CHAPTER I

INTRODUCTION.
Until late sixties the application of polymers was limited to their electrical insulating properties. In recent years polymers have applications in various fields such as electrets,\textsuperscript{1} pyroelectric polymers\textsuperscript{1,2} conductive and photo conductive polymers\textsuperscript{3} apart from their use as insulators.

A polymer is a chemical substance whose molecules are large and consists of many small repeating units covalently bonded together. For instance, polyethylene consists of essentially long chains of \((-\text{CH}_2-\text{CH}_2-\text{)}\) repeating units. The length of the polymer chain is specified by the number of repeat unit 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 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.
Most of the physical parameters discussed above play an important role as regards to the charge storage and transport phenomena in polymers.

1.1 DIELECTRICS : RELAXATION PHENOMENA

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.

Dielectrics, by definition are those materials having negligible or small electrical conductivity. They possess the ability to be polarized in the presence of an electric field (Figure 1.1). If the polarization persists for a longer time in a dielectric, the dielectric is termed as an 'electret'.

The relaxation process is defined as the approach to equilibrium of a system which is initially out of thermodynamic equilibrium. Dielectric relaxation is due to hindrance of the motion of the permanent dipole and free charges of polymers by frictional forces. Therefore, upon the application, or, removal of an electric field a polar molecule is neither charged nor discharges immediately.

A dielectric material subjected to the electric field may be polarised due to four different processes.

(A) ELECTRONIC

When electrons of the atoms are displaced relative to the
FIG. 1.1  FIELD AND TEMPERATURE PROGRAMME FOR THE FORMATION OF POLYMER ELECTRETS
atomic nucleus, the "electronic polarization" ($\alpha_e$) results.

The corresponding displacement of atomic nuclei in a molecule, when its constituent atoms are of different type, gives rise to "atomic polarization" ($\alpha_a$).

(C) ORIENTATION

The asymmetric charge distribution between unlike constituents of a molecule, gives rise to permanent dipole moment. These dipoles are orientated at random in the absence of an electric field and they tend to orient themselves in the direction of the field when it is applied. Due to orientation of these dipoles a polarization results, which is known as "orientational polarization" ($\alpha_0$) or "dipolar polarization" ($\alpha_d$).

The above three types of polarization are due to charges which are locally bound in atoms, molecules or the structure of the dielectric.

(D) SPACE CHARGE

The free charge carriers present in a dielectric move towards counter electrodes in the presence of electric field and give rise to space charge polarization ($\alpha_s$).

(I) INTERFACIAL OR BARRIER POLARIZATION ($\alpha_1$)

This type of polarization is the characteristic of the systems with a heterogeneous structure which results from the formation of charged layers at the interfaces due to unequal conduction currents within the various phases.

(II) EXTERNAL POLARIZATION ($\alpha_{ex}$)

A space charge polarization of extrinsic origin may be additionally created in a polymer subjected to high fields when
excess electronic or ionic charge carriers are generated by the injection mechanism from electrodes (Schottky emission) or from Townsend breakdowns in the surrounding atmosphere.

A complete pictorial view of the various types of polarization is shown in figure 1.2.

The total polarization due to above four processes can be written as

\[ \chi = \chi_e + \chi_n + \chi_o + \chi_s \quad (1.1) \]

The relaxation nature of the polarization is demonstrated by the fact that immediately after the application of an electric field an absorption current varying with time is observed. It takes a finite time for the current to reach the steady value. It results in time lag between applied field and polarization under a.c. fields giving rise to dielectric loss.

Relaxation time of a polarization process may be defined as the time in which the polarization decays to 1/e (e is the natural logarithmic base), times its original value, on removal of the applied field\(^{11}\). Relaxation time decreases with increasing temperature and so does the saturation polarization. Relaxation times in solids are usually much longer than in liquids because a solid presents a more rigid barrier to internal motion\(^{12}\). Since the relaxation times for various processes responsible for different types of polarization are different, the mechanism attributed to them will dominate in different frequency ranges. Consequently, the dielectric dispersion would be obtained in the different regions of the frequency spectrum.

Debye\(^{13,14}\) has given an elegant picture of relaxation of
Fig 1.2: Polarization mechanisms in dielectric materials
dipolar polarization with a single relaxation time. This model assumes a set of identical, non-interacting dipoles free to rotate against some viscous resistance in a fluid like medium.

Another more useful relaxation is given by Frohlich's bistable model\textsuperscript{15}. In this model, charged particles (bistable dipoles) can jump between two preferred orientations separated by a potential barrier 'E' by thermal excitation. The relaxation time is given by

\[ \tau = \tau_0 \exp \left( -\frac{E}{KT} \right) \]  \hspace{1cm} (1.2)

Recently, a universal law of dielectric relaxation covering a wide range of solid dielectrics has been proposed\textsuperscript{16,17}. This law which is valid upto GHz frequencies is of the form

\[ \chi(\omega) \propto \omega^{n-1} \text{ where } (0 < n < 1) \]  \hspace{1cm} (1.3)

Here, \( \omega \) is the frequency and \( \chi \) is the imaginary part of the dielectric susceptibility.

Polymers exhibit structures covering the entire range from amorphous to crystalline, and also fine textures which consist of complex combinations between the two forms. The complicated architecture of atomic arrangements and fine textures are vital factors which affect the structure, properties and chemistry of the solid polymers\textsuperscript{18}. Delicate balance of structural features is needed to achieve the desired combination of properties.

1.2 STRUCTURE OF POLYMERS

In a polymer, a large number of molecules called monomers are joined together to form a long macromolecular chain, which can assume various conformations in space\textsuperscript{18}. These chains may either be separate macromolecules, or they may more or less be cross linked by chemical bonds and thus form a three dimensional
network. A general formula, which fits a number of polymer chain may be represented in the form -

\[
\begin{array}{cccc}
R_1 & R_4 & R_1 & R_4 \\
\text{-- C -- C -- C -- C --} \\
R_2 & R_3 & R_2 & R_3
\end{array}
\]

\( R_1 \) to \( R_4 \) are molecular groups. The polymer chain generally consists of 100-1000 single repeating monomer units as shown above.

Generally polymers exhibit heterogeneous structure comprising both the crystalline and amorphous regions \(^{19-21}\). Many of the unique properties of polymeric substance, glassy and crystalline as well as in liquid state as due to the flexibility of the long chain molecules are conferred by internal rotation around C-C-bonds\(^{22}\).

**1.2(A) AMORPHOUS POLYMERS**

In amorphous polymers the molecules are tangled up in a completely random manner. According to Kargin\(^{23}\) amorphous polymers are partially ordered systems and are made up of illobules or bundles of polymer chains. Within the bundle, the polymer chains are ordered, but the bundle are tangled. The major transition of an amorphous polymer, namely the glass transition, can be explained qualitatively by both the hypotheses\(^{24}\). The polymer liquid \( T > T_g \) is considered to be quasi-crystal. Although the motion of the chain - segments in the liquid is chaotic, at any given instant the segments are grouped in small quasi-crystals with holes\(^{25}\) in between.
1.2(B) CRYSTALLINE POLYMERS

Some polymers crystalize when cooled from the melt. A crystalline polymer is distinguished from an amorphous polymer by
(I) The presence of sharp X-ray lines superimposed on an amorphous halo. Amorphous polymers yield the halo alone\(^{25, 26}\).
(II) The presence of polycrystallite aggregates known as spherulites which are usually large enough to be seen in optical microscopes\(^{27}\).
(iii) The occurrence of a first order transition, the melting point.
(iv) Schematic comparison of the electronic band structure of crystalline and amorphous dielectric is shown in figure 1.3

1.2-1 STRUCTURAL MODIFICATIONS IN POLYMERS

Polymerization process\(^{29}\) and time\(^{30}\) affect the microscopic properties of the material. Glass transition temperature (\(T_g\)) is also affected by the degree of polymerization (n). Decrease in n lowers the \(T_g\) and hence increases the mobility of charge carriers although the activation energy remains the same\(^{30}\).

The following relation has been found to hold good.

\[ T_g = T_g^0 - \frac{K}{M_n} \]  \hspace{2cm} (1.4)

Where, \(T_g^0\) is the glass transition temperature at infinite molecular weight, \(M_n\) is the molecular weight of the polymer with a degree of polymerization and \(K\) is the constant.

The addition of plasticizer usually reduces stiffness, hardness and brittleness and has similar effect on other mechanical properties, since interchain forces are effectively reduced. These changes are also accompanied by a reduction in \(T_g\).
**FIG. 1.3—**

Comparison of the electronic band structure of crystalline (A) and amorphous (B) dielectrics.
Plasticization is usually restricted to amorphous polymers\textsuperscript{29}.

The requirement of good optical properties\textsuperscript{31}, especially in massive pieces impose severe limitations on the structure of polymers. Achievement in low dielectric loss over a wide frequency range, is possible on the basis of low polarity.

An efficient control over electrical properties of polymers is achieved by doping. Polymer with suitable dopant\textsuperscript{32-34} forms a donor - acceptor complex with the host material. Carrier transport in polymers is also markedly affected by doping. Gill\textsuperscript{35} investigated in detail the transport properties of Trinitrofluorenons dispersed in poly (vinyl carbazole) - PVK. Doping of iodine improves the conductivity of the polymers due to the formation of charge transfer complex. Some times doping causes reduction in trapping of charge carriers and increase in mobility.\textsuperscript{30}

From the technological point of view, new polymeric materials - polyblends, copolymers, and inter-penetrating polymer network (IPN) promise a versatile route to superior combinations of useful properties from the existing polymers\textsuperscript{36}.

If the constituent polymers in the blend are cross linked, the resulting material is known as interpenetrating polymer network (IPN).\textsuperscript{38} In IPN'S the phase separation is not as extensive as would be otherwise, due to the permanent entanglements occurring between the constituent polymers, a graft copolymer results. If the differing monomer units are arranged linearly in segments covalently bonded to one another along one chain, a block copolymer results\textsuperscript{37}. Phase separation generally occurs more in block copolymer than in polyblends\textsuperscript{38}.
1.2-2 TRANSITIONS AND RELAXATIONS IN POLYMERS

The characteristic features of polymers are largely due to their extra rotational degrees of freedom compared with other solid types. The manifestation of each kind of molecular motion that leads to appreciable changes in the temperature dependence of physical properties is customarily interpreted as thermally stimulated transition. The most prominent change in the microscopic behaviour of amorphous polymers takes place at the glass transition temperature $^{39-42}$.

The polymer structure undergoes physical deformation at certain critical temperature known as glass transition temperature. It is called glass transition temperature because the polymer has two states, the glassy state and rubber like state.

<table>
<thead>
<tr>
<th>Glassy State</th>
<th>Rubbery State</th>
<th>Viscous Fluid State</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Brittle Plastic)</td>
<td>(Though plastics and rubbers)</td>
<td>(Polymer metals)</td>
</tr>
</tbody>
</table>

$T_g$ (Glass transition temp.) $T_f$ (Flow temp.)

The glassy state of polymers can be interpreted as a state in which segmental mobility is frozen. Thus the glassy state is of relative equilibrium, (i.e., a metastable state)$^{43}$.

At this transition temperature, the mechanical strength of the polymeric material decreases rapidly, there is an abrupt change in the thermal dilation temperature curve. The thermal conductivity, mechanical loss at periodic stress and dielectric properties change appreciably by passing through this
temperature. In amorphous polymers transitions are of relaxation nature. It is customary to denote these transitions starting with high temperature ones by the Greek letters $\alpha$, $\beta$, $\gamma$ and $\delta$. The $\alpha$-relaxation involves the main chain segmental motion and occurs at the glass transition temperature of the polymer. The $\beta$-relaxation is attributed to the motion of the side groups or elements of chain-backbone and it takes place at temperatures below glass transition temperature. The $\gamma$ and $\delta$ relaxations may have a complicated nature and they have been observed at ultra low temperatures. The temperature transitions encountered by each polymer are determined by its chemical structure. General relation between chemical composition and structure with glass transition is reviewed by Boyer.

1.2-3 POLARIZATION IN POLYMERS

When solid polymeric materials are subjected to an electric field, polarization phenomena occur, i.e. application of an electric field brings a net dipole moment over the bulk in its direction. In a non-polar material the dipole moment is due to the induced dipoles whereas in a polar material it is due to the orientation of dipoles in the field direction.

Mechanism responsible for the polarization of polymer depends upon the properties of polymer, electrode material and technique of excitation.

Since most of the polymers contain both amorphous and crystalline regions (or phase) whose conductivities are different, Maxwell-Wagner-Sillar's effect is expected to contribute to the polarization of all polymers. Different technique which can be used to investigate polarization phenomena.
(I) Thermally Stimulated Discharge Current (TSDC)

(II) Spontaneous current emission measurement (SCE)

(III) Electrical Conduction (EC).

1.3 THE ELECTRET STATE IN POLYMERS — (A Brief Survey)

An electret can be simply defined as a dielectric material which possesses a semi-permanent polarization.\textsuperscript{50,51} The term electret is an electric counterpart of a magnet since they carry opposite charge on other 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 thermoelectrets\textsuperscript{52-55}, photoelectrets\textsuperscript{56-58}, thermophoto-electrets\textsuperscript{59,60}, radioelectrets\textsuperscript{61,62}, magnetoelectrets\textsuperscript{63-65} prepared under the simultaneous treatment of electric field and heat, electric field and light, electric field and heat and light; electric field and high energy radiations; magnetic field and heat respectively.

Heaviside\textsuperscript{66} was the first who got the idea of an electret. Eguchi\textsuperscript{52,53} 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\textsuperscript{67} introduced the concepts of "heterocharge" and "homocharge". According to Gemant's terminology a charge on the electret of the same sign as 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\textsuperscript{68} classified electrets into two groups, viz., those comparatively high conductivity yielding heterocharges only and those of much lower conductivity capable of developing homocharge.

Electret research gradually moved to organic substances and polymers where fundamental solid state properties could be correlated with electret behaviour\textsuperscript{50,69,70}. Recently electret phenomena have received more attention because of their applications in electret microphones\textsuperscript{71} electrophotography\textsuperscript{72}, electrostatic voltage generators,\textsuperscript{73} radiation dosimeters,\textsuperscript{74,75} etc.

A large number of workers have reported the electret effect in inorganic solids\textsuperscript{76-78}, Organic solids\textsuperscript{79-82}, liquid crystals\textsuperscript{83,84}, polar polymers\textsuperscript{85-92} non-polar polymers,\textsuperscript{93-95} copolymers\textsuperscript{96-98} and biopolymers\textsuperscript{99-101} etc. This literature one lectret has been reviewed by Gutman,\textsuperscript{102} Johnson,\textsuperscript{103} Perlman\textsuperscript{549} and Pillai et al.\textsuperscript{55,83}.

1.3-1 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. Vanderschueren\textsuperscript{103} and others\textsuperscript{55,104-106} have shown that when an electret is exposed to high humid atmosphere, their charge decreases. Several workers\textsuperscript{107-109} 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.\textsuperscript{109-110} Grass and DeMoraes\textsuperscript{74} observed that on exposing a thermoelectret to Co\textsuperscript{85} I-rays, its charge decreases. Linear relationship has been established between the loss of charge and dosage of high energy radiation\textsuperscript{80,111} and this effect has been explained on the basis of degradation of cross linking of the polymer on irradiation.

Khanna\textsuperscript{112} and Perlman\textsuperscript{113} 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.\textsuperscript{114-116} A good correlation between the surface charge and the work-function of the metal used as electrode has been reported.\textsuperscript{114, 115}

1.3-2 INVESTIGATION OF ELECTRET STATE

Measurement of charge has a special importance in the study of electret phenomena. Many techniques such as induction method\textsuperscript{53,67,108} dissectible capacitor\textsuperscript{117,118} generating voltmeter method\textsuperscript{119} vibrating electrode method,\textsuperscript{120} electron beam method,\textsuperscript{121} etc. have been employed. However, none of these methods could provide a deeper insight into the electret phenomena. A significant break through was achieved in the study of electret phenomena with the discovery of heat accelerated decay of electret charges.\textsuperscript{50} It is known that a dielectric 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, therefore, it is useful to stimulate the
discharge of the polarized dielectric at a higher temperature. The method is popularly known as Thermally Stimulated Discharge Current (TSDC) method.

1.3-3 CHOICE OF MATERIALS FOR ELECTRET FORMATION

There are two obvious choices; polar and non-polar polymers. Polar polymers have a distinct dipole reorientation, whereas in non-polar polymers no such dipoles are present. Polar polymers show\textsuperscript{122} a high ohmic conduction, since this arises partly from absorbed water, which may amount to a few percent in polar materials. The high polarity will also enhance the formation of free carriers by facilitating the dissociation of impurities. Part of these carriers will be piled up near the electrodes during the formation and so form excess charges. Consequently, in polar polymers, we might expect storage of dipoles and excess charges. Non polar polymers show no dipole relaxation effects. But this is true for only pure sample.

1.4 POLYMER BLENDS (Polyblends)

Polyblends are simple physical mixtures of the constituent polymers with no covalent bonds occurring between them. There may be homogeneous (single-phase) solid solutions or heterogeneous (multi-phase) mixtures\textsuperscript{123} in polymers, the latter case is by far the most prevalent due to the thermodynamic incompatibility of most polymers.\textsuperscript{36-38} There is relatively small gain in entropy upon mixing the polymers due to restrictions imposed by their large chain length. Criterion for blend miscibility in a single, composition depends on the glass transition temperature.\textsuperscript{124-126} Optical clarity\textsuperscript{125} method is also used for predicting polyblend miscibility.
The glass transition temperature \( (T_g) \) of polyblend can be predicted by the mixing rule of Couchman.\(^{126}\)

\[
\log T_g = \frac{\sum C_{pi} \bar{\theta}_i \log T_{gi}}{\sum C_{pi} \bar{\theta}_i}
\]

Where, \( T_{gi} \) is the glass transition temperature of the homopolymer, \( \bar{\theta}_i \) is its mass fraction and \( C_{pi} \) is its glass transition increment of isobaric heat capacity.

An important application of polyblends is impact improvement, in which small particles of a rubbery polymer are dispersed in the matrix of a glassy polymer. Another commercially important application of polyblending is improvement in reactivity. Other such commercial applications include improvement of chemical resistance, weatherability, flammability etc.

Blending of two polymers usually leads to a class of materials whose properties are due to the presence of two phases, with two glass transition temperature, and usually unique. The degree of compatibility is determined by the size and distribution of the phases, i.e., how finally one polymer is dispersed within the other. Compatibility occurs as a result of an exothermic interaction between the component segments. The incompatibility is due to the small gain in energy upon mixing the two constituents because of the restrictions imposed by the chain length. High compatibility is often desirable for the case of blending, but some degree of incompatibility often leads to useful properties. Both miscible and immiscible blends have their own advantages and applications depending on their requirements. One well known commercial blend is (poly vinyl chloride) -
Nitrile Rubber system. In this system, one of the component Nitrile Rubber acts as a polymeric plasticizer. Another blend which has gained commercial importance is poly styren - poly (phenylene oxide) (PPO). The blend of this system has shown better thermal resistance due to PPO and the procesability has become much easier and the production cost has also been lowered compared to that of PPO, because of the easy availability of PS. Blends of (Poly vinylidene fluoride) - PVDF and (Poly-methyl methacrylate) - PMMA offer combination of toughness and resistance to chemicals along with very useful pyro, pyezo and dielectric properties. The applications of immiscible blends include rubber blends in tires impact modified plastics and thermo plastic estomers.

The work reported in this thesis was carried out on pure Ethyl Cellulose (EC), Poly Methyl Methacrylate (PMMA) and blended samples. The details of polymers used in the present investigation are given as under.

1.4-1 ETHYL CELLULOSE (EC)

Commercial grade EC used in the present investigation was supplied by M/S Kasliwal Brothers Indore (India). Its degree of substitution (DS) lies between 2.4 – 2.6. Ethyl Cellulose is well known for its properties of physical and chemical nature its structural formula is: \[ \text{CH}_2\text{OH} \]
EC is a polar polymer. Its main chain is -C-O-C-. The side groups have a structure of the like (-C-O-C-) form but their electronegativity nature is different than those in main chains. The reported glass transition temperature $T_g$ for atactic EC lies between 60-72°C and the softening and melting temperatures of EC (DS=2.5) lie between 135-145°C and 165-175°C respectively.\textsuperscript{151D}

Experimental observations on the polymer used in the present investigation gave the values of softening and melting temperatures around 120°C and 160°C respectively. Hence the present study was conducted within a temperature range from 25 to 160°C. The dielectric strength of EC lies between 350-500 volts/mil.\textsuperscript{151E}

1.4-2 POLY METHYL METHACRYLATE (PMMA)

In the present work poly methyl methacrylate (PMMA) is taken as one of the constituent polymer of the polyblend. It is amorphous and polar polymer, having high impact strength and good weatherability. PMMA can be obtained in different stereo-regular forms depending on the polymerization method. The properties of the different stereo-specific forms of PMMA are summarized in

<table>
<thead>
<tr>
<th>Type</th>
<th>Density</th>
<th>Glass Transition Temp. ($T_g$)</th>
<th>Melting Temp. ($T_m$)</th>
<th>Stereo-regular form</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.19</td>
<td>115°C</td>
<td>200°C</td>
<td>Syndiotactic</td>
</tr>
<tr>
<td>II</td>
<td>1.22</td>
<td>45°C</td>
<td>160°C</td>
<td>Isotactic</td>
</tr>
<tr>
<td>III</td>
<td>1.20-1.22</td>
<td>60-95°C</td>
<td>170°C</td>
<td>Stereoblock Copolymer</td>
</tr>
<tr>
<td>Conventional</td>
<td>1.188</td>
<td>70-105°C</td>
<td>-</td>
<td>Pairly high degree of syndiotactic character.</td>
</tr>
</tbody>
</table>
The value of $T_g$ for 'conventional' PMMA has been reported between 70 to 105°C. This variation may be due to the difference in stereo-regularity between different samples.

Transitions and relaxations in PMMA have been studied extensively by several workers\textsuperscript{135-137}. Five relaxation processes 0, B, OB, I and $s$ have been reported in PMMA. However all of them are not observed simultaneously.

I. MAIN CHAIN SEGMENTAL MOTION ($\alpha$-relaxation)

$\alpha$-relaxation arises due to the main chain segmental motion and occurs around and above glass transition temperature, $T_g$ (\(\geq 105°C\)).\textsuperscript{138}

II. CARBOXYL SIDE GROUP ROTATION ($\beta$-relaxation)

A large peak at 35°C generally through due to $\beta$-relaxation in PMMA, arises from the hindered rotation of the COOCH\textsubscript{3} group about the C-C bond which links it to the main chain\textsuperscript{139}. In methacrylate polymers, the O-methyl group is thought to interfere sterically with the C = O of the carboxyl group. The details of the motion are not clear but the most common conjecture is that a hindered rotational motion is involved.

$\beta$-relaxation is unaffected by increasing the length of the ester-alkyl group or by incorporation of plasticiser, whereas both of these changes serve to lower the $\alpha$-relaxation($T_g$).\textsuperscript{135,140}
III. β-RELAXATATION

It has also been observed that the α and β processes coalesce around glass transition temperature and give a single relaxation - (α β) process. Pressure has been applied to split α and β processes.139.

IV.O -METHYL GROUP ROTATION (γ-relaxation)

A small mechanical loss peak in PMMA by Sinnott141. is assigned to the rotation of the methyl groups attached directly to the main chain (O-methyl group). This rotation of methyl groups does not result in a directional change in their net dipole moments. It is not observed directly. However it was most easily observed in n.m.r. line width because of the large magnetic dipolar interaction within the CH₃ group.21

V. ROTATION OF THE METHYL GROUPS IN THE ESTER SIDE CHAIN(γ-relax.)

Both dynamic mechanical and n.m.r. studies have indicated that the rotation of the CH₃- group about the o - C bond in the COOCH₃ side group sets in at extremely low temperature, since the energy for the motion is small.21

1.5 STUDIES UNDERTAKEN

Studies of spontaneous emission of current, Thermostimulated discharge current (TSDC) and steady state electrical conduction in various polymers throw a great amount of light on the origin of charge carriers in them and mechanism of charge transport. Since most of the polymers fall under the group of semi-insulators, the study of dielectric relaxation and polarization mechanism also constitute an integral part of the experimental studies and will go a long way in understanding the behaviour of
polymer under DC and AC electric strain. Brief ideas about these studies are as follows.

1.5-1 THERMALLY STIMULATED DISCHARGE (TSD) CURRENT

The TSD technique because of its high sensitivity and high resolving power has become a powerful tool for obtaining information on trap depth and relaxation processes in polymeric materials. This method is analogous to thermoluminescence (TL).\textsuperscript{142-144} TL is suitable for those materials which show natural phosphorescence, or which have been made phosphorent by doping with activators (acceptors) and coactivators (donors).\textsuperscript{145,151}

The TSD current method involves the following steps: Electrodes should be made on both the sides of a polymeric film (any dielectric in general), elevate its temperature, apply an electric field across the electrodes, cool the specimen to room temperature keeping the field on. The specimen now possesses polarization. If the temperature of the specimen is increased at a linear heating rate, the discharge current is generated. A plot of this current as a function of temperature is a TSD thermogram.

(TSD gives a complete picture of temperature dependant relaxation and allows the parameter of dipolar relaxation time and activation energy to be determined from a single measurement with higher accuracy than the conventional dielectric measurements.)

There are numerous ways of analysing the TSD spectra. They are based on the nature of the curve on the low temperature side,\textsuperscript{147} the precise shape of the peak\textsuperscript{148,149} and the way it moves with different heating rates.\textsuperscript{150}
1.5-2 ELECTRICAL CONDUCTION IN POLYMER FILMS.

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 process of charge transport in polymeric semiconductors is a complex phenomenon. The actual nature of conduction mechanism in a variety of polymeric films is still a matter of speculation. Although the information on the study of electronic properties of polymeric materials is enormous, no comprehensive theoretical approach, which can adequately interpret 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 he 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 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.
Current density (J) \( \frac{(I)}{(A)} \) \( \text{Id} \)

Electric Field (F) \( \frac{(V)}{(d)} \) \( \text{VA} \)

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 ease 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 orders 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/em for polyvinyl chloride to \( 10^{-18} \) S/em for polystyrene, which are many orders of magnitude below the conductivities associated with metals.

1.5-3 SPONTANEOUS CURRENT EMISSION :-

Polymers sandwiched between vacuum evaporated electrodes are found to generate electric current on beating. This phenomenon of generation of current is called spontaneous current
emission (SCE). Several workers\textsuperscript{153-156} while performing experiments on TSD (Thermally stimulated discharge) measurements have noticed that at certain temperatures many unpolarized polymers generate a "dark current".\(^{(}\) Then a polymer film sandwiched between two electrode metals similar or dissimilar is heated with a uniform heating rate, then the system generates a current which has a maximum value at certain temperature ranges. Turnhout\textsuperscript{157} called this current as "parastic current" and he attributed it to a weak electrochemical potential which arises due to increasing contact of metallic electrodes with a polymer film.\(\)\)

Ideally the electrode-dielectric contact should be electrically "invisible" for investigating intrinsic relaxation properties but by heating with a constant rate, current may give rise to a peak (or peaks) as a result of electrochemical potential between electrodes and the sample. They are also influenced by transitional changes of the polymer\textsuperscript{153} (or a biopolymer) Polar polymers whose glass transition temperatures are in higher temperature ranges possess several mechanical and dielectric relaxations at certain fixed temperature ranges. On the other hand biopolymers such as gelations or proteins have a large influence on their relaxation processes from structurally absorbed water traces. Now a days a trend of doping of polymers with some suitable impurities has grown up and thus the SCE of doped samples may give some more information about the formation of complexes. Detailed investigations of SCE on pure and iodine doped PVP films are necessary to find out the origin and nature of this current which may prove to be more interesting from
scientific and technological points of view.

(I) PROCESS RESPONSIBLE FOR THE ORIGIN OF SCE.

It seems that one or more of the following four processes may be responsible for the origin of SCE.

(A) Electrochemical Process  (B) Water Activated Process
(C) Rotation of Dipoles & Molecular Complexes  (D) Electronic Process

(II) SOME IMPORTANT FACTORS WHICH AFFECT SCE

(A) Effect of Moisture Content  (B) Effect of Heating Rate
(C) Effect of Thickness.  (D) Effect of Impurity
(E) Effect of Time Interval Between two Sucoesive Heatings.
(F) Effect of Electrode Metals

All the above mentioned points are discussed in Chapter 5.

1.6 AIM AND SCOPE OF THE PRESENT INVESTIGATION

Polymers are widely used in many areas of electrical and electronic devices in diverse application 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 structure in a local or a general way. The fundamental understanding of various phenomena occurring in these materials are important for future applications.

Earlier electret investigations were mostly performed with wax, resin, natural raw products and their mixtures, in which neither the mechanism was understandable nor their structures were well defined. Further, these materials are not very much useful for a variety of applications because they acquire a smaller magnitude of charge and are sensitive to ambient conditions.
conditions. The interest in polymer electrets is due to the fact that these show excellent charge-storage capabilities and are relatively stable to environmental conditions.

Polymers, EC and PMMA have a special significance because of their excellent properties. Although a few studies on EC and PMMA have been made in the past, but a clear and coherent picture has not yet been emerged for explaining various observations in these materials. As regards to the charge storage and transport phenomena in these polymers, an atmosphere of controversy is still prevailing to a great extent. The work presented in this thesis essentially probes into the mechanism of charge storage and transport in EC, PMMA and EC:PMMA blend films.

Blending of polymers is a very simple and inexpensive method to obtain new types of materials with a wide diversity of properties intermediate to those of the pure components. In blends, however, compatible blends have received significant attention because of their superior properties. In the present investigation, in order to understand how blending affects the charge storage and transport phenomena, the TSD current and d.c. conductivity studies of compatible EC:PMMA blends in various weight proportions have been carried out.

The information obtained from these studies would promote the understanding of persistent polarization and charge transport phenomena in polymers, and particularly in EC, PMMA and EC:PMMA blends and prove useful in the design and fabrication of certain devices based on these polymers.
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