Chapter-7

Correlation
of different studies
CORRELATION OF DIFFERENT STUDIES

It is well known that many dielectrics including polymer such as PS, show a polarization which is out of phase with polarizing field. This leads to electrets in the case of a persistent or semipersistent polarization or to the dielectric absorption, manifestations of which are short circuit currents or open circuit voltages. Many physically different mechanisms may be responsible for these effects. Among them are interfacial polarization, ionic polarization due to migration of ionic carriers over macroscopic distance, movement of space charges perhaps due to carrier injection from electrodes or other inhomogeneities and dipole orientation effects.

Dielectric loss measurement of PS film shows a peak round 85°C. TSC spectra of PS exhibits peak round 105°C. These are well near the glass-transition temperature of PS. Due to doping of PS with iodine, loss maxima as well as TSC peak is shifted to a lower temperature. The activation energy of relaxation process is increased. Iodine incorporation in PS enhances its conductivity. Photo depolarization current is also increased due to mixing of iodine in macro molecular substance.
Dielectric loss maxima may be attributed to the motion of phenyl group. However, it is not possible in TSC because of the relatively high temperature (20-40°C) up to which the electrets were cooled during the formation. At these temperatures, the local motion of the phenyl group remains mobilized and are not frozen-in during the cooling phase of electret formation. On the other hand, TSC peak lies in the main relaxation region of the polymer. Its origin cannot be assigned to dipole reorientation only because of the fact that PS is a nonpolar polymer and moreover, the dipolar contribution calculated from Debye's equation does not correspond to the released charge. It may be partly due to the detrapping of charge carriers. Thermoluminescence experiments are also interpreted in terms of electron detrapping. Phenyl group provides a deep trap site and enhances electret stability. New traps are created due to mixing of iodine in the matrix.

Charge storage in doped matrices can take place on three structural levels.

Primary level- The traps are on the molecular chains themselves and the charge is stored at atomic sites.
Secondary level—Electrons can become caged within groups of atoms in neighbouring molecules and are held there due to the charge affinity of these groups.

The release of charge at a primary level. individual atomic motions are necessary while at the secondary level it is independent of the motion of groups of atoms.

Tertiary Level—Charge may be stored in both crystalline and amorphous regions of the matrix or at the boundaries. Charge released in this case depends on main chain motion.

Charge stability at the primary level i.e. along the molecular chain is determined by both the electro negativity of the ions and symmetry along the chains. Charge stability at the secondary level is better, higher the packing density and lower the branching. At high temperatures, the trapping site itself may be destroyed due to increased molecular motions.

In high insulating polymer like PS, intrinsic carrier generation resulting from Boltzmann’s factor is negligible at temperatures below polymer decomposition. Marked dependence of current on electrode material, linear dependence of charge
stored on applied field and the superlinearity of steady-state current-voltage characteristics suggest carrier injection from electrode. Charge transfer from metal depends on electron levels in which the carriers shift freely under the influence of field. Polarization and depolarization of doped films in the presence of UV Radiation indicate that incident photon eject carriers from electrodes which are injected into the film. Correspondingly, effect of electrode variation was studied in TSD, photo depolarization and current voltage measurements. The decrease in current due to increase in metal work function implies that electron injection decreases with increasing metal work function. The thickness of the charged layer at the electrodes which arises as a result of injected carriers depends on the potential difference and on the density of traps. It is of the order of about 500Å, a relatively high value which is of consequence in the analysis of electrical properties of films. The process of charge injection also depends on time, therefore, surface states are taken into account which can take up charge directly from the metal surface. From the surface state the injected carrier diffuses under its own field or under the external field into the bulk of the film where it is again trapped in the volume traps. Electrical conductivity
study suggests a uniform distribution of traps. The trapping sites exert a strong influence on the current flow i.e. the concentration of free carriers and their mobility. Mobility values in polymer are very low suggesting strong trapping. Increase in conductivity due to incorporation of iodine may be due to increase in mobility. Dependence of mobility on temperature points to a hopping process. Hopping is connected with charge jumps brought about by motions of chain elements and the process is related to the so called chain hopping mechanism. In the present investigation chain-hopping and trap-hopping mechanism may be invoked.

Photo depolarization experiments of films suggest that carrier generation occurs via excitons. The electrons are deeply trapped and the dissipation of polarization is bimolecular in nature.

The charge storage capability of a polymer electret and the different mechanisms contributing to storage of the charge are greatly influenced by the structure of the forming polymeric matrix. The effect in polymers can be produced not only by the conventional procedures but can also be obtained by making some structural changes by doping of the matrix with
suitable impurities like iodine. All the four studies of doped films reveal that the electret forming characteristics of PS can be greatly modified by doping it with iodine even in very small quantity. Doping facilitates molecular chain motion as is apparent from the shift to lower temperature of TSC and dielectric loss maxima. The conductivity and dielectric loss are enhanced due to doping, resulting in marked space charge peaks which have been observed in TSC. The foreign molecules i.e. guest molecules are undoubtedly responsible for the presence of deeper traps. The trapping activity of guest molecules depends on their electron affinities and ionisation potentials. The shallow traps are those from which carriers are released thermally and deep trapping levels occur where charge carriers stay longer.

The effect of doping may also be described in term of charge transfer complex formation. Charge complex is an aggregate in which bond formation between two molecules occurs. In terms of donor-acceptor levels, in the absence of radiation, the donation of an electron causes n-type conduction. In the same material, however, irradiation may create a pair of carriers at the level of the valence band due to high energy an electron can be transferred to the conduction band and trapped in trapping sites,
thus leading to a p-type conduction. Acceptor levels should be considered as a hole in the valence band which may result from electron trapping, leading to p-type conduction. In the same material, radiation induced conduction is n-type if a hole is trapped from the pair of created carriers and the electron is transferred to the conduction band.

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