CHAPTER I

GENERAL

INTRODUCTION
1.1 INTRODUCTION

Since the formation of the earth over 4 billion years ago, in its giant laboratory "Nature", elements like carbon, hydrogen, oxygen and nitrogen have been combining to form complex molecules. Such a combination triggered off the most intriguing and fascinating process called life, the material basis for whose origin was a polymer. Thus, the human life was associated with polymers in the form of food, clothing, wood etc.

In the laboratory, polymers have obviously not been discovered overnight. They came out of long and persevering studies by a host of motivated scientists whose work has enriched human life. Today, the overall insight into polymer science and technology is so deep that a material scientist can create an almost limitless range of new materials. Just as an architect, a polymer scientist can produce innumerable plastics, rubbers, foams, fibres, etc. by judiciously combining various chemicals to react under desired conditions.

In recent times studies in polymers in the form of thin films have gained attention, due to their fascinating properties, disordered structure, potential applications and growing need of solid state devices. Polymer thin films are being used in a number of exploratory electronic technologies such as thin film triodes, thin film memory circuits, cryotron logic and associating storage circuits etc., apart from their use as insulators. Also, these are finding many technological applications such as electret
microphones, electrostatic voltage generators, air filters [1], IR detectors and transducers.

The physical properties of all polymers are not alike. The polymer properties depend on average molecular weight and molecular weight distribution of the polymer. But even these two parameters do not fully characterise a polymer. Two polymer samples can have the same chemical structure and almost similar molecular weight distributions, but may have different properties due to the difference in structure. All properties depend on intermolecular and intramolecular interactions of polymer chains in the aggregated state. Such interactions are caused by forces, such as dispersion force, induction force, dipole interaction and hydrogen bonding, acting within various parts of the same molecule as well as between the neighbouring molecules. The nature and the magnitude of such interactions force depend apart from the chemical characteristics of the monomer on the manner in which these monomeric units are linked with each other in the polymer [2], whereas the number and chemical nature of monomeric units forming the macromolecule gives an overall picture of the polymer chain, the manner in which they are linked gives the finer aspects of the picture. The number of monomeric units depicts the macrostructure and the mode of their interlinking indicates the microstructure of the polymer molecule. The polymers can be classified basing on the chemical structure; organic or inorganic, depending on whether the chain backbone is made
essentially of carbon-carbon (C-C) links or not. Polygermane is an inorganic polymer.

1.2 POLYMERIC MATERIALS

A polymer is a chemical substance whose molecules are large and consists of many small repeating units covalently bonded together. For instance, polyethylene consisting of essentially long chains of \((-\text{CH}_2-\text{CH}_2-)\) repeating units. The length of the polymer chain is specified by the number of repeat units in the chain and is called degree of polymerization which may vary over a wide range from few units to several thousand units in a chain. Unlike other materials, polymers do not have a unique molecular weight but are described in terms of average molecular weights.

Polymers are generally classified into two groups, viz., the non-polar and the polar polymers. The non-polar polymers have no permanent dipole moment whereas the polar polymers possess permanent dipole moment.

Polymers can exist as amorphous materials, as crystalline materials or a mixture of crystalline amorphous materials. Even highly crystalline polymers contain considerable amount of amorphous material. The properties of the polymer are determined by its structure, molecular weight, degree of crystallinity and chemical composition. The most prominent change in the physical properties of the polymers takes place at their glass transition temperature which is the characteristic property of an individual polymer.
Vast use of organic polymers has attracted scientists, engineers and technologists, all over the world, for studying their various, properties and characteristics. Synthesis, mixing and blending of different polymers have given them to play around with the characteristics to suit their specific requirements. Polymers are inexpensive and hence affordable by all. These days polymers have become the most important commodity without which it is difficult to sustain the life.

In early days, polymers in the form of plastics were regarded electrically as simply good insulators. But now, observations as substitutes in electrical response have shed a great deal of light on their molecular and charge particle dynamics. Such studies have enabled the development of materials which meet exacting electrical engineering requirements. Research along these lines has demonstrated the feasibility of obtaining materials with entirely novel set of properties. Also, such a research has led to the discovery of 'electret' displaying an unusual electrostatic phenomenon. Electrets made of different polymers have a very important use as transducers in electret microphones [3,4]. Subsequent researches led to permanent electrification of electrets. Such electrets are utilised in xerographic reproduction techniques [5], gas filters [6], relay switches [7], medical appliances like radiation dosimeters [8], optoelectronic devices like video/TV cameras [9], maritime devices like hyrophones [10], electret motors [11], electret generators [12], tachometers [13], vibrational fans, thin film transistors and thin film memory circuits [14,15] and many other areas.
Such scientific, technological and commercial applications have led to an explosive activities of research in polymers for different phenomena like charging and discharging, charge transport in polymer and the formation behaviour of electrets.

The polymers have contributed a great deal in electrical insulation, but high fields yield these polymers causing electrical breakdown. Although the causes of breakdown have been attempted to be explained in a number of ways in terms of models, understanding of high field transport in polymers is far behind and needs to be studied in greater details. Of the many factors which cause the electrical breakdown, composition of polymers, electrical stress applied, charge transport in the bulk and temperature are some of the important factors. There are ways and means of improving the performance of a polymer by mixing or blending/doping of other suitable polymers.

1.3 CHARGE STORAGE IN DIELECTRIC MATERIALS

Polymers or in general dielectrics when placed in an electric field undergo polarization, which involves the appearance of electronic charges on the surface of the dielectrics. These charges, known as induced charge, are not free and they generate a field in the dielectric called depolarization field whose direction is opposite to the direction of the field causing polarization.

Any material is made up of atoms and is treated as an electronic system consisting of positively charged nuclei surrounded by negatively
charged electron clouds. By the application of external field, electron cloud experiences a displacement relative to the nucleus, causing induced dipole moments in the material. This is called "electronic polarization (P_e)".

Molecules are made up of different atoms that contain charges with different signs. The external field acts upon them and causes their equilibrium position to change. This is an induced polarization known as "atomic polarization (P_1)".

If the centres of gravity of the positive and negative charges in a molecule, made up of different atom, do not overlap, then the molecule will have a permanent dipole moment. On application of external field, dipoles align themselves in the direction of the field which results in the appearance of "orientation" or "dipole polarization (P_0)".

The above mechanisms of polarization are due to the charges that are locally bound in atoms or in molecules. But the free charge carriers which are present in the bulk of the material displace themselves in the dielectric on the application of the electric field, causing various types of polarization. In the dielectric the intrinsic charges during their motion may be trapped at some centres such as grain boundaries, defects, etc. and hence it may result in the "Maxwell-Wagner or interfacial polarization (P_i)". The excess charges deposited or injected from the electrode results in space-charge polarization (P_s). A complete picture of different types of polarization is shown in Figure 1.1
Atomic polarization

Dipolar polarization

Interfacial polarization

Space polarization

External polarization

Fig. 1.1: Polarization mechanisms in dielectric materials
1.4 POLARIZATION IN POLYMERS

Application of electric field to a solid polymer material produces polarization phenomena which brings a net dipole moment over the bulk, in its direction. In case of non-polar materials, the dipole moment is due to the induced dipoles where as in a polar material it is due to the orientation of dipoles in the field direction.

1.4-1 DIELECTRIC DISPERSION PHENOMENA IN POLYMERS

Dielectric A.C. Bridge measurements have been used as an effective tool in characterizing the molecular motion and the dielectric relaxation behaviour in polymers [16-28]. A lot of work has been done on various dielectrics by this technique.

When a solid dielectric material is subjected to an alternating electric field, polarization phenomena occur and the resulting dielectric constant is given by -

\[ \varepsilon = \varepsilon' - i \varepsilon'' \] ...

(1.1)

\( \varepsilon' \) and \( \varepsilon'' \) are real and imaginary part of dielectric constant. Interfacial polarization is observed at very low frequencies. Dipolar polarization generally occurs in the frequency range \( 10 \) to \( 10^6 \) Hz. Atomic and electronic polarizations are observed in the IR and optical frequency ranges (Fig. 1.2).

The displacement of polar groups of polymers require some time and is thus dependent on the frequency and temperature which lead to different dispersion phenomena according to the segmental motion of the
Fig. 1.2: (a) Variation of permittivity with frequency for simple dielectric

(b) Variation of loss tangent with frequency for simple dielectric.
polymer chain or orientation of the polar side groups. Actually at frequencies and temperatures where dispersion occurs, only a part of the electrical energy is stored while some of it is dissipated as heat. The electrical energy stored per cycle is proportional to the real part of the permittivity and the energy loss per cycle is proportional to the imaginary part of permittivity. The loss factor exhibits a maximum at frequencies at which dielectric permittivity $\varepsilon'$ shows a dispersion (Fig. 1.3).

Technique employed for the characterization of relaxations in polymers influences the molecules of a polymer in a different way and thus the response of a system to different stimuli may be very different.

1.4-2 FACTORS AFFECTING DIELECTRIC RELAXATION BEHAVIOUR OF POLYMERS

(a) Effect of polar group

The $\alpha$-relaxation is basically dependent on the intra and inter molecular interactions. The greater the inter molecular interaction, the less mobile are the molecules and the higher is the relaxation temperature at which maximum loss occurs and larger is the relaxation time. Exchange of non polar substitutes increases dipole-dipole interaction.

(b) Effect of substituents

Introduction of very bulky substituents into the side chains or increasing the side chains decreases the mobility sharply.

(c) Effect of side group isomerism

In case of isomers, magnitude of $\alpha$ and $\beta$ relaxation are different.
Fig. 1.3 Behavior of dielectric constant ($\varepsilon'$) and loss factor ($\varepsilon''$) for polar polymers as a function of frequency (broadening of loss curve is caused by multiple relaxation times and is shown by the dotted line).

- $\varepsilon_0$ - Static dielectric constant
- $\varepsilon_\infty$ - High frequency dielectric constant
- $\tau$ - Dielectric relaxation time.
- 1 - Dipole contribution
- 2 - Electronic contribution
(d) **Effect of stereoregularity**

The dielectric properties of polymers are substantially dependent on the stereoregular nature of the polymer, because the percentage, the length and quantitative proportion of syndiotactic and isotactic sections have a significant effect on the molecular mobility of polymers.

(e) **Effect of plasticizers**

Dielectric relaxation of polymers shift towards lower temperature side on the addition of plasticizers. This is because plasticizers (i) increase molecular mobility, (ii) increase free volume, (iii) decrease $T_g$ of the polymers.

(f) **Effect of crosslinking**

Cross linking always decreases molecular mobility and increases temperature and relaxation time of $\alpha$ process.

(g) **Effect of copolymerization**

Dielectric properties of copolymers vary according to the composition and the ratio of monomeric units.

(h) **Effect of pressure**

Pressure influences the relaxation time of the process in which the intermolecular interaction plays an important role.

1.5 **THE ELECTRET STATE IN POLYMERS**

Here, we discuss some important aspects of electrets and types of electrets.
When a dielectric or polymer piece is subjected to an electric field, the polymer piece exhibits electrical charge storage even after the applied field is removed. This charge is temporary in nature and decays with respect to time. Such a dielectric piece is known as the electret.

The electret charge may consist of 'real' charge, such as surface-charge layer or space charge; it may be a 'true' polarisation; or it may be a combination of these. This is shown in Fig. 1.3a.

While a true polarisation is usually a frozen-in alignment of dipoles, the real charges comprise of layers of trapped positive and negative carriers, often positioned at or near the two surfaces of the dielectric respectively. On metallised electrets, a compensation charge may residue on the electrode, unable to cross the energy barrier between metal and dielectric. Mostly, the net charge on an electret is zero or close to zero and its fields are due to charge separation and not caused by a net charge [29].

An electret not covered by metal electrodes produce an external electrostatic field if its polarisation and real charges do not compensate each other everywhere in the dielectric. Such an electret, thus in a sense, is the electrostatic analogue of a permanent magnet, although electret properties may be caused by polar and monopolar charge while magnetic properties are only due to magnetic dipoles.

An electret can be simply defined as a dielectric material which possesses a semi-permanent polarization [30-31]. The term electret is an electric counterpart of a magnet since they carry opposite charge on either
Fig. 1.3 An dielectric with various types of charges
side. Many types of electrets have been discovered and the names of these electrets are given on the basis of the method by which they are prepared. They are termoelectrets [32-35], photoelectrets [36-38], thermophotoelectrets [39-40], radioelectrets [41-42], magnetoelectrets [43-45], prepared under the simultaneous treatment of electric field and heat; electric field and light; electric field, heat and light; electric field and high energy radiations; magnetic field and heat respectively. The thesis deals only with termoelectrets.

Heaviside [46] was the first who got the idea of an electret. Eguchi [32-33] made the first thermoelectret by using a mixture of carnauba wax, bees wax and resin. He melted equal parts of carnauba wax and resin, along with some bees wax, and permitted the substance to solidify in a strong electric field. He found that disks prepared in this way exhibited a strong negative charge on the face which had been in contact with the anode and vice-versa. Later Gemant [47] introduced the concepts of "heterocharge" and "homocharge". According to Gemant's terminology, a charge on the electret of the same sign is the polarity of the adjacent electrode is called a homocharge, and a charge of opposite sign to the polarity of the forming electrode is called a heterocharge.

Mikolo [48] classified electrets into two groups, viz., those comparatively high conductivity yielding heterocharges only and those of much lower conductivity capable of developing homocharge.
The first attempt towards the theory of the electret was made by Adams [49] and subsequently developed by Gemant [47], Gross [50-51] and Perlman and Meurier [52].

Electret research gradually moved to organic substances and polymers where fundamental solid state properties could be correlated with electret behaviour [30,53,54]. Recently, electret phenomena has received more attention because of their applications in electret microphones [55], electrophotography [56], electrostatic voltage generators [57], radiation dosimeters [58,59], etc.

A large number of workers have reported the electret effect in inorganic solids [60-62], organic solids [63-66], liquid crystals [67,68], polar polymers [69-76], non-polar polymers [77-79], copolymers [80-82] and biopolymers [83-85] etc. This literature on electret has been reviewed by Gutman [86] and Johnson [87].

1.5-1 EFFECT OF DIFFERENT FACTORS ON ELECTRET STATE

Electret state of polymeric materials is highly sensitive to the environmental conditions such as humidity, pressure, high energy radiations, etc. The charge of an electret also depends on the thickness of the dielectric and electrode materials used during the preparation of thermoelectret. Vander-schuuren [88] and others [89-91] have shown that when an electret is exposed to high humid atmosphere, their charge decreases. Several workers [92-94] have found that thermoelectret charge
decreases with lowering the pressure. It is proposed that charge decrease is either due to desorption of charge sources from the surface of electret or due to spark breakdown at the electret surface [93,94].

Grass and DeMoraes [58] observed that on exposing a thermoelectret to Co$^{60}$ γ-rays [89], its charge decreases. Linear relationship has been established between the loss of charge and dosage of high energy radiation [58,95] and this effect has been explained on the basis of degradation of cross linking of the polymer on irradiation.

Khanna [96] and Perlman [97] have found that the magnitude of charge of an electret increases with its thickness. There are number of observations to the fact that electrode material used in the formation of electret plays an important role in the electret [98-100]. A good correlation between the surface charge and the work-function of the metal used as electrode has been reported [97,98].

1.5-2 INVESTIGATION OF ELECTRET STATE

Measurement of charge has a special importance in the study of electret phenomena. Many techniques such as induction method [33,47,92], dissectible capacitor [70-101] generating voltmeter method [102], vibrating electrode method [103], electron beam method [104], etc. have been employed. However, none of these methods could provide a deeper insight into the electret phenomena. A significant breakthrough was achieved in the study of electret phenomena with the discovery of heat
accelerated decay of electret charges. It is known that a dielectret medium takes a long time to relax to the steady state at room temperature because at such low temperature the dipoles and charges remain virtually immobile.

Gray in 1732 [105] observed the "perpetual attractive power" in a number of dielectrics particularly in waxes, resins and sulphur. Much later in 1839, Faraday [106] theorised the electret properties due to application of an external electric field when he referred to a dielectric which retains all electric moment after externally applied field was switched off. Heaviside [107] in 1892 coined it as an 'electret'.

Systematic research into electric properties began in 1919 when Japanese Physicist Eguchi [108] formed electrets from the same materials used by Gray employing the thermal method consisting of the application of an electrical field to the cooling melt. He found that the dielectrics exhibited charges on their two surfaces which changed sign after a few days from a polarity opposite to one that of the adjacent forming electrode. The charges were later named 'heterocharge' and 'homocharge', respectively, indicating their relation to the forming electrode.

Subsequently, research on photoconductors image formation by Carlson [109] led to the development of xerography. Further studies in this field were carried out by Nadjakoff [110] and Fridkin and Zheludev [111]. Selenyi's work was related with the study of breakdown of thermal charge release. During the development of xerography, a simple charging method
related to Selenyi's ion-beam technique depending on the application of corona discharge was used [109,112] and later extended to thin films [113]. In 1937, Gross [114] used the Boltzmann-Hopkinson superposition principle valid for linear dielectrics to develop a mathematical formalism for the discharge of electrode charges over the internal resistance of dielectric and for the decay of polarisation in dielectric. Further insight into the nature of charge retention was achieved from the studies of Gerson and Rohrbaugh [115] which indicated that carrier trapping could play an important role in electrets.

It is interesting to note that the first ever electret device offered for commercial use was thick electret microphone under the name "No Voltage Veloton". Its large scale application came during World War II in Japanese field equipment.

Randall and Wilkins [116] used the thermal depolarisation method for the first time for investigation of phosphorescence. In 1964, this method was applied to the case of dipole polarisation by Bucci and coworkers [117,118] who suggested the name Ionic Thermal Conductivity (ITC). It allows determination of activation energy and dipole relaxation time from the measurement of depolarisation currents obtained on linear heating of dielectric. A host of recent work has been devoted to the application of ITC methods or related thermally stimulated current techniques for investigating dipolar and space-charge respectively [119-123]. These studies have culminated in a very comprehensive treatise by van Turnhout [124]. The
early literature on electrets was reviewed by several authors notably by Fridkin and Zheludev [111] and Gross [125]. Lupu et al. [126] have carried out study of electret state on polyvinyl chloride (PVC). In the last decade phenomenal progress has been made in the field of electrets; more efficient charging techniques have been developed, new materials capable of storing more charge for considerably longer duration have been identified and synthesised, techniques with very good resolution for precise determination of charge centroid and its distribution in the material bulk have been devised, etc. [127,128].

1.5-3 TYPES OF ELECTRETS

The classical electrets were made of thick plates of carnuba wax. Presently, thin films made of polymers like teflon materials, polyfluoroethylene propylene (FEP), polvvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFF), polypropylene, polyethylene, etc. are utilised in making electrets [129-134]. Examples of different nonmetallised and metallised electrets are shown in Fig. 1.4. Various types of electrets are enumerated below:

(a) **Thermoelectret**: It is obtained by polarising a dielectric by simultaneous application of heat and electric field [135,136].

(b) **Electroelectret**: An electret prepared at room temperature by applying high electric field is called an electroelectret [137-139].
(a) A nonmetallised monocharge electret

(b) One-sided metallised electret with surface and space charges

(c) One-sided metallised electret with surface charges and charges displaced within domain

(d) Two-sided metallised electret with dipolar and space charges

Fig. 1.4: Example of electrets
(c) **Radioelectret**: An electret prepared under the simultaneous action of high energy radiation such as X-rays, β-rays, γ-rays, monoenergetic electron beams, etc. and an electric field is called a radioelectret. These are less stable comparatively [140-142].

(d) **Photoelectret**: An electret prepared by charging by an electric field under exposure to ultraviolet or visible radiation with enough energy to release carriers (either band to band transition or excitation out of deep traps). Such electret remains polarised for a much longer time when kept in dark. Photoelectrets were first prepared by Nadzhakov [143,144] and later studied extensively by Fridkin and Zheludev [145] and Kallmann et al. [146-147].

(e) **Thermophotoelectret**: A photoconducting dielectric polarised at high temperature by light radiation of high energy under an applied electric field results into a thermophotoelectret. This was first prepared by Padgett [148].

(f) **Magnetoelectret**: It is obtained by cooling the softened or molten dielectric in a magnetic field. Bhatnagar developed this for the first time [149-151].

(g) **Autophotoelectret**: Recently, Andreich [152] has observed voltage which increases exponentially with intensity of light and approaches nearly 1.0 V, when 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 was termed as an autophotoelectret, since this polarisation is achieved without applying any field.

(h) **Mechanoelectret**: An electret prepared by charging a dielectric by a mechanical effect, i.e., deformation or friction is called mechanoelectret [153].

(i) **Pseudoelectret**: These are prepared by polarising a dielectric under the action of an ionising irradiation such as γ-rays without the application of an electric field [154].

(j) **Cathodelectret**: These electrets are obtained by charging a dielectric under the simultaneous action of electric field and a beam of electrons [155-156].

(k) **Bioelectret**: Electrets prepared from biological materials and biopolymers are called bioelectrets [157].

(l) **Metal polymer electret**: Recently, a new type of electret has been formed by heat treatment of polymer layer sandwiched between two short-circuited electrodes in metal-1 polymer-metal-2 configuration. The new type of electret state has been called metal polymer electret and has been successfully used in bearings, seal corrosion durability systems, machine behaviour controls and so on [158,159].

### 1.6 MECHANISM OF CHARGING

Charging or polarisation of a dielectric for preparing an electret entails simultaneous occurrence of the following phenomena; namely,
microscopic displacement of charges, dipole orientation, macroscopic space charge polarisation, barrier polarisation, and external polarisation.

1.6-1 MICROSCOPIC DISPLACEMENT OF CHARGES

When an electric field is applied to the dielectric, it produces a small movement of charges within the atoms and molecules of a dielectric, displacing the negative electron cloud relative to the positive nucleus generating a small dipole moment. This type of polarisation is called microscopic or electronic polarisation or deformation [Fig. 1.5(a)] and its time scale cannot be changed from outside.

1.6-2 DIPOLE POLARISATION

Many dielectric including polymers have a permanent dipole moment. This dipole moment may be a deliberate part of the structure (carboxylic group, chlorinated hydrocarbons, etc.) or may be accidental or unavoidable impurities (carbonyl group in polyethylene). Under normal temperatures, the dipoles are randomly arranged and the resultant dipole moment is zero. An external electric field when applied, tends to orient these elementary dipoles along its own direction producing an electric moment of the whole body. This is called dipolar polarisation and occurs in the entire volume [Fig. 1.5(b)].

1.6-3 MACROSCOPIC SPACE CHARGE POLARISATION

All dielectrics contain a small number of free charges, i.e. ions or electrons or both. These free charges are randomly distributed and there is
(a) Microscopic polarisation

(b) Dipole polarisation

(c) Space charge polarisation

(d) Barrier polarisation

(e) External polarisation

**Fig. 1.5**: Different types of polarisation
no net dipole moment when one arranges all the charges. In such materials, the applied electric field causes displacement of the positive and negative charges, resulting in accumulation of the cations near the cathode and of the anions near the anode. If a space charge of opposite sign develops in front of an electrode, the potential distribution deviates from the linear nature; in that case, the potential drop near the electrode is larger than in the centre. This effect results into a macroscopic space charge potential [Fig. 1.5(c)].

1.6-4 BARRIER POLARISATION

In a heterogeneous dielectric, often there exists some microscopic domains or grains separated by highly resistive interfaces. In such dielectrics, the free charge carriers can move relatively freely only within the grains. This results in piling up of free charges along the barriers causing in barrier polarisation [Fig. 1.5(d)].

1.6-5 EXTERNAL POLARISATION

A dielectric can also be charged by direct injection of charge carriers when a large electric field of the order of $10^5 \text{ V cm}^{-1}$ is applied between the electrodes in intimate contact with it. Alternatively, charges may be sprayed or deposited upon the dielectric if a high voltage electrode is in contact with the dielectric and a corona discharge occurs either in the neighbouring air space at the edges of the arrangement or in the thin air space between the
electrodes and dielectric. The deposition or injection of charge on either surface produces an external polarisation [Fig. 1.5(e)].

1.7 CHARGING TECHNIQUES

There are various techniques for polarisation or charging of dielectrics, viz., thermal method, corona and other charging methods, liquid contact method, electron beam method, and photoelectric method.

1.7-1 THERMAL METHOD

In this method, an electric field is applied on a polymeric dielectric at a high temperature and thereafter it is cooled down while the field is still applied.

Eguchi [160,161] used this method for polarising a dielectric for preparing the thermoelectret. Dielectric relaxation is due to hindrances of the motions of the permanent dipoles and free charges by frictional forces. Therefore, a polar polymer is not immediately affected by the application or removal of an electric field. Only a part of its polarisation which originates from electron and ion displacement within the atoms or molecules responds almost instantaneously. Since friction is exponentially proportional to the temperature, the response time of permanent dipoles and free charges changes remarkably with temperature. By heating, the response time is accelerated and by cooling it is slowed down. In polymers, the response time changes sharply near the glass transition temperature (T_g), where the conformational motion of the main chain segments set in. Hence, polymers having their T_g above room temperature can be charged permanently by
subjecting them to a field-temperature treatment. A schematic arrangement of the method based on the above principle is depicted in Fig. 1.6.

The material is heated above the $T_g$, and is kept at this temperature for sometime (say 30-60 minutes) to reach the thermal equilibrium due to the motion of permanent dipoles and free charges. Thereafter, at the time $t_0$, an electric field of the order of $10^4 \text{ V cm}^{-1}$ or larger is applied which causes an alignment of permanent dipoles and drift of free charges to the electrodes. After some time (say approximately an hour), at the time $t_f$, the material is cooled to the room temperature $T_r$ while the electric field is still there.

1.7-2 ELECTRON BEAM METHOD

The sample polymer is charged by injection of electron of proper energy into it. When the range of electron striking the dielectric (here a polymer piece), is less than the thickness of the polymer sample, the electrons are trapped inside and sample gets charged. If the range of the electrons is greater than the polymer sample thickness, charging occurs mainly due to the secondary emission of back scattering.

1.7-3 PHOTOELECTRIC METHOD

When inorganic photoconductors like PVK-TNF are irradiated with ultraviolet or visible light under an applied field, a permanent polarisation is achieved due to the generation of charge carriers in the sample. These carriers are then displaced by the applied field eventually trapped at the
Fig. 1.6: Field temperature programme for the formation of a polymer electret
dielectric electrode interface or in the volume resulting in a two separate charge clouds of opposite sign or a single charge cloud.

1.8 TECHNIQUES FOR INVESTIGATION OF ELECTRICAL CHARACTERISTICS OF POLYMERS

The knowledge of electrical characteristics, such as type and origin of charge carriers, their storage and transport in polymer are extremely important for making stable and useful electrets. Studies of a number of methods have been carried out, viz. capacitive probe [162-165], dynamic capacitor [166,167], compensation method [168,169], split Faraday cup [170], sectioning and planning methods [171,172], light radiation release methods [173], indirect methods [174,175], thermally stimulated discharge [176], combined induction depolarisation method [177], etc. Some methods with very good resolution efficiency of determining the type and distribution of charge, such as thermal pulse method [178], pressure pulse method [179] etc. have also been devised in the last decade. However, accurate information about the electrical characteristics can be easily obtained by the following important experimental techniques:

(a) Dark conduction current measurements,
(b) Transient current measurements,
(c) Thermally stimulated discharge current (TSDC) measurements, and
(d) Dielectric measurements.
1.8(a) TRANSIENT CURRENT MEASUREMENTS

The transient current phenomena have been studied by many investigators like Spear [180], Kepler [181], Davies [182] etc. Spear carried out studies on selenium films where he measured the transient time of charge carriers and hole mobility. Kepler utilised a light pulse technique to measure the charge carrier mobility in anthracene crystals. Davies measured directly contacted electron transfer to polyethylene from a variety of metals.

Thielen, Vanderschueren et al. [183,184] carried out studies on several polymers like PMMA, PEMA, PVC, PS, etc. and came to the conclusion that at temperature lower than the glass transition temperature under low to moderate fields, the transient currents are essentially governed by dipolar mechanisms and as such are very much dependent on the temperature ranges of various molecular relaxation processes of the material under investigation.

Transient currents in dielectrics observed upon the application of a step voltage have been studied extensively to give an insight into the polarization processes in the materials undertaken for the study. It is generally accepted that the transient currents in an insulating material, on the application or removal of a step voltage, may be attributed to one or more of the following mechanisms: (i) electrode polarization, (ii) dipole orientation, (iii) charge storage leading to trapped space-charge effects, (iv) tunnelling of charge from the electrodes to empty traps, (v) hoping of charge carriers through localized states. The above processes have been reviewed by several scientists and it
has been established that the observed time dependence alone does not permit any discrimination to be made between various mechanisms. The argument for and against a particular mechanism is to be found by considering the variation of transient currents on various experimental parameters also, such as temperature, field and frequency. Polymers contain a large number of structural disorders and, therefore, contain discrete traps levels in their bulk. The role of various polarization processes and their relative contributions to the electret state of the polymer is not yet fully understood. Particularly, the space charge structure including the trap distribution of energy and also over the volume of the polymer, are still to be well understood. Such informations are also being obtained by carrying out the measurements of absorption and short circuit isothermal desorption (discharging) currents at various temperatures. The d.c. step response technique in which the current response is measured as a function of time after d.c. voltage is applied to, or removed from the sample, is the isothermal analogue of TSDC measurement, as it determines the discharging current at constant temperatures instead of varying temperatures.

Polyvinylidene fluoride (PVDF) is a polar polymer that exhibits excellent chemical resistance and good mechanical properties. Inspite of its activeness for many applications, the conduction mechanism is presently not well understood. In the present thesis, we have attempted to identify the nature of the transient conduction and thermally stimulated discharge currents in pure polyvinyl films by comparing the observed dependence on
parameters such as electric field, electrode material, temperature, time and relation between the charge and discharge currents, in the light of characteristic features of various proposed mechanisms.

1.8(a)-1 TRANSIENT CURRENTS IN CHARGING AND DISCHARGING MODES

The charging or absorption current is obtained immediately after the application of a step voltage on a dielectric specimen, while the discharging or desorption current is obtained on removal of the step voltage provided the temperature is kept constant. Both the charging and discharging currents decay approximately as $t^{-n}$, where $t$ is the time elapsed after the application or removal of the step voltage, and the exponent $n$ is a constant depending upon the properties of the material and the experimental conditions. Charging current decays with time until a steady state current, usually known as conduction current, is reached. On the other hand, isothermal discharging current decays for a long time depending upon the internal phenomena taking place irrespective of the steady state current level.

The nature of transient charging and discharging currents differ from material to material depending upon the mechanisms involved. The origin of these transient currents is still a subject of much controversy and a large number of mechanisms have been proposed. The combined effect of one or more may be responsible for the observed decay pattern of the transient currents. The discharging current is usually mirror image of charging current, provided that a steady state current does not occur. Hence,
discharging currents can yield information about charging processes even when the corresponding charging current is masked by conduction current at charging. Quantitative as well as qualitative analysis can be made on comparing the experimental values of the decay exponent obtained under various experimental conditions.

This technique is time consuming hence it is not very popular, but results of this long time technique are most consistent than any other technique because the electrical disturbances and instantaneous variations in other experimental parameters affect these experiments much less as compared to those involved in the fast discharge processes.

The origin of isothermal charging and discharging currents has not been clearly accounted for in most of the dielectric materials because of lack of experimental data covering an adequate range of experimental parameters, i.e., field, temperature, electrode material, etc. However, the results are available for many materials although covering very few experimental conditions, which are insufficient to yield clear and firm conclusions.

In view of this it becomes worthwhile to undertake a detailed study of transient currents and to correlate the results obtained with those of other studies. This is expected to give a proper clarification of the transient response of charging and discharging in polymers, which is of prime importance for the analysis of the electret effect in polymer dielectrics.
1.8(b) DARK CONDUCTION CURRENTS - AN INTRODUCTION

It was not many years ago when the interest in the electrical properties of polymers was effectively limited to their electrical insulating ability. This situation has changed very markedly in recent years. The replacement of inorganic semiconductors and metals by organic macromolecules has recently been termed "Molecular Electronics". The large number of atoms per organic molecule makes a great variety of modifications possible and therefore subtle variation in electrical properties should be possible.

The conduction in polymers is a complex process and takes place due to intrinsic charge carrier generation and charge carrier injection from the electrode contacts at high electric field. The theoretical and experimental analysis have been thoroughly carried out by Kao and Hwang [185]. The band theory, mobility theory, carrier production and transport mechanisms have been dealt with by Wintle in his monograph [186]. The review article on electrical conduction by Adamec and Calderwood [187] takes up the time dependence of the conductivity of PVC, PMMA, PC and epoxynovalac resin and gives a theory for the origin of free charge carriers.

Recent work has been done by Molitan [188] who gave the theoretical model in terms of the SP₂ dangling-band states after carrying out conduction measurements on poly(paraphenylene). Chandra and Chandra [189] studied the mixed anion effect in polyethylene oxide-based sodium-ion-conducting polymer electrolytes. Leda et al. [190] in their review
article have in detail takes up the high field conduction and breakdown of low density polyethylene, polystyrene, polyisobutylene, polyvinyl chloride, polymethyl methacrylate and elongated high density polyethylene.

The process of charge transport in polymeric semiconductors is a complex phenomena. The actual nature of conduction mechanism in a variety of polymeric films is still a matter of speculation. Although the body of experimental information on the study of electronic properties of polymeric materials is enormous, no comprehensive theoretical approach, which can adequately interpret all observations and measurements, so far has been proposed. The complexity and chemical structure of numerous long chain high mol. wt. polymers make it difficult to consider the transport behaviour in terms of generalised transport theory. In most cases models derived for conventional semiconductors are applied to polymeric systems.

The electrical conductivity (\( \sigma \)) of a solid is defined [191] as the ratio of current density (\( J \)) to the electric field (\( F \)). The conventional measuring technique consists of applying a known voltage across a sample of known dimensions and determining the current in the external circuit.

\[
\text{Electrical conductivity} = \frac{\text{Current density (} J \text{)}}{\text{Electric Field (} F \text{)}} = \frac{\frac{\text{I}}{\text{A}}}{\text{V} / \text{d}} = \frac{\text{I} \text{d}}{\text{V} \text{A}}
\]

where \( d \) and \( A \) are thickness and area of the sample, respectively.

The magnitude of conductivity depends on the number of charge carriers and their mobility. The mobility of the carriers is the measure of the case with which the carrier can pass from one molecule to another. In view
of the relatively large intermolecular spacings common to polymeric systems, mobility values are several order below to those of conventional semiconductors.

The charge carriers may be generated intrinsically or from impurities, in which case, they may be electrons, holes or ions. Alternatively, holes and electrons may be injected from the electrodes. Therefore, conduction may be of two types - ionic or electronic, i.e., current carriers are free ions or electrons.

A semiconductor is p-type with n-type depending on whether it is having excess of holes or electrons. The charge carriers are called majority or minority carriers depending on which predominates.

In general, polymers are insulating materials having conductivities ranging from $10^{-10}$ S/cm for polyvinyl chloride to $10^{-18}$ S/cm for polytetrafluoroethylene, which are many orders of magnitude below the conductivities associated with metals (Fig. 1.7).

1.8(b)-1 ELECTRICAL CONDUCTION IN POLYMERS - A BRIEF SURVEY

Saegusa [192] in 1926 was the first to measure the conductivity in paraffin wax as a function of temperature. Clark and Williams [193] in 1933 published an excellent work on the conductivity of organic solids and they were the first to establish unequivocally the exponential relation between conductivity and temperature in these materials. Fuoss [194] did similar
**Fig. 1.7:** Conductivity of various metallic, semiconductor and insulating materials.
work on a number of polymers and supported the exponential relation of Clark and Williams [193]. In 1954, Akamatu et al. [194,195] observed for the first time that some solid organic charge transfer complexes display a surprisingly high conductivity. A significant breakthrough in the study of electrical properties of organic solids occurred with the discovery of tetracyanoquinodimethane (TCNQ) ion radical salts [196]. These salts have general stoichiometric formula \( M^+ (\text{TCNQ})_n^- \) and depending on \( M \) and \( n \), the properties of these materials have been observed to vary from those of insulators to those of metals. Highly conducting polymers have been prepared by utilizing some of the knowledge gained from the studies of solid charge transfer complexes. In 1977, Shirakawa et al. [197] showed that highly conductive polymers could be prepared by adding small quantities of either electron donating or electron accepting species to conjugated polymers. The discovery [198] of poly(sulphur nitride) in 1973 as an intrinsically conducting polymer gave a tremendous boost for the search of other polymers.

The very exciting possibility for polymers has been discovered by Little [199]. He proposed that it might be possible to prepare polymers that are superconductors and these polymers could have superconducting transition temperature well above the room temperature.

All these results and speculations have led to an increasing tempo in research on electrical properties of polymers. A large number of excellent reviews of this work have been published. A particular mention should be
made about the works of Gutmann and Lyons [191], Meier [200], Kepler [201], Bogulsavskii and Vanikov [202], Seanor [203] and Skotheim [204].

A wealth of information on the process of charge transport in polymeric films can be obtained from the measurement of electrical properties as a function of temperature, electric field and frequency. There is ample evidence for ionic and electronic conduction in a variety of polymers. Von Roggen [205] and others [206-208] have reported that conduction in polymers is ionic in nature. The conduction in polyvinylchloride is reported to be ionic and is attributed to $\text{H}^+$ and $\text{Cl}^-$ ions [208]. Few workers [209,210] have suggested protonic conduction in polyamides.

Electronic conduction in polymers has been extensively studied [211-213]. Myioshi and Chino proposed electronic conduction in polyethylene [213]. A number of authors [214-218] have studied the conductivity of biopolymers. A complication in the study of biopolymers is that they contain a large amount of water. If before the measurement, the biopolymer is dried, many of its properties become completely different from those which it had in the living organism. In the study of proteins containing water it is difficult to distinguish the electronic conductivity from ionic conductivity. Consequently, the results of experimental studies carried out with different proteins are extremely contradictory. Some authors state that ionic [216] or protonic [217] conduction exists in a protein, other have concluded that proteins are electronic semiconductors [218].
Several mechanisms such as tunnelling, hopping, Richardson-Schottky emission, Poole-Frenkel effect, space charge limited current, etc. have been proposed to explain the transport of charge carriers in polymeric films. The theoretical details of these mechanisms are given in Chapter III.

1.8(c) THERMALLY STIMULATED DISCHARGE CURRENT (TSDC) MEASUREMENTS

Polymers are generally good dielectrics which are capable of storing charge in them permanently, when subjected to field-temperature treatment and are known as thermoelectrets. When such thermoelectrets are subjected to a programmed heat treatment, they give rise to a current in the external circuit which is known as thermally stimulated discharge current (TSDC). TSDC is an accurate, sensitive and convenient method for studying the charging and discharging processes in dielectrics. These currents are due to the dielectric relaxation behaviour and motion of free charges in the polymers. Hence, TSDC technique can be used to understand the low frequency dielectric behaviour and relaxation processes on the atomic scale. Because of the high sensitivity of the technique, it is also used to investigate the low concentration of the dipolar impurities, formation and aggregation of impurity-vacancy complexes, phase transitions, photographic response of silver halide, etc.

Thermally stimulated discharge current (TSD) technique is a powerful method to gain an insight into the mechanisms of charge migration and dipolar motions. The process of TSD measurement involves
the poling of the polymer film for certain values of poling parameters such as poling field \( E_p \), poling temperature \( T_p \) and poling time \( t_p \) and its heating in a specially designed cell, with a constant heating rate. The details of each step involved in this measurement are discussed below.

1.8(d) DIELECTRIC MEASUREMENT

The dielectric behaviour of polymeric films is of direct interest to both the basic studies of electrical conduction through such films and their application in capacitors for microelectronics. To obtain high values of capacitance the dielectric constant should be high and the thickness be small. Due to the difficulty of obtaining structurally continuous and stable ultrathin films, capacitor applications are generally limited to thick films. The evaluation of the dielectric properties of insulator films is carried out by measuring simultaneously the capacitance and the dissipation factor over a wide range of frequencies and temperature [218-a].

The most important property of dielectrics is their ability to be polarised under the action of an external electric field. The basic parameter of a dielectric describing its properties from the viewpoint of the process of its polarization or propagation of electromagnetic waves in it, or more generally from the viewpoint of the processes of its interaction with an electric field is the permittivity. Permittivity (dielectric constant) is the number which shows by how many times the capacitance of a vacuum capacitor will increase if the capacitor is filled with the dielectric without
changing its dimensions and shape. It is a macroscopic parameter of a
dielectric which reflects the properties of a given substance in a sufficiently
large volume but not the properties of the separate atoms and molecules in
the substance. As all the other electrical parameters of dielectrics, the
permittivity depends on the changeable external factors such as the
frequency of voltage applied to the dielectric, temperature, pressure,
humidity, etc. In a number of cases these dependences are of paramount
practical importance [218b-d].

When an electric field acts on matter, the latter dissipates a certain
quantity of electric energy that transforms into heat energy. This
phenomenon is known as 'the expense' or 'loss' of power, meaning an
average electric power dissipated in matter during a certain interval of time.
As distinct from conductors, most of the dielectrics display a characteristic
feature: under a given voltage the dissipation of power in these dielectrics
depends on the voltage frequency; the expense of power at an alternating
voltage is markedly higher than at a direct voltage, and rapidly grows with
increase in frequency, voltage and capacitance, and also depends on the
material of the dielectric. The amount of power losses in a dielectric under
the action of the voltage applied to it is commonly known as dielectric
losses. This is the general term determining the loss of power in an electric
insulation both at a direct and an alternating voltage. The dielectric loss
angle is an important parameter both for the material of a dielectric and an
insulated portion. All other conditions being equal, the dielectric losses
grow with the so called loss tangent (tan δ). Sometimes the quality factor of an insulation portion is determined, i.e. the value reciprocal of the loss tangent.

A number of reports [218e-h] on the dielectric properties of polymer films have been published. The value of tan δ exhibits a maximum at a frequency at which dielectric permittivity (ε) shows dispersion. Some polymers show polarization when compressed or distorted. The general theory of dielectric dispersion has already been elaborated. It follows from general considerations that dielectric dispersion is analogous to mechanical dispersion and similar mathematical treatment may be used to describe both these phenomena.

The maxima in dielectric loss occurs at temperatures at which motion of large segments of the main chain or different polar side groups begins. Thus, these temperatures are related to the temperature at which the same transitions are observed in mechanical studies (at the same frequency). These are, however, cases in which transition temperature differ considerably. This may result from different fields acting in both these cases. Dielectric behaviour of high polymers is generally characterized by the distribution of relaxation times. These distributions may be obtained by the procedure applied to obtain distributions of mechanical relaxation times. In many cases they are similar but not identical.
Notable progress has been made in the understanding of the mechanism of dielectric dispersion. Several phenomenological models [218i,j] have been proposed relating the main relaxation to free volume. Petrosian [218k] deduced dielectric parameters for a polymer system using the general dielectric loss theory and found values consistent with those derived from experimental results. Dielectric behaviour of amorphous polymer systems in macroscopic and molecular terms was analysed by Cook et al. [218l]. Pollock [218m] developed a theory of dielectric constants arising from electron localized states which contribute to elucidation of conductivity. Ishida [218n] reviewed the effects of stereoregularity, pressure, crystallinity, plasticizers, and so electric field an absorption due to motions of molecular chain segments (\(\alpha_c\)), micro-Brownian motion of main chain segments in amorphous region (\(\alpha_a\)), and local relaxation (\(\beta\)).

1.9 AIM AND SCOPE OF THE PRESENT INVESTIGATION

Polymers are widely used in many areas of electrical and electronic devices in diverse applications because of their extremely small size, abundance, diversity, ease of processing and fabrication. These materials are unique because of the range of structural forms that can be synthesized and the way in which changes can be made in the structure in a local or a general way.

It can be observed from the review of the available literature that charge storage phenomena is rather sensitive to the structure of the electret forming material. It has been reported that even the electret state in
a polymer can be produced not only by conventional methods, but also by merely bringing about some structural changes in the electret forming material. During the past few years, therefore, main efforts have been directed towards understanding the relationship between the structure and properties of the electret forming materials.

1.10 POLYMER USED - POLY(VINYLIDENE FLUORIDE)

The molecular origin of the transition is not the same for all the polymers. A brief description of various relaxations of poly(vinylidene fluoride) (PVDF) is given below:

(A) Relaxations in PVDF:

Lovinger [218(i)] have investigated relaxation in PVDF by studying dielectric behaviour through mechanical, NMR and piezoelectric investigations [218(i)]. Dielectric studies of PVDF in the frequency range (1 Hz - 1 MHz) shows three transitions corresponding to the $\alpha^-$, $\beta^-$ and $\gamma^-$ relaxation.

$\alpha$-relaxation: Peterlin et al. [218 ii,iii] have investigated $\alpha$-relaxation and attributed it to amorphous regions. However, Yano [218iv], Sasabe et al. [218v] and Osaki [218vi] have attributed these $\alpha$-relaxation to crystalline regions. Later Nakagawa et al. [218 vii] and Yano [218 viii] offered convincing evidence of a crystalline $\alpha$-transition. This was confirmed by nuclear magnetic resonance studies by other workers [218ix].
**β-relaxation**: β-relaxation is attributed to micro-Brownian motion of amorphous segments [218vi,iix,x]. It is related to glass transition temperature and occurs around (−40°C).

**β'-relaxation**: The β'-relaxation has been reported to occur at 50°C. This occurs in amorphous region and has been attributed to chain fold motion [218ix].

**γ-relaxation**: The γ-relaxation has been observed at around −70°C. It is attributable to amorphous phase and is associated with chain relaxations in amorphous regions [218iii,ix].

Orientation and poling of PVDF have been found to influence its relaxation behaviour. Application of pressure increases the α-relaxation temperature. The intensity of α-relaxation is found to decrease by the process of poling and orientation. Yamada et al. [218x] have reported that a crystalline α-relaxation (α_c) at about 58°C in PVDF is intensified after drawing and annealing. This has been attributed to molecular motion of crystalline regions of a well defined β-phase PVDF. A transition around 70°C has been reported for PVDF-TrFe copolymer [218xi-xvi]. In case of composites, a transition around 80°C has been observed which was absent in pure PVDF. This indicates that the relaxation and transitions in PVDF are much more complicated and depend not only on thermal history of the sample but also varies with other factors such as constituent phases, pressure, poling, orientation and the composition of the sample.
1.10-1 PHYSICAL, CHEMICAL AND MORPHOLOGICAL PROPERTIES OF PVDF

PVDF is of fundamental interest for its different crystalline phases and phase transitions. PVDF can present five distinct crystalline structures depending on the formation conditions of the polymer. Four of these phases designated as $\alpha$, $\beta$, $\gamma$ and $\delta$ are respectively by form II, I, III and IV (or IIP) are stable at room temperatures, a fifth form, $\varepsilon$, could exist just below the melting point [219] (Fig. 1.8, 1.9).

The $\alpha$-phase of PVDF crystallizes directly from the melt [220]. The $\beta$-phase is normally obtained by mechanical deformation of $\alpha$-form [221]. The $\beta$-form may also be grown from solution under special conditions [222]. Growth from solutions such as dimethyl sulfoxide or dimethyl acetamide usually leads to $\gamma$ form [223].

PVDF is inherently polar. The hydrogen atoms are positively charged and the fluorine atoms negatively charged with respect to the carbon atom in the polymer. The net moment of a group of molecules in a liquid region of PVDF will be zero in the absence of an applied field because of the random orientation of individual dipoles. In the crystal, there are $\beta$ and $\gamma$ (Form I and III) phase where the molecules are reported to form a planar zig-zag (all trans) conformation [224] with the dipole moments parallel in the unit cell. $\beta$ and $\gamma$ crystal forms of PVDF are, therefore, inherently polar. The $\gamma$ phase is a polar form. This is an intermediate phase between $\alpha$ and $\beta$ phase, and can be viewed as a
SCHEMATIC MODELS OF MOLECULAR CONFORMATIONS IN PDUF MOLECULES PROJECTED FROM NORMAL (TOP) AND PARALLEL (BOTTOM) TO THE CHAIN AXIS.
FIG 1.9 CRYSTAL STRUCTURES OF PVDF.
kinked all trans conformation. Mechanical orientation of \( \gamma \) phase yields \( \beta \) phase. The crystals of \( \beta \) PVDF are orthorhombic and have two CH\(_2\) CF\(_2\) monomers per primitive cell with lattice spacings \( a = 0.858 \) nm, \( b = 0.491 \) nm, \( c=0.256 \) nm. The magnitude of the dipole moment for each monomer unit is \( 7.0 \times 10^{-13} \) cm. Phase II (\( \alpha \) form) has trans-gauch-trans-gauch (TGTG\( ^{\prime} \)) conformation. It has a net dipole moment with a component normal to the molecular axis but the chains pack to form an antipolar unit cell [224]. However, phase II is not non polar under all circumstances but can have unit cell dipole moments of \( 5 \times 10^{-30} \) cm after orientation of poled films (Fig. 1.10 to 1.11). The fraction of crystal amorphous interface in the PVDF homopolymer is 0.35. Crystallinity of PVDF homopolymer is 0.63 [225].

X-rays [226] and infrared [227] results (data) indicate that poling changes morphology in PVDF [228]. Other technique for controlling the morphology include crystallization from solution [229] and high temperature annealing [230].

Depolarization studies were carried out on PVDF electrets by Takamatsu and Fukada [231]. Depolarization studies of roll drawn PVDF films show that it can retain a large polarization and show a fairly large piezoelectric effect without being polarized electrically [232]. The depolarization current of a PVDF film prepared by solvent casting is
Fig. 1-10: Configuration of the $\alpha$ PVDF crystalline
from:
(a) Unit cell according to the structure of Bachman and Lando. Down and up chains are depicted by solid and broken lines respectively.
(b) $\text{TG}^+$: $\text{TG}^-$ chain conformation dipolar moments are indicated.
Fig. 1.11: Configuration of the $\beta$ PVDF crystalline form.
(a) Unit cell (b) zig-zag chain conformation (dipole moments are indicated)
extraordinarily large [233]. Depolarization studies of unstretched, stretched, solvent cast and doped PVDF films have been done by Tara [234].

Murayama and Hashizume [235] studied depolarization and pyroelectricity of thermoelectrets prepared from β form PVDF. Depolarization current and pyroelectric activity depends on poling time, field and temperature. The depolarization spectra obtained from different electrets have five peaks. The first peak \( P_1 \) is obtained around 60° C as a weak shoulder. This peak is related to characteristic molecular motion at this temperature [236]. The second peak depends on polarizing temperature and shifts towards higher temperature with increasing poling field \( E_p \). Therefore, it is due to trapped charges, \( P_3 \) and \( P_4 \) appear near the melting temperature, \( P_3 \) is polarization responsible for piezo-electricity, \( P_4 \) gives negative depolarization current because of space charge caused by migration of charges over microscopic distances. The last peak \( P_5 \) appears in the melting temperature region and is related to phase transition. Charge storage capacity of PVDF films can be increased by doping [237].

The electrical conductivity by PVDF depends on ionic impurity concentration, which in turn depends on sample history [238] and field strength [239]. Typically the resistivity \( \rho \) is \( 10^{-14} - 10^{-15} \) cm for PVDF at room temperature and the relative permittivity \( \varepsilon_r \) is 10-15 [236].

The high dielectric constant of PVDF and its copolymers make them potential candidates for energy storage devices [240]. Recently, Jow and
Cygan have found that dc breakdown strength of PVDF is very high and ac breakdown strength is very low. Low ac breakdown strength of PVDF relative to its dc breakdown strength can be attributed to its specific dielectric properties, namely the piezoelectricity and ferroelectricity. The injected space charge that exists at the surface of polarized zones is the reason for PVDF's high dc breakdown strength. Large interval stress existing at the boundaries of the polarized zones plus the space charge mentioned will induce breakdown near any defect in the sample under ac conditions.

PVDF exhibits extraordinary piezoelectric, dielectric, ferroelectric and pyroelectric properties [241]. Piezoelectricity means change in polarization on application of stress or strain. The electrets of PVDF show a piezoelectric strain constant more than $10^{-6}$ cgs esu [242]. The $\beta$ phase has the highest piezoelectric activity. The piezoelectricity depends on crystal form and stretching conditions. The piezoelectricity of PVDF electrets is quite stable at room temperature [243].

It was suggested by Murayama [244] that piezoelectricity can be explained on the basis of trapped charge theory. Recently, Schaffner and Jungnickel [245] have studied the dielectric moment contribution to the piezoelectricity of PVDF.

Pyroelectricity is the effect which exhibits a change in polarization when the temperature of the sample is changed. Pyroelectricity in PVDF is studied by many workers [246-248]. Pyroelectric material exhibits a
spontaneous polarization. True (reversible) pyroelectricity originates from
the temperature dependence of spontaneous polarization. As the polar
pyroelectric materials are also piezoelectric, a strain originating from a
thermal expansion may also provide a secondary pyroelectric effect which
is, however, small in comparison with the primary pyroelectric effect.

Ferroelectrics constitute a special class of dielectrics which has a
spontaneous polarization which can be switched by action of an external
electric field. Ferroelectrics belong to a subgroup of pyroelectrics which
belong to a subgroup of piezoelectrics. PVDF and its copolymers with other
polymers exhibit ferroelectricity. Ferroelectricity in PVDF and copolymers of
PVDF and TrFE (Trifluoro ethylene) has been studied using different
methods [249].

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### TABLE - 1.1

**CHARACTERISTICS OF 5-CRYSTALLINE FORMS OF PVDF:**  
\( \alpha, \beta, \gamma, \delta \) and \( \varepsilon \)

<table>
<thead>
<tr>
<th></th>
<th>( \alpha ) form</th>
<th>( \beta ) form</th>
<th>( \gamma ) form</th>
<th>( \delta ) form</th>
<th>( \varepsilon ) form</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystalline form</strong></td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2 cm</td>
<td>CM2M</td>
<td>Cc</td>
<td>P2cm</td>
<td>Cc</td>
</tr>
<tr>
<td><strong>Chain conformation</strong></td>
<td>TG(^+) ( \text{TG}^- )</td>
<td>TT</td>
<td>T3G(^+) ( \text{T3G}^- )</td>
<td>TG(^+) ( \text{TG}^- )</td>
<td>T3G(^+) ( \text{T3G}^- )</td>
</tr>
<tr>
<td><strong>Polar conformation</strong></td>
<td>Antipolar</td>
<td>Polar</td>
<td>Polar</td>
<td>Polar</td>
<td>Antipolar</td>
</tr>
<tr>
<td><strong>Dipolar moment/monomer</strong></td>
<td>( \mu = 3.4 \times 10^{-30} \text{ cm} )</td>
<td>( \mu = 0 )</td>
<td>( \mu = 3.4 \times 10^{-30} \text{ cm} )</td>
<td>( \mu = 4.0 \times 10^{-30} \text{ cm} )</td>
<td>( \mu = 4.0 \times 10^{-30} \text{ cm} )</td>
</tr>
</tbody>
</table>
| **Elementary cell** | a = 4.96 A  
  b = 9.64 A  
  c = 4.62 A | a = 8.59 A  
  b = 4.91 A  
  c = 2.56 A | a = 4.96 A  
  b = 9.58 A  
  c = 9.23 A | a = 4.96 A  
  b = 9.64 A  
  c = 4.62 A | a = 4.96 A  
  b = 9.58 A  
  c = 9.23 A |
| **Density**        | 1.92 g/cm\(^3\) | 1.97 g/cm\(^3\) | 1.94 g/cm\(^3\) | 1.92 g/cm\(^3\) | 1.94 g/cm\(^3\) |
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