CHAPTER I

GENERAL INTRODUCTION
1.1 Introductory Remarks

Miniaturization of solid state devices used in electronic instruments has provided a new field of investigation which is interesting as well as promising. Organic insulating materials in thin films form are being extensively studied so that they may be suitably used in microelectronics devices.\(^1, 2\) Polymers with their high insulating properties may play an important role in the fabrication of such devices. Recently sufficient attention is being paid in understanding the structures of biopolymers \(^3, 4\) also, in the form of thin films with different types of investigations i.e., conductivity measurements,\(^5\) dielectric relaxation behaviours \(^6\) or spontaneous current emission \(^7\) or thermally stimulated discharge current measurements.\(^8\)

Polymer films are generally insulating but by doping with suitable impurities, the conductivity values of these films may be modified\(^9\) and therefore doped samples may have the values of the order of inorganic semiconductors. On the other side generally biopolymers \(^5, 10\) like proteins, hemoglobin etc. have higher order of conductivity values due to sorbed water or absorbed water traces.

It has been reported by Ciaing \(^11\) that conducting polymer can be obtained by doping poly acetylene with halogen impurities. Conducting filter polymer composites \(^12\) are also reported in the
literature. Polymer films are also employed for making suitable electrets. Electrets made of polymer films/foils are now widely used in microphones.\textsuperscript{13,14} Knowledge of electrical conductivity, dielectric loss measurements, spontaneous current emission and thermally discharge current for pure and doped polymer films (PVP) are necessary for making new applications in the field of electronics, medicines, photographic materials etc. Poly vinyl pyrrolidone has a new growing applications in pharmaceutical sciences\textsuperscript{15,17} hence it is necessary to collect the exact behaviours of this polymer in the form of thin films in different investigations and these informations may be helpful in underlying the new field of applications in different branches of sciences.

1.2 The Electret State

An electret is a piece of dielectric material exhibiting a quasi-permanent electrical charge. The term "quasi-permanent" means that the time constant characteristics for the decay of the charge are much longer than that of the periods over which studies are performed with the electret. Shortly electrically polarized dielectrics in which the polarization persists for a long time even after the polarization field is removed, is called electret.\textsuperscript{19} The electret charge may consist of "real" charges, such as surface charge layers or space charges, it may be a "true" polarization or it may be a combination of these two phenomena. This is shown in Fig. 1.1 for a dielectric plate, while the "true polarization" is
Fig. 1.1 (A) & (B) –

(A) - Schematic cross-section of a one sided metallized electret having deposited surface charges, aligned dipolar charges and compensation charges.

(B) - Schematic cross-section of two sided metallized electret with dipolar and space charges.
usually a frozen-in alignment of dipoles, the real charges comprise layers of trapped positive and negative carriers, often positioned at or near the two surfaces of dielectric respectively. The electret charges may also consist of carriers displaced within molecular or domain structures throughout the solid, resembling a true dipole polarization. If the charges are displaced to domain boundaries, they are referred to as Maxwell-Wagner polarization. On metalized electrets a compensation charge may reside on the electrode, unable to cross the energy barrier between metal and dielectric. An electret not covered by metal electrodes produces an external electrostatic field if its polarization and real charges do not compensate each other every where in the dielectric such an electret is thus a sense the electrostatic analogue of a permanent magnet, although electret properties may be caused by dipolar and non-polar charges while magnetic properties are only due to magnetic dipoles. The existence of an external field and corresponding analogy with a magnet has often been used to define the electret.

1.3 Electret Research

Electret properties are described in different terms by Gray in 1732 and latter by Faraday. Later on the word "Electret" was first coined in 1902 by Heaviside. Systematic research into electret properties began in 1919 when the Japanese physicist Ikuchi formed electrets from essentially the same
material used by Gray by a thermal method consisting of the application of an electret field to the cooling melt. He found that the dielectrics exhibited charges on their two sides which changed sign after a few days from a polarity opposite to the one equal to that of forming adjacent forming electrodes. These charges are named as "Heterocharges" and "Homocharges" respectively indicating their relation to the forming electrodes. Bellenyi in 1928 found that such process depends on the injection of electrons or ions into insulators. In 1940s, in the fundamental studies by Gross revealed a lot of informations about the two different types of charges. The two charge theory was subsequently used by Swann. On the basis of the phenomenological theory of open circuit charge decay, extended latter by Gubkin to short circuit conditions. In 1954, thermal depolarization method was applied to the case of dipole polarization by Ducii and Co-workers who suggested the name of ionic thermal conductivity (ITC). ITC also allows the determination of activation energy and dipolar relaxation time from depolarization current measurements obtained upon linear heating of the dielectric. In the following decades electrets from wax materials and a number of other substances (polymers) are produced by charging techniques different from Equchi's thermal method. Most of recent work has been devoted to the application of ITC method and other related thermally stimulated current techniques for investigating dipolar and space
charge phenomena.\textsuperscript{33,37} Much of newer experimental work is done on polymer electrets, which although chemically not so well defined, as many other materials, have gained importance due to their usefulness in practical applications. These experiments have culminated in a very comprehensive treatment by Van Turnhout.\textsuperscript{39} Vanderschuren\textsuperscript{39} invented a new technique of partial polarization of the dielectric and from this he concluded a distribution in frequencies of dipolar peak. The biological and other polymeric materials are investigated by Fukada\textsuperscript{40-42} and others in 1950s and 1960s. Pillai and Hollah\textsuperscript{43} have found a thermo induced current from water activated phenomenon in cellulose derivatives even in unpolarized samples. The similar work of TSD of unpolarized PAN films has been reported by Stupp and Carr\textsuperscript{44} and more recently SCE of unpolarized samples of PVA (poly vinyl alcohol) has been investigated by Sareef \textit{et al.}\textsuperscript{7}

TSD measurements on many polar and non-polar polymers have been reported separately by different workers. P.G. Mehendru and his coworkers reported several papers on TSD of polycarbonates,\textsuperscript{45} poly vinyl butryal,\textsuperscript{45} poly vinlidene fluoride\textsuperscript{8,47} etc. The impurity doped polymer samples have also importance due to its morphological informations and growing uses of doped polymers as a charge transfer complexes.\textsuperscript{9,46} Mostly the iodine doped polymer films are tested by different workers\textsuperscript{9,45,47} for TSD measurements in the last decade.

On the other side, during the development of xerography,
corona discharge was used and latter extended to thin films also. The charging of polymers by irradiation is reported by R.A. Cresswell and M.M. Perlmann and the distribution of trap levels was found in polyethylene. Some of polymers in thin films are being used in the field of electronics and also as passivative layers in the integrated circuits. Recently, work on use of dosimeters, transducers, pyroelectric detectors, prosthetic and switching devices, gas filters and other instruments is being performed by a number of laboratories and a series of commercial applications have been reported. A general discussion of different types of electrets is also described below.

1.4 Different types of Electrets

(a) Thermoelectret - Thermoelectret is obtained by polarizing a dielectric by simultaneous action of heat and electric field.

(b) Electroelectret - An electret prepared at room temperatures by applying a high electric field is called electroelectret. Generally the dipolar materials which contain polar side groups are also polarized at room temperature, although the suitable polarization conditions in these polar polymers are found at higher temperatures.

(c) Photoelectret - In 1937, C. Nadzhakov discovered the phenomenon of persistence internal polarization in poly crystalline sulphur, produced by
simultaneous action of an electric field and light. This electret was named as photoelectret. Major contribution in the understanding of photoelectrets is due to Nadzhakov,\(^5^4\) Fridkin and Zholudev.\(^5^5\)

(d) Radioelectret\(^5^5,5^7\) - If the dielectric is polarized by simultaneous action of high energy radiations like X-rays, \(\beta\) rays, \(\gamma\) rays and electric field, the electret thus formed is called radioelectret. In 1953 Gross and Murphy\(^5^5\) polarized the carnauba wax by using \(\gamma\)-rays in presence of electric field.

(e) Thermo-Photoelectret\(^5^3\) - A photo conducting dielectric polarization by simultaneous application of an electric field, heat and a suitable high energy radiation is called thermo-photoelectret. This term was first introduced by Padgett.\(^5^3\)

(f) Magneto-electret\(^5^9,5^0\) - Magneto electret was prepared by Bhatnagar\(^5^9,5^0\) by cooling molten carnauba wax in the presence of a magnetic field. Latter on this affect was observed in some plastic materials\(^5^0\) also.

(g) Auto-Photoelectret State\(^5^1,5^2\) - Recently Andrichin\(^5^1,5^2\) observed a voltage which increases exponentially with increase of light and approaches to 1.0 volt when an Al-As\(_2\) \(S_3\)-Pt configuration is illuminated. This photo emf persists for a long time in dark. Persistence of photo
induced voltage in dark is termed as "auto-photo-electret" since
the polarization is achieved without applying field.

1.5  An Introduction - Long Chain Polymers

In a polymer, a large number of molecules called
monomers are joined together to form a long macromolecule chain
which can assume various confirmations in space. Polymers are
generally form a long chain network structures which seem to be
polymerized by their monomers and due to several bonds of main
and side chains (as the case may be). They are not easily
characterized as amorphous or crystalline materials. Some polymers
are structurally known as paracrystalline materials while the
disordered polymers are mostly classified as more amorphous and
less crystalline.

In polymers, there are terminating sequences of primary
valance bonds and neighbouring chains are hold together by
mechanical entanglements, although in some cases there may be
bonding of magnitudes of Vander-Wall forces between the
neighbouring chains. In this consequence the polymers locally
behave like a liquid while from bulk point of view they seem to be
solid. The behaviour of polymer up to a certain temperature is
different and a volume expansion of polymer occurs (densification)
and thus polymer behaves like a rubbery structure above to this
temperature. Polymers are known from its group i.e. acrylic
polymers, cellulose polymers, polyanides, polyesters, vinyl polymers, vinylylene polymers, vinylidene polymers etc. The polymers can be classified as polar and non-polar polymers. 
Polar polymer possesses some polar side groups in its structure which may be responsible for polar properties (as dipoles). The side groups are acetate, nitrate, and pyrrolidene in PVAc, PAN and PVP polymers. The other class of polymers has a linear symmetric structure (like PE or PS) which is known as non-polar polymer. In non-polar polymers the primary relaxation process is simply related to phase transition behaviour of the long chain structure, while the other class of polymer (polar) has different relaxations at different temperature ranges in TSC or TSD currents of the samples. These relaxations are termed as primary, secondary etc., according to its behaviour at different temperatures. Oftenly, a polymer may has major relaxation near rubber-glass transition temperature (Tg) whereas secondary relaxation may be possible in certain lower temperature conditions.

The vinyl polymers have great interest among research workers since last many years due to its much interesting properties with wide applications. The polymer structures like PVC, PVAc, PVF and PVDF are characterized as a network of different crystalline and amorphous phases and these different phases are extended into each other. These polymers have the distribution of traps which are available in some cases for trapping of charge carriers. These traps are available due to difference in energy
levels of amorphous and crystalline phases and thus the trapping and detrappling of charge carriers are the usual phenomena in large number of polymers. 71

Recently, the injected charge carriers may also be get trapped in some polymer structures. From injecting nature of electrodes the injection of charge carriers (electrons/holes) may be possible. 71

1.5.2 Trap Model in Polymers

Usually the trapping or detrapping of electronic charge carriers is analysed with the help of band gap model developed for crystalline solids. However, most of the polymer electrets are amorphous or at least partly crystalline in nature. The high degree of positional and compositional disorder in the materials results in many localized states in the forbidden energy gap 72,73 (Fig. 1.2) The trapping sites differ in number and depth, the higher the disorder, the lower these are and the deeper tail off into energy gap. The energy gap is thus replaced by a pseudo-gap in which the density of states remains finite. As a result the band edges are blurred so that it is difficult to make the energy at which a carrier is completely non localized. Mott et-al. 72 have therefore proposed to base the definition of the transport bands in amorphous materials or the mobility of carriers. This is illustrated in Fig. 1.2, the critical energy Ec at the mobility edge separates from delocalized states. Clearly it is only above Ec, that electrons can move through the solid
Fig. 1.2 (A) & (B) -

(A) - Energy diagram for a polymer, $T_e$ electron traps, $T_h$ hole traps.

(B) - Density of states $N(E)$ for a polymer, localized states are shaded and $E_v$ and $E_c$ mobility edges.
without the help of thermal energy. In addition to the disorder induced band tail states, clearly recognizable gap states may be formed by intrinsic structural defects. In polymers, intrinsic defects are e.g., branching, chain entanglements, chain ends, pendant groups etc. 73,74

By heating a trapped carrier may undergo, after its thermal release from trap. On its way to the electrodes it meets another trapping centre and recombination with an opposite charge may be possible, when it is caught by a recombination centre. Recently a successful alternative "Trap limited band transport" model was proposed in which the transport is assumed to be produced by multiple trapping.75 Experiments 75 clearly indicate that structural modifications and not impurities are responsible for trapping sites for which activation energies of 1.2 to 1.7 eV were derived. Measurements show an increase of carrier mobility with the number of unsaturated terminal groups, indicating the contribution of these groups to carrier trapping. Trapping effects in a series of substituted polyolefins have been investigated by Creswell et-al.75 and Perlmann.77 These experiments indicated the presence of three different structural trapping levels known as primary, secondary and tertiary, but no trapping is due to impurity centres. Recently in several disordered polymers the trapping of charge carriers have been observed by different workers.45,73 Calculations of this kind show (also in PVP) that structural defects such as carbonyl groups
of double bonds yields shallow or intermediate trapping levels of depths up to about 1.0 eV while foreign molecules function as deeper traps. 78

1.5.1 Poly vinyl pyrrolidone (PVP)

Several electrets are used as transducers 77 since from a long time but recently strong, highly active polymer films notably PVC, PVF, PVDF, PVA and PVAc etc have been recognised for their potential values as thermo electric and electro chemical transducer materials. 18 PVC is well known disordered polymer from its structure while PVF and PVDF are known as semi-crystalline in behaviour exhibiting piezo and pyrro electric properties. 30,31 If the monomer of the structure is symmetric the polymer can be considered semi-crystalline or crystalline in nature (i.e., PE, PVF, PETF etc.) but in the polymers like PVC, PVA or PVP, the asymmetric monomers are present in their structures, hence these can be treated as disordered or amorphous polymers, although at certain higher temperatures (greater than Tg ) the vinyl polymers may change as partly crystalline in structures.

In the same manner as described above PVP (poly vinyl pyrrolidone) also exhibits asymmetric structure of monomer and possesses a side group (as pyrrolidone ring). Similarly, PVP can be treated as disordered polymer up to a certain higher temperature (Tg value).
PVP was first developed in Germany by W. Renée of I.C. Farben during the 1930s and was widely used in same country as a blood plasma extender during the Second World War. Though the usual form of PVP is amorphous, because of the nonstereospecific addition of monomer units during polymerization and several workers have reported the activeness of its amide and carbonyl groups in complexing with other materials. Although the structural formula of PVP indicates that it should be neutral but its aqueous solution is slightly acidic in nature (pH value 4 - 5).

PVP can be easily treated up to 220°C because the heating curves on a differential scanning calorimeter measurement (under air or nitrogen) from 35°C to 220°C shows no exotherm or endotherm. A thermally state high Tg of a glass like PVP polymer may be found useful in high temperature applications. In literature several conflicting values of a glass-transition temperature (Tg) are found ranging from 140°C to 175°C. According to Tan et-al. these different values of Tg of PVP reported by different workers may be due to a influence of absorbed water molecules and a correct rubber-glass transition of zero water content of PVP is 175°C. According to them the different Tg values are due to its different amount of water content. A conclusion can be drawn that PVP is a hygroscopic material and the lower values of Tg possibly may be due to
homogeneously absorbed water in it. Recently electrophoretic experiments show that PVP (K = 40) solution slowly migrates to anode. The measurements of electrical conductance in CHCl₃ / CH₃ COOH show that protonation of PVP increases with acid content. More recently, the intermolecular (segmental) mobilities of poly vinyl pyrrolidone and poly vinyl carbolactum in solutions have been investigated by *Washermann and his coworkers* using the spin level technique. The rotational co-relation times of the order of 4.2 to 5.2 nento second have been observed for different segments in solutions of both the polymers.

1.5.2 Complexes of PVP

There are several complexes of the apparent adsorption of PVP on a variety of substances and in some cases the adsorption becomes sufficient to form complexes. Several materials have formed different complexes with PVP such as iodine, phenols, dyes etc. The complexes of iodine with PVP are being marketed because of its excellent germicidal properties combined with the greatly reduced toxicity and absence of staining action of iodine. The iodine is held so tightly in the complex that it is not removed by extraction with chloroform and no appreciable vapour pressure of iodine is apparent above the complex. Recently the complex formations between poly phenols and PVP have been explained by *Bublevskii et-al.*
The I.R. study of PVP shows the fact that two absorption bands for the carbonyl group of amide bonds are found to be present in the spectra (corresponding to free group and combined with a hydrogen bond). These facts about the morphology of poly complexes confirm the general concept of PVP according to which chain sections links co-operatively to one another coexist with free sections. 84, 82

1.7 Present investigations of pure and iodine doped PVP films.

PVP is known to be growing pharmaceutical importance because of its ability to form complexes with various drugs which in turn makes the drugs soluble or dispersible or delays the degradation of tablets. The thin film form of PVP is still lacking the informations and thus there is a sufficient scope in this field of electret work. Vacuum evaporated electrodes of different metals are used here in the present investigations and in this way these results have informations about the different mechanisms of thermally stimulated discharge currents. The different workers have reported the different hypotheses for complex formation between PVP and other materials such as phenol, iodine etc. but still there is a incomplete information about the dielectric relaxation about iodine doped PVP films and about the nature of complex formations (CTCs). The nature of charge transfer complexes can be explained with the help of these results of doped samples. The electrical conduction in the form of thin film of pure and
iodine doped PVP is not found in the present literature which may be necessary to explain the insulating properties of thin films on account of its wide uses in pharmaceutical sciences.

The proposed study of spontaneous current emission (SCE) of unpolarized samples of pure and iodine doped may also possesses the different important informations about its toxicity behaviour even at higher temperature conditions.

The proposed electrical conduction measurements of PVP films with different asymmetric electrode configurations may also possess the informations about the space charge and ionic conduction mechanisms. In F3O, it is proposed to make a detailed investigations of electret forming conditions, electrical conduction mechanisms and other related mechanisms.

The different chapters of this work have been organised in this way for different investigations and the complete research work is accompanied with experimental techniques and obtained results about pure and doped PVP films.
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