CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

This chapter includes the review of literature along with basic introduction about the polymers. Molecular structure and arrangements of polymer chains is also discussed for determining the properties of polymers. To highlight the interaction of ionizing radiations with matter, the detailed study of interaction processes, along with the ion range, electronic stopping power, heavy ion stopping powers, delta rays, track formation models and nuclear stopping power have been discussed. The mechanisms of radiation induced processes like cross-linking of polymer chains, chain-scission, oxidative degradation and changes in unsaturations, evolution of gaseous products are included. Motivation and objectives of thesis are also explained in this chapter.

1.1 Introduction

For many centuries, naturally occurring polymers deduced from plants and animals have been used. Numerous polymers have been groomed using new scientific tools. Due to low cost and ease of shaping, the utilization of polymers is enhancing. They are unusual resourceful class of materials; having different values of given property and sometimes different physical states are designated to the same polymer (Bower, 2002). The energetic growth of polymer science and the wide usage of polymeric materials in all fields of technology have aroused the interest towards various problems of physics and chemistry of polymers. The consequences of high energy ion irradiation in polymers have captured extensive attention for the application of polymers in radiation environment and also in the advancement of new electronic devices (Tahara et al., 1997; Zhang et al., 1997). A broad research has been focused on swift heavy ion irradiated polymers of precise nature of heavy ions and their prominent penetration length in polymers. An extensive diverseness of material modifications in polymers has been analyzed using ion irradiation technique (Lee, 1999; Ruck, 2000; Balanzat et al., 1994; Boufford et al., 1995). Earlier studies by the different research groups across the globe have investigated induced modifications of polymer (Rizk et al., 2009; Singh and Prasher, 2006; Phunkan et al., 2003; Biswas et al., 1999). These
modifications are due to changes in the micro structural properties such as phase
distribution and chemical bonding. The characterization using different techniques has
been done to relate the changes produced in optical, thermal and structural properties
due to swift heavy ion irradiation.

1.2 Polymers

Polymer word is broken as poly means many; and mero’s means parts. Polymers
are the compounds of very high molecular weight comprised by aggregating large
number of unit structures called monomers and the process of formation of polymers
from several monomers is known as polymerization,

A polymer resulting from polymerization of a single monomer is known as
homopolymer, whereas the polymeric compound made up of two different types of
monomers in the same polymer chain is named as copolymer. Polymers can be
classified in number of ways as:

- On the basis of polymerization, polymers can be distinguished as homopolymer
  and copolymer.
- On source of availability, polymers are classified as natural and synthetic
  polymers.
- On the mode of synthesis, polymers are sorted out as addition and condensation
  polymers.
- Based upon molecular forces acting between the molecules, polymers are
  classified as thermoplastic, thermosetting, elastomers and fibres.

(a) Thermoplastic: Thermoplastics are the polymers which soften on heating
    and on reversing harden e.g. Teflon, PVC and Polyethylene.

(b) Thermosetting: These polymers undergo irreversible or permanent
    change on heating e.g. Polyester and Polysiloxanes.

(c) Elastomers: These polymers possess elastic character e.g. Natural rubber.

(d) Fibres: In these polymers chains are held together by H-bonds, dipole-
dipole interaction.
Polymers are also classified as linear; cross linked and branched polymers on the basis of their structure.

Organic polymer, inorganic polymer and elementoorganic polymer are the types of polymer based upon the chemistry of polymers.

Amorphous and crystalline polymers exist depending upon the morphological behavior.

Polymers are also sorted as charged polymers, having some free functional groups and uncharged polymers.

1.3 Molecular Structure and Arrangements of Polymer Chains

The important factors for determining the properties of polymers are the molecular structure and the arrangements of polymer chains. Polymers are prepared at several distinct levels as given below (Fink, 2004):

- Primary structure is the monomer chemical structure specified with given functional groups and associated electronic structure.

- Secondary structure is the chain specified by the spatial arrangements of some $10^2$ to $10^6$ repetitive units in the polymer chains.

- Tertiary structure is the global form of macromolecule as determined by weak Vander Waals forces, hydrogen bonds and the sum of conformational constraints. The molecular chains in general are dressed in zigzag or helical shapes. Usually the chains are not linearly stretched but wrapped up. The shape of molecules can be thread-like, cross-linked either as single distinguished units or intertwined with each other through covalent bonds.

- This leads to amorphous or crystalline arrangements (1-10 μm) as the quaternary structures. Most polymeric single crystals consist of many lamellae placed one over the other in decreasing order of size. Here the long chains are fitted into narrow lamellae having length around 100-1000 nm and thickness around 10 nm.

- These lamellae may arrange globally in still larger units, having size around 100 μm, known as spherulites.
Polymer properties are effectively influenced by its geometrical arrangements and its side groups. The infinite number of shapes of a given polymer chain exists due to its large size and the rotational degree of freedom of most covalent bonds that gives rise to a random and strongly entangled arrangements of the polymer chains.

The role of polymers in our daily life has become indispensable as modern synthetic polymers have substituted the metals in number of applications (Bahadur and Sastry, 2007). The tremendous role of polymers in everyday life has challenged the scientists to bring out new developments in the field of polymer science.

1.4 Interaction of ions with matter

When an ion passes through the matter it loses energy either by elastic or inelastic collisions. The energy loss of a charged particle after travelling a distance $\Delta x$ in matter is denoted by $\Delta E$. In practice at least three different values of energy loss appear that can be named as: mean energy loss, median energy loss and the most probable energy loss. Generally the differential energy loss per distance traversed $dE/dx$ can be replaced by $\Delta E/\Delta x$. This entity $dE/dx$ is called the stopping power ($S$).

1.4.1 Interaction Processes

The interaction processes contributing to slowing down of energetic charged particles in matter are as follows:

- Electronic stopping power involves inelastic collisions with the atomic electrons of the media. In this case the number of individual collisions is large but the path of the ion is practically unchanged.
- Nuclear stopping power involves elastic collisions with the target nuclei. The ion can lose most of its energy in a single collision and its direction can change considerably.
- Radiative stopping power includes processes not included in above mentioned processes, namely bremsstrahlung emission, Cerenkov radiation and nuclear reactions which are notable only at high particle energies.
1.4.2 Electronic Stopping Power ($S_e$)

When the energetic ions pass through material, atoms are not displaced from their locations and get excited or ionized due to interaction of electrons with the highly energetic radiations. The theory of electronic energy loss was first given by Bohr (Bohr, 1913). The expression for ($S_e$) was derived on the basis of a model which viewed the target as the group of harmonic oscillators and the study was extended to relativistic ions by Bethe (Bethe, 1930) and Bloch (Bloch, 1933). The expression given by them is known as Bethe-Block formula which describes the electronic energy loss of a highly energetic ion in the material quantum mechanically as follows:

$$S_e = -\frac{dE}{dx} = \frac{4\pi\hbar^2 Z_p^2 Z_t N_t}{m_e v^2} \left( \log_e \left( \frac{2m_e v^2}{I} \right) - \log_e \left( 1 - \frac{v^2}{c^2} \right) \right) \left( 1 - \frac{v^2}{c^2} \right)$$

Where $v$ and $Z_p$ are the velocity and charge of projectile ion, $I$: is the ionization potential of target material and $Z_t$, $N_t$, $m_e$, and $e$ are atomic number, number density of target atoms, rest mass of electron and charge of electron respectively.

Equation (1.1) is generally valid for different types of ions until velocity of these ions is quite large as compared to velocity of orbital electrons in the target material. The reason behind this fact is that if velocity of ion is less, the ion will spend greater time in the vicinity of electron. Hence more energy and impulse will be transferred to the electron.

1.4.3 Nuclear stopping power ($S_n$)

Nuclear energy loss occurs when an energetic ion collides elastically with target nuclei and causes atomic displacements. When a colliding particle imparts energy greater than displacement threshold energy, which is the amount of energy required to overcome the binding forces and to deviate from its original site, atomic displacement comes into play. In formulating the nuclear interactions involved in nuclear stopping, the interactions between the charged particles and the target atoms are described by a screened Coulomb potential
where $F_s$ takes into account the screening caused by electrons.

### 1.4.4 Heavy Ion Stopping Powers

The commonly employed procedure for predicting heavy ion stopping powers is by scaling from proton or alpha particle stopping powers. The simplest scaling law is (Raisanen, 2003):

$$ S_{HI} \propto \frac{Z_{22}^2}{Z_{21}^2} \frac{S_{H1}}{S_{HI}} \frac{Z_2}{Z_1} $$

(1.3)

It should be noted that the velocities of protons and heavy ions must be the same. This is valid only if the effective charge of heavy ion does not change during the slowing down process. A more appropriate procedure is to adopt the effective charge formulation. In this scheme the heavy ion stopping power is obtained from

$$ S_{HI} = S_{H1} \frac{Z_1^2}{Z_2^2} = S_{H1} Z_{HI}^2 \gamma^2 $$

(1.4)

where $\gamma$ is the so-called effective charge of the ion.

### 1.4.5 Delta Rays

An energetic ion undergoes two types of collisions with the target electrons, while moving in the solid. The first one is known as glancing collision, which involves inelastic scattering and the other is called knock-on collision and it refers to elastic scattering. Each glancing collision occurs quite frequently and involves a small energy loss. On the other hand knock-on collisions occur very infrequently and impart a large amount of energy to a target electron. According to theoretical and experimental evidences approximately electronic energy loss due to glancing collision and knock-on collision is shared equally. The energy transfer occur in both cases is either by electronic excitation or by ionization. The ejected electron is often called delta ray or secondary electron. The delta ray can further produce excitation and ionization if it carries enough energy.
1.4.6 Ion Range

The distance travelled by a penetrating ion before it loses all its kinetic energy via elastic or inelastic collisions is known as range of that ion. In other words, the range of an ion in the target material is the average depth of penetration of an ion into the target material before it loses all its kinetic energy and stops. The range of an ion is inversely proportional to the stopping power of the target, mass of the ion and is directly proportional to the energy of the ion. The nuclear energy loss occurs in discrete amounts, in contrast to electronic loss which occurs continuously. The energy transfer process has probabilistic nature, thus the amount of energy loss varies from one collision to the other and contributes to a straggling of the ion range.

1.4.7 Track Formation Models

While traversing through the matter an energetic heavy ion leaves permanent changes in a small volume around its path. The high energy deposition gives rise to the formation of a chemical or structural defect cluster of cylindrical shape, known as ion track. The two different mechanisms are proposed for the track formation by swift heavy ions:

- Ion explosion spikes
- Thermal spikes

In the Coulomb ion explosion theory, it is considered that the ion creates a cylinder of highly ionized matter, which is unstable due to Coulomb repulsion between charges. Core Plasma model, the shock-wave model and the modified lattice potential model were derived from this theory (Lesueur and Dunlop, 1993; Fleischer et al., 1975).

In thermal spike model, energy from the bombarding ion to the lattice is transferred in two steps:

(a) Thermalization of energy deposited in the electronic system via electron-electron interaction and
transfer of this energy to the lattice via electron-phonon coupling/interaction (Toulemonde et al., 1993, 2004; Szenes, 1996).

The interaction between electron and phonons originate from the phenomenon of local polarization. It is assumed that a melt is formed in a localized zone of few nanometers, when the temperature exceeds the melting point of the crystal. The rapid thermal quenching of the hot region induces an amorphous track along the ion path in a short span of time \(10^{-11}\) s having diameter of typically few nm. The narrow cylinder of material that was heated quickly to high temperature and then quickly quenched by thermal conduction, results in modifying or disordering in track core. In new developments, one more model named as compound model is there to explain the track formation in materials (Rana, 2007; Chadderton, 2003).

1.5 Radiation stimulated Processes in Polymers

The peculiar radiochemistry of ion interaction with solid, starts with in \(\sim 10^{-16}\) s after the ion’s traversal through the polymer. The processes like cross-linking of polymer chains, chain-scission, oxidative degradation and changes in unsaturations, evolution of gaseous products etc. are resulted due to irradiation of polymers (Marletta, 1990; Kulshrestha et al., 2006; Calcagno et al., 1992; Balanzat et al., 1996; Trautmann et al., 1999). The magnitude of these processes relies upon the nature of the polymer, irradiation and post irradiation conditions. The parameters of the projectile particle, atmosphere and temperature are mainly incorporated in irradiation conditions. The ionization and excitation phenomena occur due to transfer of energy to the medium during irradiation. Polymers endure bond cleavages after the absorption of energy and results in the formation of non-saturated fragments called free radicals, hence are responsible for most of the chemical transformations detected in polymers (Chapiro, 1988). The various ion induced functional chemical entities created (Lee, 1999) are as shown in Figure 1.1.
1.5.1 Chain scission and Cross-linking

The chain scission due to irradiation leads to the decrease in molecular weight of polymer due to dispersal of volatile elements (H, O and N) or groups (CH$_3$, CO and CO$_2$) from the irradiated zone. In the absence of oxygen or other reactive elements and in case of high concentration of primary radicals, the scission polymeric bonds have opportunity to react with each other, thus ensuing in either recombining, or initiating cross-linking or end-linking, or the creation of double bonds (C = C). Cross-linkages are the covalent bonds which modify the properties such as tensile strength, modulus and molecular weight. The properties of PVC get modified due to radiation induced crosslinking, and have successfully been used in industries widely for cable and wire insulation (DeHollain 1980; Abdel-Fattah et al., 2002). Scission has a converse effect on the physical properties of the polymer ensuing in softer materials with reduction in molecular weight. In general, scission and cross-linking take place simultaneously. However, the ratio of these two processes is dependent on the chemical structure, physical state and irradiation conditions of the polymer. Depending upon the chemical structure, irradiation can cross-link or degrades the polymer. The polymers such as polyethylene, polypropylene and polyvinyl chloride cross-links due to irradiation and polymers such as cellulose, polyvinyl alcohol, poly methylmethacrylate undergoes degradation. Figure 1.2 A and 1.2 B demonstrates two generalized polymer structures: the tertiary backbone carbon atom highlighted and the quaternary backbone carbon
atom high-lighted. Polymer chains with tertiary carbon atoms are likely to crosslink, while polymer chains with quaternary backbone carbons are likely to scission (Coffey et al., 2002).

![Fig. A (cross-linking)](image1)

![Fig. B (chain scission)](image2)

**Figure 1.2:** Structure of irradiated polymer

where R may be a different atom or group other than H-atom. Radical-radical reaction is responsible for cross-linking (Charlesby and Fydelor, 1972). After the initial primary process of excitation and ionization, a free radical and a hydrogen atom are formed and with the abstraction of some hydrogen atom in the near vicinity secondary polymer radicals are yielded. Radiation and abstraction leads to the formation of pair of adjacent radicals, which cross-link readily with minimum probability of disturbance by other molecules. The hydrogen atom, which is not abstracted in first few collisions, is thermalized and can pass through long distances and experiences several collisions before abducting second hydrogen to provide a second free radical. The chains can move into the suitable arrangement by the slow movement of trapped radicals from within the crystallite into amorphous region, as the cross-linking takes place most voluntarily in the amorphous regions between polymer crystallites. The scission phenomenon of the polymer having quaternary carbon atom prevail in the main chain with R’ and R” are groups other than hydrogen atom. Such polymers having weaker C-C bonds at quaternary carbon, preferring bond scission at this location, are sterically emphasized and have low heat of polymerization. The presence of quaternary carbon forbids radical movement along the polymer chain and steric hindrance obstructs radical grouping ensuing in either the dissociation of the radicals engineered by bond scission at quaternary carbon atom. Irradiation of poly methylmethacrylate at room temperature leads to the main chain scission and cross linking that occurs more frequently in the amorphous sample of gamma irradiated LDPE in vacuum at room temperature (Dole, 1973).
1.5.2 Trapping of Ions and Radicals

On irradiating the polymers with ionizing radiations, ions and radicals are produced (Chapiro, 1988). Ions that resulted from electron abstraction are positively charged. If the molecules of the medium contain groups with significant electron affinities, these may capture the electron to form negatively charged species and as a result of bond scissions, free radicals are formed in pairs. The life time of these species in a liquid is very short, and these species aggregate as a result of very fast radical-radical matching and positive ion interactions with either electrons or negative ions. Similar situation is fulfilled in the polymer above its glass transition temperature, where the high mobility of its segments favours encounters of several reactive species. In contrast, in the irradiated polymer, mobility is substantially decreased and the trapping of ions and radicals takes place. The life time of the trapped species is reliant on glass transition temperature, farther is the system from glass transition temperature, longer is the life time of the species. Crystallinity of polymer is also responsible for the trapping of transient species particularly radicals.

1.5.3 Evolution of Gaseous Products

The gaseous products are formed due to the side-chain abstraction, and the constitution of polymer can be pondered by the nature of the gas. Different gases are evolved during irradiation in different polymers as shown in Table 1.1.

Table 1.1: Gases evolved due to irradiation in polymers (Chapiro, 1988).

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Polymer</th>
<th>Gases evolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Polyethene</td>
<td>H₂</td>
</tr>
<tr>
<td>2.</td>
<td>Polyvinyl chloride</td>
<td>HCl</td>
</tr>
<tr>
<td>4.</td>
<td>Polymethylacrylate</td>
<td>H₂, CO, CO₂, CH₄</td>
</tr>
<tr>
<td>5.</td>
<td>Polypropylene</td>
<td>H₂, CH₄</td>
</tr>
<tr>
<td>6.</td>
<td>Polyisobutylene</td>
<td>CH₄</td>
</tr>
</tbody>
</table>
1.5.4 Oxidation

The oxidation process uses the oxygen that diffuses into the polymer during or after irradiation. In ion irradiated polyimide, peroxy radicals, hyperoxides and carboxylic acids are produced due to oxidative process (Sun et al., 2002). Oxygen reacts with free radicals created during irradiation, and instigates oxidation processes. Oxidation reactions may result to radiation degradation in polymers, rather than to conventional cross-link in the absence of oxygen (Chapiro, 1988). Apel reported that chemically active radiolysis yield in heavy ion tracks undergo post-irradiation oxidation reactions. As a result of this, significant increase in track etch rate is observed due to storage of tracked polymers in air (Apel, 2003; Guillot and Rondelez, 1981; Benton and Henke, 1969; Tretyakova et al., 1980).

The concentration of oxygen in the polymer facilitates to figure the rate of oxidation, which is influenced by the solubility of, and permeability to, oxygen in the material and the pace at which oxygen enters. The factors like structural-morphological characteristics of the polymer, the microstructure of amorphous and defect areas, pressure of oxygen, dose rate, the thickness of sample, and temperature during irradiation govern the efficiencies of these processes (Woods and Pikaev, 1994).

A significant role is played by post irradiation oxidation in degradation of polymers. Post irradiation takes place by radicals trapped in the crystalline regions of the polymer, as the radicals in the amorphous regions react quickly with oxygen that disseminates comparatively easily into these sections of polymer. Radicals trapped in the crystalline regions of the polymer slowly diffuse to the surface of crystallites, where they react with oxygen to give peroxy radicals.

1.5.5 Changes in Unsaturations

Formation of double bonds may arise as a result of Chain scission (Chapiro, 1988). in The radiation induced formation of main-chain unsaturated groups (-C=C-) polyvinyl chloride has been effectively used in gamma and electron beam dosimetry (Abdel-Fattah et al., 2002). Establishment of triple bonds has also been evidenced in irradiated polymers (Sun et al., 2003a).
1.5.6 Changes in Chemical Resistance

The amount of cross-linking of polymers may be increased spectacularly by irradiating them with energetic ions, and highly cross-linked polymers demonstrate more resistance to solvents (Davenas and Thevenard, 1993; Calcagno and Foti, 1991; Calcagno et al., 1995). In ion irradiated polymers the cross-linking and chain scission competes with each other. Hence, cross-linking increases the resistance to chemical attack. Due to irradiation with energetic ions or other ionizing radiations, many chemically active species i.e. free radicals and unsaturated bonds are formed in irradiated polymeric material. These species react with other molecules and new chemical structures are produced in the polymer surface that changes its surface properties. At low and medium fluences, ions irradiation produces an extra free volume in the irradiated layer that may help penetration of gases or liquids into the radiation damaged material. If the ion fluence is increased up to certain value the cross-linking, carbonization and compaction of the irradiated material prevail and the highly degraded, compact surface layer may serve as an efficient diffusion barrier preventing the penetration of different agents from the outside (Fink, 2004; Davenas and Thevenard, 1993).

1.5.7 Changes in Optical Properties

It has been observed that ion irradiation introduces changes in optical properties of the polymers. The value of optical refractive index increases in gamma ray or low ion fluence irradiated polymer (Fink, 2004). Later these effects became the subject of special investigations (Fink et al., 1988; Guzman et al., 1985; Elman et al., 1985; Davenas et al., 1985). Ion irradiation produces adsorption centers in the UV and visible region of spectra. With increase in ion fluence the irradiated polymer changes its color from yellow to dark brown (Singh et al., 2008c). Although after irradiation with lighter projectiles even up to higher fluences, the color changes are evidently reversible, but the highly energetic swift heavy ion irradiation mostly induces irreversible color changes (Guzman et al., 1985).
1.5.8 Effect of Temperature

The temperature of sample during irradiation plays a significant role. Irradiation of polyethylene at liquid nitrogen temperature prevents the formation of allyl double bond. The free radicals produced during the irradiation are frozen into solid and react when the sample is heated to higher temperature. Irradiation of polyethylene in molten state causes the formation of more cross-links than irradiated at room temperature (Khoylou and Katbab, 1993).

1.6 Applications of Polymer Irradiation

Swift heavy ion irradiated polymers have been widely studied, because the modified physical, chemical and structural properties of polymers are used in the determined way in industrial applications (Mazzoldi and Arnold, 1987), as polymers and polymerization are the backbone of many industrial applications. In terms of technological improvements of properties and in furnishing an environmental-friendly process option, an ion implantation technique proved to be a powerful instrument in arousing the industrial and medical applications of polymers (Iyer and Markovic, 1995). Polymers with specific properties that can be achieved by irradiating (i) with gamma rays, energetic electrons and protons, or (ii) with swift heavy ion beams (Marletta et al., 1991). There are following applications of the irradiated polymers:

- Polymers may be exposed to a low level, extensive irradiation with deleterious effect after a long period of service time. These polymers are frequently used as ingredients in nuclear reactors, particle accelerators, radiation sources and space vehicles etc. A loss of mechanical and electrical properties may have serious consequences on the functions of these materials. Here, the primary interest is the detection, monitoring and stabilization of radiation effect (Singh, 2008).

- A significant role is performed by polymers in health science. The sterilized medical disposables are used to amend the health care quality by reducing accidental transmissions. The sterilization of medical disposables is done by radiation processing, as it is a dry process and sterilization of prepackaged items is done with extremely high degree of certainty (Singh and Silverman, 1992).
A macroscopic degradation effect is demonstrated by some fluorinated polymers, such as poly tetrafluoroethylene (PTFE) induced by incident ions. The produced micro channels can be utilized to develop micro filters or pierced micro pipes (Singh, 2008).

Various scientific projects are frequently figured out by track-etch membranes. For studying transport of liquids, gases, particles, solutes, electrolytes (Pasternak et al., 1995) and electromagnetic waves (Mitrofanov and Apel, 1989) via narrow channels, one-pore (DeBlois and Bean, 1970; Fischer and Spohr, 1983) and multi-pore samples can serve as unique models. The role of templates can be served by track membranes, for making exclusive micro- and nano-structures (Martin, 1994; Whitney et al., 1993; Zhitariuk et al., 1995). Electrically switch-able ion selective membranes and sensors can be developed by utilizing small-pore track membranes as matrices (Nishizawa et al., 1995)

The doors to the growth of several commercial methods of surface modifications were opened by the merger of the track-etch method with electroplating, plasma deposition, sputter coating, lamination and other technologies (Fischer and Spohr, 1983). The enhanced thermal and mechanical stability, of flexible polyimide-copper composites have been obtained and proposed for the yield of printed circuit boards (Apel, 2003).

In cell culture and laboratory filtration, track membranes are commercially utilized (Apel, 2003). For the usage in tissue culture and domain called cell, a series of products were formulated in the recent years. The substantial advantage for cultivating cells and analyzing the cellular activities such as transport, absorption and secretion are supplied by porous membrane filters. Laboratory filtration is a traditional application of track membranes but the examples of analytical applications are bacteria enumeration, blood separation or capture of latex micro-particles.

During ion irradiation, a hydrogen atom is lost in polyethylene (PE), which is a hydrogenated polymer, and at higher fluence, polymer becomes rich in carbon. Hence, high chemical stability and high electrical conductivity is presented by the
residual polymer. To make homo-compatible surfaces or conductive channels in insulators, treated polymers can be used (Mazzoldi and Arnold, 1987).

- By grafting of p-NIPAAM or other hydro-gels to PET track membranes, the so-called stimulus responsive membranes were obtained in the past decade. The flow rate and the transmittance of small and large molecules through these membranes are checked by altering the environmental factors (Yoshida et al., 1997). The membranes are considered as promising technological achievement and are extended for the controlled release of drugs.

- Cross-linking induced in polymers by the electron beam is a demonstrated industrial technology, particularly in heat shrink materials, vulcanization of elastomers, processing of foamed plastics, cross-linking of cable insulation, tubes, pipes and mouldings (Mehnert, 1995).

- The novel capacitor foil FRACAP is a PET foil with fractal structures made of porous aluminium banked on both sides. The PET foil is ion-irradiated and chemically engraved. For the capacitance of composite foil, as high as possible, the surface porosity and the treatment depth should have been chosen. The thickness of this foil is smaller than the thickness of offered anode foils made of engraved bulk aluminium and with this thickness, the capacitance, of the capacitor, having same dimensions and voltage stability increases.

- A prominent role is played by the electron induced grafting, in the industrial applications. Properties such as adhesion, wet ability, thermal stability, biocompatibility, flammability and resistance to certain chemicals can be mended by grafting of polymer surfaces.

- A substantial concern in connection with medical and biological applications has been fascinated by porous materials for micro-electro-mechanical systems (MEMS). These polymers based porous MEMS devices are generally found by consolidation of the pre-fabricated membranes into final device (Bohm et al., 2000). Transport of fluid micro-volumes and at the same time, separation of particles and molecules are
furnished by these devices (Apel, 2003). The ways to fabricate the monolithic structures, having micro- or nano-pores are opened by ion track technique.

- In industry, radiation curing and thermal drying are competent to each other. Although radiation process extends substantial advantages over thermal process:
  - consumption of energy reduces
  - production rates are high
  - no solvent release
  - space requirement is small
  - Moderate temperature is required during curing (Singh, 2008).

Electron beam curing of solvents coatings, inks, paints and adhesives have benefitted recognition as fertile and environment favorable technology.

- Bar code has become an essential part of the modern interaction between manufacturers, whole-sellers, transportation services and end users for the identification of a product. It is based upon the optical properties of polymer foil, containing arrays of etched ion tracks. Any specific piece of track membrane is a unique three dimensional structure qualified by number of pores, their diameter and length, their positions and angle of incidence. It is practically impossible to reproduce such a micro-structure using optical, mechanical, lithographic or xerographic methods (Apel, 2003).

1.7 Literature Review

Modifications induced in polymers due to swift heavy ion irradiation have gained much significance in the field of science and technology in recent years. Different studies of effect of ion irradiation on polymers revealed that the modifications occurred in structural and chemical properties such as main chain scission, creation of carbonaceous clusters and formation of volatile fragments (Fink et al., 1995; Fink et al., 1996; Singh and Samra, 2008; Singh et al., 2012; Steckenreiter et al., 1997) are due to high electronic energy loss of heavy ions in the target (Balanzat et al., 1996). The modifications induced in the polymers not only depend upon the ion species, but also on
the energy of the irradiating ions. The irradiating ions, after colliding with target particles, lose their energy by ionization, excitation, and collision processes (Singh et al., 2008a). The electronic stopping power of the target also plays an important role for the irreversible changes introduced in the polymer (Singh et al., 2007; Sun et al., 2003b). All these processes are responsible for the changes in structural, optical, thermal and chemical properties of the polymer due to the introduction of defects inside the polymer (Mackersie et al., 2001; Nasef et al., 2003; Saito et al., 2010; Samra et al., 2011a; Senna et al., 2001; Singh et al., 2008a, 2008b). This disruption occurs as chain scission, cross linking, carbonization, degassing of volatiles, as well as oxidation processes upon exposure to air (Nasef et al., 2003; Samra et al., 2011a, 2011b; Seguchi et al., 1999; Mishra et al., 2000; Calcagno, 1995; Beardmore and Smith, 1995; Balanzat et al., 1995). The irreversible changes triggered in the polymer, due to swift heavy ion irradiation, are quite different from those induced by low ionizing particles (Singh et al., 2008c). The swift heavy ion irradiation introduces both physical and chemical defects in the polymers (Nasef et al., 2003). At very high ion fluences, carbon clusters are formed (Duraud and Moel, 1995).

In the present work, the effects of swift heavy ion irradiation on the structural, optical and thermal characteristics of Ethylene-Chlorotrifluoroethylene (E-CTFE), Poly methyl methacrylate (PMMA), Polyethylene naphthalate (PEN) and Poly vinylidene chloride (PVDC) were studied. E-CTFE imparts in combination of properties delivered from both fluorocarbon and hydrocarbon polymers including heat resistance, mechanical stability and superior resistance to common solvents in addition to high resistance to radiation and fatigue (Radice et al., 2005; Nasef et al., 2003). Gamma irradiation of E-CTFE leads to change in mechanical properties (Luo et al., 1981) and hardening Agarwal et al., (1996). The gas emitted from E-CTFE induced by synchrotron radiation was studied by DeCastro et al., (2001). Their results showed that HCl was the most intensely emitted gas. Comparison of γ ray sensitivities of E-CTFE with other fluorinated polymers for its use in space environments was studied by Dargaville et al., (2006).

PMMA is an atactic, amorphous polymer, having $T_g = 112^\circ$C, with non-aromatic pendant groups (Mort, 1980). Earlier reports on irradiation of PMMA included studies
of the physical and chemical changes induced by 70 MeV carbon ions (Virk et al., 2010); effect of 145 MeV Ne$^{6+}$ ions on physico-chemical and structural properties of PMMA (Kumar et al., 2011); changes induced in the photoluminescence properties of swift heavy ion irradiated ZnO/PMMA nanocomposite films (Sharma et al., 2011) and formation mechanism of volatile products during ion beam irradiation of PMMA (Fragala et al., 1998); The effect of temperature on the mechanism of radiation induced degradation of PMMA (Ichikawa, 1995); gamma irradiation effects on thermal, rheological and thermogravimetric properties of PMMA composites (Silva et al. 2010); modifications induced in crystalline structures and micro hardness indentation of polymer composite films using 120 MeV Ni$^{10+}$ ions (Qureshi et al., 2008); effect of the addition of a nanofiller into a polymer matrix for characterizing thermal and optical properties of PMMA/CaCO$_3$ nanocomposites (Elimat et al., 2008) and modifications induced in optical band gap, activation energy and free volume parameters of electron irradiated PMMA (Ismayil et al., 2010) have also been studied.

Polyethylene naphthalate (PEN) is a semi-crystalline transparent polymer and has many applications due to its good optical and mechanical properties. The naphthalene ring in the main chain of PEN accounts for higher modulus, melting temperature and glass transition temperature (Nakamae et al., 1993). The study of properties of PEN has been described in number of research papers (Buchner et al., 1989; Cheng and Wunderlich 1988; Jackson, 1983; Murakami et al., 1996), however, a little about the effects of irradiation on PEN have been found in literature. Starosta et al. (1999) studied tracks induced in PEN films with pore size in the range 0.1-0.5 μm due to UV radiations. Track to bulk etch ratio in radiation induced PEN films were studied for producing micro and nanostructures (Apel et al., 2001) but Bartnik et al. (2011) suggested that the form of structure depends upon the type of polymer and UV exposure. Suppression of the loss of light elements (H, C, N, O) after aluminum coatings were observed in case of proton irradiated PEN films (Saito et al., 2010). The energy deposition and modifications by MeV light ion and UV laser induced luminescence of PET films revealed the reduction of luminescence centers by irradiation (Nagata et al., 2010). Electrical properties of gamma ray irradiated PEN films were discussed by Mackersie et al. (2001).
Poly vinylidene chloride (PVDC) is a co-polymer which is hydro halogenated. Irradiation of PVDC induced scission between the carbons of main chain and side substituent. This led to cross linkages and creation of double bonds in main chain. Parada et al., (2007) determined the chemical species in PVDC films irradiated with 1MeV proton using in-situ Residual Gas Analyzer (RGA). The effect of both the electronic and nuclear stopping power on ion bombardment (Evelyn et al., 1997) and the structural changes in PVDC irradiated with KeV and MeV energies at several fluences were reported (Parada et al., 2006). The Photoluminescence phenomenon in PVDC due to irradiation with 84 MeV Oxygen ions and 120 MeV Silicon ions (Samra et al., 2011a) and enhancement of conductivity in poly aniline-[Poly(Vinylidene Chloride)-co-(Vinylacetate)] blends of varying composition irradiated by gamma rays (Bodugoz-Senturk and Guven, 2011) were studied. Ionic desorption from PVC and PVDC polymers stimulated by the photon gives strong selectivity in the formation of chlorine ions (Faraudo et al., 2006). The effects of bombardment of MeV $\alpha$-particles on PVDC in their tracks were mapped using thin polymer film stacking technique (Evelyn et al., 1998).

1.8 Motivation and objectives of Thesis

In the light of above literature, it has been observed that a little work has been done to investigate the modified opto-structural and thermal properties in SHI induced E-CTFE, PMMA, PEN and PVDC. So an effort has been made to analyze modifications introduced in the properties of swift heavy ion irradiated Ethylene-chlorotrifluoroethylene (E-CTFE), Polymethyl methacrylate (PMMA), Poly ethylene naphthalate (PEN), Polyvinylidene chloride (PVDC) polymers. In order to have better understanding of radiation induced modifications, the optical, chemical, thermal and structural properties were analyzed. The earlier mentioned polymers were irradiated with lithium (50 MeV), carbon (85 MeV), nickel (120 MeV) and silver (120 MeV) ions having fluence range of $1\times10^{11}$ ions / cm$^2$ to $3\times10^{12}$ ions / cm$^2$. The irradiated polymers have been examined using different characterization techniques i.e. XRD (X-ray diffraction), FTIR (Fourier transform infrared), UV-visible, differential scanning calorimetry (DSC) and TGA (thermo-gravimetric analysis).