials:

Polymers play a very important role in human life. In fact, our body is made of lot of polymers, e.g. Proteins, enzymes, etc. Other naturally occurring polymers like wood, rubber, leather and silk are serving the humankind for many centuries now. Modern scientific tools revolutionized the processing of polymers thus available synthetic polymers like useful plastics, rubbers and fiber materials.

1.2.3.1 Thermo plastics

Application: Refrigerator lining, lawn and garden equipment, toys, highway safety devices.

2. Acrylics (polymethyl-methacrylate) Characteristics: Outstanding light transmission and resistance to weathering; only fair mechanical properties.
Application: Lenses, transparent aircraft enclosures, drafting equipment, outdoor signs

3. Fluorocarbons (PTFE or TFE) Characteristics: Chemically inert in almost all environments, excellent electrical properties; low coefficient of friction; may be used to 260°C; relatively weak and poor cold-flow properties.
Application: Anticorrosive seals, chemical pipes and valves, bearings, anti-adhesive coatings, high temperature electronic parts.

4. Polyamides (nylons)
Characteristics: Good mechanical strength, abrasion resistance, and toughness; low coefficient of friction; absorbs water and some other liquids.
Application: Bearings, gears, cams, bushings, handles, and jacketing for wires and cables.

5. Polycarbonates
Characteristics: Dimensionally stable: low water absorption; transparent; very good impact resistance and ductility.
Application: Safety helmets, lenses light globes, base for photographic film

6. Polyethylene
Characteristics: Chemically resistant and electrically insulating; tough and relatively low coefficient of friction; low strength and poor resistance to weathering.
Application: Flexible bottles, toys, tumblers, battery parts, ice trays, film wrapping materials.

7. Polypropylene
Characteristics: Resistant to heat distortion; excellent electrical properties and fatigue strength; chemically inert; relatively inexpensive; poor resistance to UV light.
Application: Sterilizable bottles, packaging film, TV cabinets, luggage

8. Polystyrene
Characteristics: Excellent electrical properties and optical clarity; good thermal and dimensional stability; relatively inexpensive
Application: Wall tile, battery cases, toys, indoor lighting panels, appliance housings.

9. Polyester (PET or PETE)
Characteristics: One of the toughest of plastic films; excellent fatigue and tear strength, and resistance to humidity acids, greases, oils and solvents
Application: Magnetic recording tapes, clothing, automotive tire cords, beverage containers.

1.2.3.2 Thermo setting polymers
1. Epoxies
Characteristics: Excellent combination of mechanical properties and corrosion resistance; dimensionally stable; good adhesion; relatively inexpensive; good electrical properties.
Application: Electrical moldings, sinks, adhesives, protective coatings, used with fiber glass laminates.

2. Phenolics
Characteristics: Excellent thermal stability to over 150°C; may be compounded with a large number of resins, fillers, etc.; inexpensive.
Application: Motor housing, telephones, auto distributors, electrical fixtures [1-5].

1.3 What others have done:
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 [6]. 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 [7]. Most recently, PVA has been used in pharmaceutical and biomedical applications for controlled drug release tests due to its degradable and non-toxic properties [8]. Chemical crosslinking is highly versatile method to create and modify polymers, where properties can be improved, such as mechanical, thermal and chemical stability [7, 9].
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 [10]. The X - ray diffraction data [11, 12] 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 [13]. In the gel form, isotactic PVA is much softer as compared with atatic and syndiotactic PVA due to intermolecular hydrogen bond [14]. In earlier works, several authors have reported infra red and Raman spectra of isotactic PVA [15, 16]. Wunderlich et. al. reviewed experimental measurements of heat capacity of PVA [17].

A study of normal modes and their dispersion in polymeric system is essential to understand the dynamical and thermo dynamical 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.

Poly (vinyl alcohol) (PVA) is nontoxic water soluble synthetic polymer, which is widely used in biochemical and medical applications because of its compatibility with the living body [18]. Like all vinyl polymers PVA may exist in two main tactic modifications: isotactic, where the –OH groups are on the same side, and syndiotactic, where the –OH groups are on alternating sides of the main chain. It is well known that tacticity may have a great influence on preferred polymer confirmation and on its physical properties such as glass transition temperature in vinyl polymers [19]. An increase in the syndiotacticity of PVA has been reported to improve the physical properties such as heat resistance, tensile strength, and the modulus [20-22].
In particular, the solubility in solvents and the melting temperature of PVA are significantly influenced by the tacticity. For example, syndiotactic PVA is insoluble in boiling water [23], which is well known to be good solvent for atactic PVA. Furthermore, the melting temperature of PVA is increased with increase in both the syndio and isotacticities [24]. The crystallinity of PVA [25] suggests that all the –OH groups which are located alternate in the opposite side of the plane i.e. syndiotactic PVA shows the planar zigzag configuration. In earlier works [26-29], several authors have reported IR and Raman spectra of syndiotactic PVA.

In the present study, we report a complete normal mode analysis of syndiotactic PVA using Urey - Bradley force field, phonon dispersion and heat capacity obtained via the density-of-states derived from dispersion curves.

Poly (vinyl butyral) (PVB) is a resin usually used for applications that require strong binding, optical clarity, adhesion to many surfaces, toughness and flexibility [30-32]. The macroscopic physical properties of PVB are known to be intimately related to the polymer molecular dynamics, which is strongly influenced by water molecules in the polymer [33]. It was synthesized by condensation of poly (vinyl alcohol) with butyraldehyde. Preparation and characterization of PVB/grapheme Nano composite was reported in a recent publication [34]. Worldwide 65 % of all PVB used in automotive application. With increasing material costs and demands for pollution control becoming more important there is an incentive to recycle plastic waste [35, 36]. In the case of PVB, there is a possibility to improve mechanical properties by mixing nano fillers with PVB. However, the optical and adhesive properties of PVB would not be to significantly change after mixing nano fillers. The decomposition mechanism of PVB is complex because PVB is a copolymer and decomposed products are very complicated [37].
The morphologies and structure of PVB/silica nano fibers were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), thermo gravimetric analysis (TGA), FTIR, and energy dispersive spectrometer (EDS) [38]. The pyrolysis of PVB binder and other organic additives in thermoelectric green tapes are analyzed through differential thermal analysis, TGA and FTIR [39]. The possibility of using PVB film wastes as the adhesive component of cotton, adhesive sealing materials was reported by Artemenko et. al. in 2008 [40]. In all these studies, to the best of our knowledge, no one has reported the vibrational dynamics and heat capacity of poly (vinyl butyral). The present study reports a complete normal mode analysis of PVB using Urey-Bradley force field, phonon dispersion, and heat capacity as a function of temperature via the density-of-states derived from the dispersion curves. The experimental data of FTIR reported by previous authors have been used [41].

1.4 Techniques that can be used:

The structure of these systems can be studied experimentally as well as theoretically. Experimental techniques such as X-ray diffraction, NMR, I.R. absorption and Raman scattering etc. are often used. X-ray diffraction can provide information about the fixation of the position of the atoms on the crystal lattice and the measurements of the distances between atoms and the associated internal symmetry. It has been successfully employed in elucidating the structure of several polymers [42-54] but it focuses attention on only crystalline parts of a polymer. The conformation of polymers which exist in their functional state in solution is studied by a combination of light scattering and hydrodynamic techniques, both of which yield information on their shape and dimensions.
NMR spectroscopy [55] in the broad sense is the resonance absorption of electromagnetic radiation by an atomic nucleus when placed in a strong magnetic field. The NMR spectra have found great applications in revolutionizing structural determination technique. Fourier transform technique in the pulsed nuclear magnetic resonance spectroscopy has been introduced by Ernst and Anderson [56] in 1966 which started a new era in this branch of spectroscopy. Presently versatility and maneuverability of the NMR is being used for structural elucidation of various polymers [57, 58]. Several reviews discussing the theory and physical principal behind the newer techniques in modern FT-NMR spectroscopy are available [59, 60]. In addition to NMR spectroscopy, the mass spectroscopy has also made amazing progress during the last decade in its applications in the structural analysis of polymers.

The spectrum of a polymer is to a first approximation that of its repeat unit, it follows immediately that the spectrum is an aid to qualitative analysis, i.e. finding out what kinds of repeat units are present in a sample of an unknown polymer. In addition to providing information about the chemical structure of a polymer, vibrational spectroscopy can also give useful information about the physical structure, which always influences the properties of a polymer [61]. A detailed analysis of the vibrational spectra has provided a deeper understanding of the structure and interactions in polymers [62 - 64]. The information contained in the entire spectrum is, therefore, sensitive indicator of the three dimensional structure. Infrared and Raman spectroscopy, in combination with normal mode analysis, with which the work described here is directly concerned, provide a powerful approach for the conformational analysis of polymers. These modes can be calculated from a knowledge of the three dimensional structure of the molecule and of its vibrational force field. A comparison of observed
frequencies with those calculated for a specific secondary structure could provide a method for testing structural hypothesis in great detail.

Flow birefringence and the measurement of the intrinsic viscosity have been used to study conformations in solution [65]. Optical rotation is a very useful technique for the study of the structural properties of the polymers [66-71]. The variation of the optical rotatory power with wavelength termed as optical rotatory dispersion provides the information that may be correlated with structure and therefore offers a basis for the study of conformation and conformational changes. The measurements of circular dichroism also provide considerable information [72-75]. In particular the electronic circular dichroism has become very important for qualitative characterization of vinyl polymers.

1.5 Techniques used in the present work:

Theoretically the vibrational dynamics of polymers can be studied by normal mode analysis. Among all the techniques stated above the vibrational spectroscopy provides useful information concerning the conformation of polymers. It is a very important tool for probing into conformation through conformational sensitive modes. In general, the IR absorption, Raman spectra and inelastic neutron scattering from polymeric systems are very complex and can not be unraveled without the full knowledge of dispersion curves. One can not appreciate without it the origin of both symmetry dependent and symmetry independent features. Further, the presence of regions of high density-of-states, which appear in all these techniques and play an important role in thermo dynamical behavior, are also dependent on the profile of dispersion curves. The lack of this information in many polymeric systems has been responsible for incomplete understanding of polymeric spectra. Dispersion curves also provide information on the extent of coupling along the chain together with an understanding 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 systems continues to be of topical importance. We feel that a study of the normal modes and their dispersion is essential to understand dynamical and thermo dynamical behavior of some vinyl polymers.

1.6 Chapter wise summary:

The present thesis comprises of 6 chapters including the introduction which is chapter 1. Chapter 2 explains the complete experimental and theoretical approaches used in the next three chapters.

Chapter 3, 4 & 5 deal with the complete vibrational dynamics of isotactic poly (vinyl alcohol), syndiotactic poly (vinyl alcohol) and poly (vinyl butyral) respectively. In this work, studies have been made on complete normal mode analysis using Urey-Bradley force field, phonon dispersion and heat capacity via the density-of-states derived from the dispersion curves for isotactic poly (vinyl alcohol), syndiotactic poly (vinyl alcohol) and poly (vinyl butyral).

Chapter 6 is the conclusion of the entire work. This is the last chapter which includes the merits and shortcomings of the present work.
1.7 References:


