CHAPTER - 4

DIELECTRIC PROPERTIES
4.1 **INTRODUCTION** :-

The dielectric behaviour of polymeric films is of direct interest to both the basic studies of electrical conduction through such films and their applications in capacitors for micro-electronics. 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 ultra thin films, capacitor applications are generally limited to thick films.

The evaluation of dielectric properties of insulator films (259-263) is carried out by measuring simultaneously the capacitance and the dissipation factor over a wide range of frequencies and temperatures. As all the other electrical parameters of dielectrics, the permittivity depends on the changeably external factors such as the frequency of voltage application, temperature, pressure, humidity etc. In a number of cases these dependences are of great practical importance.

Recently dielectric properties of several polymers (264-279) polar and non-polar have been investigated. Some general relations between dielectric properties have been discussed, distinguishing between resonance phenomena that commonly occur in the optical region and relaxation phenomena which occur in polymers at the lower frequency regions. It has been shown how the real and imaginary parts of the complex dielectric constant are related. In nonpolar polymers, the dielectric constant depends primarily on the density, but little is known regarding the nature of the dielectric loss. Attention has also been paid to
polar polymers. After some preliminary remarks on the nature of dielectric dispersions, some phenomenological notions of dielectric dispersions have been considered. Attempts have been made to relate theory and practice. The topics, such as phase transitions, anisotropy and inhomogeneity have been dealt with.

Dielectric relaxations in polyvinyladene fluoride were studied by Sasabe et al (266). They observed three distinct absorption peaks ($\gamma,\beta,\alpha$) in the frequency range from 0.1 to 300Hz in the temperature range -66 to 100°C. The $\gamma$ absorption is related to molecular motion in the crystalline region. The $\beta$ absorption can be interpreted as due to the micro-Brownian motion of the amorphous main chains. The $\alpha$ absorption is attributed to local oscillations of the frozen main chains. Kakutani and Ashina (267) studied low-temperature absorption of polyvinyl chloride and concluded that the $\gamma$ and $\beta$ processes are the results of molecular motion in crystalline and amorphous regions of the polymer respectively. Low temperature dielectric relaxation in polyethylene and related hydrocarbon polymers was investigated by Phillips (280). He uses a simple quantum mechanical model of relaxation process to explain the experimental results. According to this process, a particle in a double potential well tunnels from one well to the other with emission or absorption of a phonon. Results of Kawamura et at (264) on dielectric properties of co-polymer of methyl-methacrylate with n-bityl methacrylate lead to the following conclusions.

1: The loss peak temperature attributed to side chain relaxation varies
with the comonomer ratio when the comonomer does not have a methyl group but remains almost unchanged for comonomer having methyl group.

2: In both cases, the θ-peak height decreases with increasing ratio of comonomer. It is suggested on the basis of the above facts that the moving unit in the side chain relaxation consists of single side chain with a segment of the backbone chain and that the change in mobility of the side chain upon copolymerization results from the distortion of the helical structure of the backbone chain due to random distribution of methyl groups.

Though there is a wide literature available on dielectric properties of polymers, yet a few reports (281-283) exist on impurity doped polymers. Kokasi and Ieda (281) have doped high and low density polyethylene. One of them has the loss maximum dependent on the amount of the impurity and is related to the relaxation of a dipole orientation of the impurity. Another shows an odd behavior named retrogressing phenomenon near the melting point of polyethylene and can not be detected in the amorphous polystyrene doped with the same impurity. An interfacial polarization is proposed assuming a model which is justified semi-quantitatively. The retrogressing phenomenon is explained by the change of the layer thickness that affects the dielectric relaxation time of the model. Kulshretha and Srivastava (282) doped polystyrene with chloranil and Srivastava et al. (283) with copperphthalocyanine and observed interfacial polarization in the measurement of dielectric losses of the polymer.
Fig. 4.1 Capacitance Vs frequency at various temperatures for 1g/l pyrene doped PS
Fig. 4.2 Effect of pyrene concentration on capacitance Vs temperature
Fig. 4.3 Capacitance Vs pyrene concentration at various temperatures
Fig. 4.4 Effect of pyrene concentration on $\tan \delta$ vs temperature at 500 Hz.
Less has been reported on dielectric properties of doped PS (284) and it seems to carry out further investigations to understand the dielectric behaviour of the doped polymer. This chapter reports on capacitance and dielectric loss factor of pyrene doped PS films as a function of temperature and frequency in audio frequency range.

4.2 RESULTS:

Dielectric properties of polymers are investigated by measuring simultaneously the capacitance and the losses at regularly varying temperature and frequency. Capacitance as a function of frequency for 1g/l pyrene doped PS film at 30, 60, 90 and 120 °C is shown in fig 4.1. There is no variation in capacitance with the frequency in the range (0-15 KHz). Due to increase in temperature capacitance is increased. Similar results were also found for other concentrations of pyrene incorporation (not shown). Fig 4.2 illustrates the effect of pyrene concentration on capacitance Vs temperature. A plot for PS film is also included in fig 4.2 for the sake of comparision. Due to doping capacitance is increased which is further increased due to increase in pyrene loading. Fig. 4.3 exhibits capacitance versus pyrene concentration at 30, 60, 90 and 120°C temperatures. Capacitance increases with the increase in pyrene concentration as well as with the increase in temperature. Fig 4.4 illustrates the effect of concentration of pyrene incorporation in PS on tanδ (loss tangent) versus temperature at 500 Hz. For the sake of comparision the plot for pure PS film has also been included in fig 4.4. For PS a loss
Fig. 4.5 Tanδ Vs Temperature for PS at various frequencies.
Fig. 4.6 $\tan \delta$ Vs temperature for $5\text{g} \text{l}^{-1}$ doped PS at various frequencies.
Fig. 4.7 Log $\log f_{\text{max}}$ Vs $10^3/T$
Fig. 4.8 Activation energy and tanδ Vs Pyrene Concentration
maxima at 85°C is observed. Due to doping, this loss maxima is shifted to a lower temperature. For concentration 0.5, 1 and 3g/l the loss maxima occurs at 78, 70 and 66°C respectively. Loss is increased due to doping which is further increased due to increase in dopant concentration. Fig 4.5 shows tanδ Vs temperature for pure PS film at 200 Hz, 500 Hz and 1 KHz. As the freqency is increased tan δ decreases. Loss maxima shifts to a lower temperature due to decrease in frequency, Fig 4.6 exhibits tan δ Vs temperature for 5g/l pyrene doped PS at 200 Hz, 500 Hz, 1 KHz, 2 KHz and 3 KHz. Loss maxima shifts to a lower temperature due to decrease in frequency. Similar results (not shown) were also observed for other concentrations of pyrene incorporation. In fig 4.7 log f_{max} versus 10^3/T has been plotted for PS and 5g/l doped PS. The plots are straight lines. The value of activation energy is calculated to be 0.68 eV for pure PS and 1.28 eV for doped PS. Due to doping activation energy is increased. Activation energy and tan δ versus pyrene concentration have been plotted in fig 4.8. Both are straight line plots.

4.3 DISCUSSION :-

Permittivity is the basic parameter of a dielectric describing its properties from the view point of the process of its polarization or propagation of electromagnetic waves in it, or more generally from the point of view of the processes of its interaction with an electric field. Permittivity 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. There are three well know
types of polarization: Electronic, ionic and dipole polarization.

Electronic polarization is the displacement of electrons with respect to the atomic nucleus, to be more precise the displacement under the action of an external field of the orbits in which negatively charged electrons move around a positively charged nucleus. This type of polarization occurs in all atoms or ions and can be observed in all dielectrics irrespective of whether other types of polarization are displaced in the dielectrics. One specific feature of electronic polarization is the fact that when an external field is superposed, this type of polarization occurs in a very short interval of time (of the order of $10^{-15}$ seconds) i.e the time of the period of oscillation of ultraviolet rays.

Ionic polarization is the mutual displacement of ions forming heteropolar (ionic) molecules. A shorter time is required for the process of ionic polarization to set in, but is longer than that of electronic polarization, i.e. $10^{-13}$-$10^{-12}$ seconds. On the whole the process of electronic and ionic polarization have much in common. Both phenomena may be regarded as the varieties of polarization caused by deformation which is a displacement of charges with respect to each other in the direction of the field. Apart from a very high velocity mentioned above with which the state of polarization sets in, it is important to bear in mind that the process of deformational polarization is practically unaffected by the temperature of the dielectric and is not connected with an irreversible dissipation of energy. The electric energy required to polarize a molecule is completely returned to the energy source after the voltage is removed. For this reason
deformational polarization does not entail any dielectric losses.

Polar dielectrics (285-288) exhibit a tendency towards dipole or orientational polarization. The essence of this kind of polarization can be reduced in a simplified manner, as has been first suggested by Debye, to the rotation of the molecules of a polar dielectric having a constant dipole moment in the direction of field. If orientational polarization is considered more strictly, it must be understood as the introduction by an electric field of certain orderliness in the position of polar molecules being in uninterrupted chaotic 'thermal' motion, and not as a direct rotation of polar molecules under the action of a field. For this reason, dipole polarization is connected by its nature with the thermal motion of molecules, and temperature must exert an appreciable effect on the phenomenon of dipole polarization.

After a dielectric is energized, the process of establishing a dipole polarization requires a relatively long time as compared with practically almost inertialess phenomena of deformational polarization. More or less time is needed in any individual case. As distinct from deformational polarization, dipole polarization and also other kinds of relaxation polarization dissipate electric energy which transforms into heat in a dielectric i.e. this energy causes dielectric losses.

In polymers dielectric loss behaviour may be attributed to the deformation of polymer chains (289-291). The molecular flexibility of chains are responsible for this characteristic property of the polymers. The other important mechanism for the dielectric losses in the polymers is considered
to be the internal motions or the local movements of the molecular chains of the polymer. At high temperature, especially at the glass transition temperature of the polymer such segmental motions are prominent. However, at low temperature these motions become less significant.

4.3 (a) **FREQUENCY DEPENDENCE OF CAPACITANCE:**

The capacitance and hence the dielectric constant of (fig. 4.1) pyrene doped PS remains constant with the change in frequency. This is so because the polarization settles itself during a very short period of time as compared with the time of voltage sign change. Dielectric constant of non polar polymers remains invariable with frequency. In case of polar polymers, the dielectric begins to drop at a certain critical frequency and at very high frequencies it approaches the values typical of non polar polymers. In amorphous polymers structural polarization (i.e related to the loose structure of matter) is also possible. For this type of polarization, the capacitance falls with the increase in frequency (292).

4.3 (b) **TEMPERATURE DEPENDENCE OF CAPACITANCE:**

The increase in capacitance above the room temperature (Fig. 4.2 & 4.3) may be partly due to the expansion of the lattice and partly due to an ionic mechanism of polarization. The molecules can not orient themselves in polar dielectrics (293) in the low temperature region. When the temperature rises, the orientation of dipoles is facilitated and this increases dielectric constant. Addition of pyrene may form charge transfer (CT) complexes with the polymer and so the increase in capaci-
tance with temperature is enhanced.

4.3 (e) VARIATION IN LOSS TANGENT :-

Temperature transition corresponding to Alpha- relaxation process has been observed near the glass transition temperature of PS (Fig. 4.4, 4.5 & 4.6). The Alpha-relaxation process in polymers is observed at temperatures above the glass transition of the polymer. Though at glass transition temperature the segmental motion is expected but at the temperatures above the glass transition temperature some thing larger than segments and possibly the entire molecular chain motion is expected. Polymers are considered to be the mixtures of amorphous and crystalline regions. Above the glass transition temperature they seem to loose the intermolecular cohesive bondings and the association and dissociation processes involved are governed by thermodynamical equilibrium. Therefore, Alph-relaxation process may be attributed to the motion of the more mobile molecular chains in which the intermolecular forces between the crystalline regions are weakened due to thermally activated process. This weakening of forces causes the motion of the entire molecular chain and hence the occurrence of Alpha- relaxation.

Incorporation of pyrene in PS softens the viscosity of the system and causes the Alpha-relaxation to shift to the region of lower temperature. The view is further supported by the observation that the increase in pyrene concentration has an effect of displacing the loss maxima to a lower temperature.

Logarithm of frequency at which loss maxima occurs, has been
plotted against inverse absolute temperature in (fig 4.7) for pure and pyrene doped PS films. The activation energy is calculated to be 0.68 eV for PS and 1.28 eV for 5gl⁻¹ pyrene doped PS. Incorporation of pyrene has an effect of increasing the activation energy. Besides molecular chain movements, the losses also occur due to electrical conduction which increase with the decrease of frequency. This is also what has been observed presently. Mixing of pyrene in PS increases the conductivity of the film and so the doped films exhibit more pronounced increase in losses with the decrease of frequency.

4.4 **CONCLUSIONS:**

The present investigation on dielectric behaviour of pure and pyrene doped PS films helps to conclude:

1. Dipole polarization involving ionic motion is prominent in PS. Doping of the matrix with pyrene enhances the process of polarization.

2. Alpha-relaxation in the polymer is due to the motion of polymer chains. Addition of pyrene reduces the viscosity of the system shifting Alpha-relaxation peak to lower temperature.

3. Doping causes conduction losses.

4. Above the glass transition temperature of the polymer, main chains are mobilized and the mobilization is facilitated due to incorporation of pyrene.