CHAPTER I
GENERAL INTRODUCTION
1.1 INTRODUCTION

Ion irradiation in solids results in creation of a variety of defects, typically vacancies, interstitials and dislocations. The range of radiations may include photons to various high energy heavy ions. The possible types of radiations may come from the natural environment of space, the operating environment of a nuclear accelerator facility, or the controlled irradiation from an accelerator. Ions incident on matter experience two different stopping processes which cause them to lose energy as they traverse the host material/1,2/. These stopping processes arise both from the electrons and the nuclei of the host material medium and are termed as the electronic stopping and nuclear stopping respectively. High energy ions dissipate most of their energies in electron excitation rather than nuclear collisions. Through the Coulomb interaction with the electrons of the lattice ions the irradiating high energy ions may produce their tracks in some insulating or semiconducting materials provided some basic kinematic considerations of the host material and the heavy ions are satisfied. The observation of the structure of tracks so produced is important not only in the development of nuclear materials and of solid state detectors for high energy ions, but also from the fundamental standpoint to elucidate the mechanism of track formation/3/. Passage of a heavy ion in a material used as a solid state nuclear track detector (SSNTD) creates large scale lattice defects or radiation damage along the path of the heavy ions. These extended lattice damage may
remain stored in the host material as latent tracks /4-6/. Exchange of energy between electrons and nuclei is inhibited by the large mass discrepancy, but is an important component of radiation damage. The transfer is primarily one way, with electrons driving nuclear motion. Transfer of nuclear energy to electrons does occur but is less clear in its consequences. Electrons produce sparse damage with widely separated point defects dominating while heavy ions produce clusters of damage and the debris of cascades /1/.

Ion beams have been used to modify the electrical, electronic and optical properties of polymers by depositing energy in the material. Further, bond breakage of organic molecules in general results in the formation of an ensemble of smaller molecules many of which may be volatile /2,7/. As a result during the irradiation, some material is expelled from the original solid thereby producing an irreversible change.

Some of the experiments on high energy ion-polymer interactions have been summarized in Fig. 1.1 as a function of the ion dose of a heavy ion like Ar⁺ /2/. In certain polymers new carbonaceous material is formed with enhanced electrical conductivity. Considerable research efforts have gone into studying the conductivity of polymers under a range of conditions other than during radiation, e.g., with a strong applied electrical field. Studies using radiation have notable advantages, as irradiation is known to enhance the electrical conductivity together with wider ranging modifications on the
Fig. 1.1 Typical ion–polymer interactions phenomena observed as a function of dose for a typical heavy ion, Ar⁺, at 2 MeV energy.
dielectric properties because of absorbed energy /8, 9/. Different mechanisms, such as electronic excitation, electronic ionization and atomic displacement are claimed to influence the electric and dielectric properties.

1.2 ION BEAM EFFECTS IN ORGANIC MOLECULAR SOLIDS AND POLYMERS:

Ion irradiation leads to irreversible changes in organic films and polymers and hence it is important to understand the damage mechanisms in these solids /1, 2, 10/. Effects of ion beam irradiation at low and high fluence have attracted large interest in the last decade and have been investigated in different laboratories /11/. The large change induced in electrical conductivity has been studied by Forrest et al. and by Wnek et al. who have characterised the temperature dependence and some doping effects induced in polymers by different ions. Marietta et al. have found a correlation between chemical structure modifications and electrical change of some polymers like polystyrene, polyimide and polyethersulfone. Aleshin et al. have reported the electrical behaviour of ion irradiated polyimide. Polymer films darken upon irradiation with energetic ion beams. At high doses (10^{16} - 10^{17} \text{ cm}^{-2}) of 2 - \text{MeV Ar}^+ ions, the resistivity of these insulating films decrease dramatically to the order of 10^{-3} \text{ }\Omega \text{cm}. Furthermore, over a wide range of doses (10^{14} - 10^{15} \text{ cm}^{-2}) these films exhibit a temperature - dependent resistivity characteristic of carrier transport via hopping between isolated conducting islands /12/. Along with
different chemical changes of polymers as an effect of ion irradiation, dramatic changes in their optical and structural properties have also been observed and widely studied / 12 , 13 / . Amorphous polymeric and organic materials have been studied as well as highly ordered crystalline polymers. Ion irradiation provides a mechanism for radically modifying their electronic, transport and optical properties.

The formation of radicals in irradiated polymers is a sequence of a series of events initiated by the absorption of energy from the incident radiations. Not always is the electron ejected from the parent molecules recaptured by the polymer molecule to give a radical, it may become a mobile electron, away from its parent molecule, or it may be trapped and released far later. These electrons are liberated uniformly through the specimen and one can find out the effect of temperature and dose rates / 14 / . The behaviour of electrons in irradiated polymers may provide valuable information of the behaviour changes in heavy ion irradiated solids in general and polymers in particular.

1.3 RADIATION DAMAGE IN POLYMERS:

Energy transfer from ionizing radiations to large molecules, results in primary ionization and excitation / 1 , 11 / . In polymer samples it induces breaking of original bonds, production of excited and ionized species, and radicals; and bond rearrangements, which are responsible for the most observed chemical modifications / 2 , 15 , 16 / . Fig. 1.2 represents the passage of a ionizing
Fig. 1.2 Passage of an ionizing particle in a polymer.
These effects are due to the large amount of energy storage in the electronic molecular environment, which overcomes the binding energies of simple organic molecules.

In a short time (10^{-13} \text{s}) the ion energy is transferred to the electrons in the polymeric chain, within a small volume surrounding the ion track. The energy spike is very high, reaching values of the order of 100 \text{eV/atom} for a single ion track. For ions in the MeV/amu energy, the energy transfer occurs only through electronic ionizations and excitations, over extension up to 100\AA\ for energetic secondary electrons (or \delta rays)/11/.

As regards the second step, the electronic energy decay produces intermediate species (ionized and excited species, radicals, etc.) which may recombine or react within a volume much larger than the ion track, due to diffusion effects. Because these reactions involve molecular group species of the same ion track, the average distance of ionization events inside the ion track is an important parameter. For high energy particles this distance is very small (1 - 10 \text{\AA} \ ) and reactions between different subionizations can occur producing nonlinear effects. This picture suggests that ion polymer interaction is a complex process where a lot of primary and secondary effects are involved.

In general the energy deposited by the incoming ion in the polymer film, in steady state condition, results in crosslinks or scission of the original chain. The prevalence of one effect on the other depends on the
polymer structure. For example, Poly (methyl methacrylate) [PMMA] undergoes scissions because the tetra-substituted carbon atoms tend to degrade the main chains, while the presence of benzene rings in the PS structure increases its stability by trapping the excitation energy. Together with crosslinks and scission production, gas depletion from polymer is always observed /11,17/.

1.4 THEORY OF LATENT PARTICLE-TRACKS IN POLYMERS:

Chadderton et al. /18/ proposed an atomistic model which accounts for the rate of accumulation of ion-induced radiation damage in the form of latent nuclear tracks in polymers. The theory specifically applies for incident ion energies $E \geq E_{\text{max}}$, where $E_{\text{max}}$ is that energy corresponding to the peak in the electronic stopping power for particular ion/target combination. Latent charged particle track production in polymers is essentially due to chemical bond-breaking events along the ion trajectories. Ion-beam induced scission of polymeric chains typically produces charge redistribution along the skeletal backbone of a polymer molecule /19/. This gives rise in turn to chemically unsaturated bonds and a variety of topological cross-linking rearrangements of polymer fragments. This is also a simultaneous generation of free radicals which often diffuse rapidly to the surface of the ion beam modified polymer. The energy loss process, particle to polymer, is radiophysical. Subsequent developments in the radiation damage process itself, however, are
primarily radiochemical, characterized by continual irreversible steps as commulative polymer degradation proceeds. Isolated bond-breaking events, extended regions of damage, and implanted impurity atoms, all play key but competing roles in a diffusion scenario leading towards aggregation and growth of macroscopic radiation damage.

1.5 THE PRESENT STATUS OF POLYMERIC TRACK DETECTORS:

Some solid-state materials are in use as nuclear particle track detectors for their good track sensitivity and track storing property. CR-39 (PADC) is one such solid-state nuclear track detector (SSNTD). Tracks are not formed in metals and good semi-conductors. In general, only materials having resistivity values greater than 2000 ohm cm. can store tracks. Heavy ions passing through insulating solids ranging from crystals to glasses and high polymers produce extended lattice defects. In metallic or low band-gap semiconductors such tracks are not formed.

It has been observed that only high band gap semiconducting materials are capable of storing latent tracks, produced along the heavy ion trajectories. According to the ion spike model, along with conductivity i.e. the free carrier density and their mobility, the dielectric property and elastic strength of the material are other equally important physical attributes which determine whether the material is a track detector or not. The various physical properties of a track detector are related as per the ion spike model as
where \( \varepsilon \) is the dielectric constant for the material, \( \varepsilon_0 \) is the permittivity of free space, \( e \) is the electronic charge, \( a_0 \) is the interatomic spacing, \( n \) is average ionization of unit charges and \( Y \) is the Young's modulus for the mechanical strength of the material. The latent tracks are basically the sites of lattice damage. The lattice vibrational time \( t \), and carrier mobility \( \mu \), should also bear the relation \( \mu < r_0^2 e / 4 \pi k T t \) for the latent track to be stored at any temperature \( T \), where \( r_0 \) is the track radius. The criteria for track formation can thus be expressed as

\[
n^2 > \frac{4 \pi \varepsilon_0 \varepsilon a_0^4 Y}{10 e^2}
\]

In general, for polymers

\[
0.01 \geq \frac{4 \pi \varepsilon_0 \varepsilon a_0^4 Y}{10 e^2}
\]

and for inorganic crystals

\[
1 \geq \frac{4 \pi \varepsilon_0 \varepsilon a_0^4 Y}{10 e^2}
\]

Thus it is seen that a systematic study on the changes or modifications of conductivity, dielectric constant and structural composition of a track detector in its pristine state and after the passage of heavy ions through it, should provide a basic insight to the track formation mechanism itself.

### 1.6 CR-39 PLASTIC DETECTOR:

The CR-39 detector is made of allyl diglycol carbonate plastic. The material used in this work is manufactured by Pershore Mouldings, England. This material is commercially referred to as CR-39 polymer, CR for Colombia Resin with registered type no. 39.
The chemical composition is $\text{C}_{12}\text{H}_{18}\text{O}_7$ and the molecular formula is:

$$\begin{array}{c}
\text{O} \\
\text{CH}_2\text{CH}\text{CH}_2\text{O}\text{C}\text{O}\text{CH}_2\text{CH}_2\text{O}\text{CH}_2\text{CH}_2\text{O}\text{C}\text{O}\text{CH}_2\text{CH}_2\text{O}
\end{array}$$

CR-39 is a thermoset plastic that combines the optical properties of glass with mechanical and physical properties superior to other plastics.

i) **Absolute clarity**: Cast CR-39 has optical properties comparable to those of optical glass. The surfaces of CR-39 sheets are equivalent to polished glass in surface lustre, smoothness and chemical resistance. Its index of refraction is only slightly lower than the refractive index of crown glass.

ii) **Stability of optical properties**: CR-39 maintains its excellent optical properties through a wide variety of difficult environments and conditions of use. It does not crack internally or at the surface as a result of age, stress, or contact by most solvents. It possess excellent photo-elasticity, exhibiting no loss in optical properties resulting from strain.

iii) **Chemical and solvent resistance**: CR-39 is immune to the effects of virtually all solvents including acetone, benzene and gasoline, and to most chemicals other than highly oxidizing acids.

iv) **High heat resistance**: CR-39 resists distortion due to heat. In tests it has shown distortion of 35 to 65 mils at 130 °C, at which temperature acrylcs are fluid. CR-39 has a burning rate only one-fourth than that of cast acrylics materials, and under some conditions is rated as self-extinguishing.
v) **Resistance to gamma irradiation**: CR-39 withstands about fifty times as much radiation as acrylics materials before physical properties are reduced to the 50% level. The transmittance loss of CR-39 is only 5% after 100 million röentgens exposure, compared to 45% loss for acrylics subjected to the same exposure.

vi) **Light weight**: CR-39 is a comparatively lighter material having a specific gravity slightly lower than that of most plastics and approximately one-half that of glass.

vii) **Response and sensitivity of CR-39**: CR-39 is the most sensitive and uniform SSNTD with a high charge resolution and good optical properties. It can record very low REL (Restricted energy loss) events to reveal cores upon etching. This means that its threshold etchable ionization is very low.

viii) **Some physical properties of CR-39 Allyl Dicycol Carbonate**:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity, 25 °C</td>
<td>1.32</td>
</tr>
<tr>
<td>Refractive index at 20 °C</td>
<td>1.50</td>
</tr>
<tr>
<td>Specific heat, cal/g °C</td>
<td>0.55</td>
</tr>
<tr>
<td>Thermal conductivity J/cm²/s/°C</td>
<td>7.53</td>
</tr>
<tr>
<td>Water absorption, 24 hrs/25 °C</td>
<td>0.2</td>
</tr>
<tr>
<td>Density g/cm⁻³</td>
<td>1.32</td>
</tr>
</tbody>
</table>
1.7 EFFECT OF AMBIENT CONDITIONS ON CR-39:

i) Effect of ageing: It has been reported in the literature /20 - 23/ that the sensitivity and response of CR-39 and other SSNTD's depend on the environmental conditions like temperature, total ambient pressure and/or partial pressure of oxygen before, during and after the exposure to the particle radiation. Response of CR-39 does not vary noticeably with the time lapsed between irradiation and etching or on ambient temperature and humidity during ageing as long as oxygen pressure profile is constant /23/.

ii) Effect of registration temperature: It is now well established that the response of SSNTDs depends critically on the ambient temperature during the exposure /24, 25/. It has been seen that higher the ionization, larger is the rate of change in the response.

The sensitivity of a polymer /26/ to the registration of particle tracks is closely related to its sensitivity to the formation of chain scission under irradiation. It suggests a means by which useful track-storing polymers may be identified, and also provides strong evidence that chain scission is of primary importance in the track formation process in such materials. Low temperature during irradiation is one important factor which affects the registration sensitivity of plastic track detectors /24/.
1.8 MOTIVATION OF THE PRESENT STUDY :

A correlative study of these physical attributes i.e. electrical conductivity and dielectric property of a track detecting material with the various parameters of the track forming ion beams is of significant importance in track formation mechanism.

Although quite a good amount of work in this regard is reported /8, 27–29/, still the data are not comprehensive enough for making point to point correspondence between track formation mechanism and physical attributes of the track detecting material. Keeping these objectives in mind the present research study has been undertaken.

1.9 OUTLINE OF THE PRESENT WORK :

In view of the present status of the work as has already been mentioned, it has been proposed to make a detail experimental study in the pristine and variously irradiated conditions of PADC SSNTD on
(a) d.c. conductivity mechanism under different ambient conditions
(b) dielectric response under different ambient conditions
(c) structural investigations using XRD, UV-Vis and FTIR spectrometry.

As a result of this study it is expected that the experimental data concerning the various physical attributes will suitably supplement the existing knowledge for a comprehensive understanding of the track formation
mechanisms in terms of electrical conductivity, dielectric properties and structural modifications in irradiated samples.