Chapter-1

Introduction

This chapter deals with the importance of irradiation in the field of material science, historical development of polymers, structure and morphology of polymers, effect of radiation on polymers, applications of polymers, fundamental principles of the interaction of swift heavy ion with polymeric materials and present work done.

Contents

CHAPTER 1

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1.1 Importance of Irradiation in the Field of Material Science

Modern high technology industry moves into ever more advanced methods of preparation and processing of advanced materials. This is especially true in the microelectronics and opto-electronics industry, due to the economic driving force of information technology market. Often developments pioneered in micro-electronics are transferred and modified for use in other industries, for example, advanced coatings for bearing surfaces.

In the development of mankind polymers have played a very important role. They are widely used in science and technology particularly in space and nuclear technologies in addition to the various applications in day to day life. The extensive utilization of polymeric materials and the rapid development of polymer science have created an increased interest in various problems of the physics of polymers. They have achieved the highest production status as compared to conventional materials like metals and ceramics. In addition to this, their economic superiority, vast spectra of physical properties, wide nature of mechanical parameters, flexibility, lightness, optical transparency, easy processing etc, also helps the polymer industry to achieve highest growing rate among others. The impact of such developments is very mild in developing countries like India, on the basis of per capita consumption rate.

Polymer properties can be tailor made by adding some additives (Physical modification) or by changing its chemical structure (chemical modification). It is known that when polymers are exposed to ionic radiation its properties e.g. mechanical, optical, thermal, electrical etc change rapidly. Radiation causes chain scission (brittleness, lower thermal property, higher solubility etc) or cross-linking (flexibility, better dielectric and thermal property) or both. The effectiveness of these changes depends on the structure of polymers and the experimental condition of the ions implantation like ion species, energy, fluence etc.

Ion irradiation offers a possibility to modify the properties of the materials in a controlled way on a microscopic scale. Ionizing radiations have a definite range of penetration; a high local confinement of deposited energy can be generated conveniently in great quantity. The created damage zones can be stored indefinitely in many insulators and can be used to initiate a phase transformation process that modifies the materials along the latent track. One ion suffices to induce physically and chemically – a submicroscopic change in the target material and thereby can render it susceptible to the development process. Thus the study of the properties of these materials before and after irradiation with different radiation fluences and at different temperatures is very important. Prior to this, one must know the historical background of polymers and their development with the understanding of their structural and morphological nature.

1.2 Historical Background of Polymers

As described above polymer science grew and developed in the middle of the last century. The advent of polymers is an important industrial revolution of the 20th century. In 1877, Kekule gave the first hypothesis of the existence of macromolecules. He proposed that natural organic substances derive their special properties from the very long chain of molecules of which they are made up. Records show that cast mouldings were prepared from shelloc by ancient Indians. Despite Indians using this technology, the first patent for this was taken in 1868. Shortage of ivory had become a major problem in and around 1868. Hence in 1868 John Wesley Hyatt of New York manufactured the first synthetic plastic producing celluloid by treating cotton with nitric acid and camphor. This material was used for the production of billiard balls.

John Trodescaut (1608-1662) introduced gutta-percha a natural resin from the east, to western civilization. Thomas Hancock discovered that if rubber was highly sheared or masticated, there is a several fold reduction in its molecular weight and it becomes a plastic and hence capable of flow. In 1839 Charles Goodyear found that rubber when heated with sulphur can retain its elasticity over a wide range of temperature and that the raw material can have, greater resistance to solvents. In 1844, he patented this. Later, this process was termed as Vulcanisation by W. Brockendon.

In 1893 Emil Fisher suggested a structure for natural cellulose having a chain of glucose units. He also postulated that polypeptides are long chain of polyamino acids. In 1909, an American Scientist, Leo Backeland from two very common chemicals

(Phenol and Formaldehyde) developed a resin (which was later named after him as Bakelite) that could be moulded into hard infusible articles. In 1912, Jacques Brandenburger introduced a famous transparent material – cellophane.

Hermann Staudinger received the Noble Prize in Chemistry in 1924, for his pioneering work in macromolecular chemistry and proposed the linear structure for polystyrene and natural rubber. As soon as the idea of macromolecules having linear structure was recognized, many materials e.g. Cellulose acetate (1927), polyvinyl Chloride (1929), Formaldehyde resins etc were discovered.

Again it needed a scientist with broad vision to provide a new concept for the development of synthetic polymers. This man was Wallance H. Carothers who gave a concept for the development of synthetic polymers and produced linear condensation polymers such as polyester and polyamides. His group including, Paul J. Flory [1-3], (who received the Nobel Prize in chemistry in 1974), made basic research efforts to study long chain molecules made from di-functional monomers, resulting in the development of Neoprene, Polyester and Polyamides. Subsequently rapid development of many important polymers e.g. Acrylics and Polyvinyl Acetate in 1936, Polystyrene in 1938, Malamine Formaldehyde in 1936, polyester and polyethylene in 1941 took place.

A brilliant scientist Kerl Ziegler of Max Plank Institute, Germany, was involved in synthetic organometallic chemistry. He observed that exposure of ethylene to some

aluminium alkyle compounds led very rapidly to polymerization of ethylene. He and Giullio Matta extended the work to other olifines. They received the Nobel Prize in 1963 for their discovery of stereo specific polymerization.

Within a decade or so, several polymers started appearing in newer and newer forms with better properties from the laboratories of scientists all over the world. In broad sense one can conclude that polymer industry came into existence only after 1900 and rapid development of polymer science has taken place during the last three decade. This period saw the development of several co-polymers and organometallic polymers. Now a days, various types of conducting polymers are growing with newer and newer forms. A large number of processing techniques accompanying them are also under development.

1.3 Polymers

Polymer is a generic name given to a vast number of materials made up of long chain molecules, composed of a large number of repeating units of identical structure having high molecular weight. Depending on their origin they can be grouped as natural and synthetic polymers. Owing to the presence of carbon in their backbone structure they can be classified as organic and in-organic polymers. They can be divided into thermoplastic and thermosetting polymers according to their response to application of heat. According to its ultimate form and use, a polymer can be classified as plastic, elastomer, fiber or liquid resin [4]

Polymers that are capable of high extension under ambient conditions find important applications as elastomers. Commercial materials, other than elastomers and fibers that are derived from synthetic polymers are called plastics. Today, polymeric materials are used in nearly all areas of daily life and their production and fabrication is seen world wide. Because of their low cost, easy processibility, low weight, high corrosion resistance, high electrical resistance, durability etc. polymers are fast replacing metals and alloys in many applications and are extensively used in industries, science and technologies, particularly in space and nuclear technology.

A kind of processing that is now routine is blending, a strategy that was first applied to amorphous polymers such as polystyrene, polyvinyl chloride and polymethyl metacrylate, an acrylic. Because they are not crystalline, such polymers have no melting point. However above a critical temperature known as glass-transition temperature, they become soft and rubbery. Amorphous polymers are serviceable only at lower temperatures, where their molecular structure is frozen and the material is glass like. Most amorphous polymers are brittle below their glass-transition temperature, although there are notable exceptions such as polycarbonate, a tough material found in protective helmets.

To increase the toughness of a brittle amorphous plastic it can be combined with another polymer, usually an elastomer. Most blends combine immiscible components, and so the material that results contains tiny particles of one polymer in a matrix of the other. Controlled mixing and cooling of the blend makes it possible to form the

particles in an optimum concentration and range of sizes. In a glassy plastic combined with a relatively small proportion of an elastomer the rubber particles toughen the material by enabling it to absorb energy more efficiently as it is fractured. Its resistance to crack propagation is hereby increased substantially.

Blending makes it possible to combine the good properties of several polymers, other methods of processing enhance the strength of a single polymer. If the bulk material is to benefit fully from the longitudinal strength of the polymer molecules, they must have a common orientation. Many rigid-rod polymers are readily oriented, but it is also possible to align the chains in a conventional flexible chain polymer through appropriate processing. The product is usually a fiber in which many of the ordinarily folded or coiled polymer chains are extended along the fiber axis, lending it great strength and stiffness.

1.3.1   Classification of Polymers:

Thousands of polymers have been synthesized and many more are likely to be produced in the future. Polymers can be assigned into one or two groups based upon their processing characteristics or type of polymerization mechanism. Specific classification can be made on the basis of polymer structure. While the chemical structure of a macromolecule depends on the chemical nature of the monomeric units, the geometrical structure depends on the spatial arrangement of the monomeric units

with respect to each other. Polymers exist only as solid or liquid but never as gas as they decompose before reaching their boiling point.

1.3.1 (A)   Classification based on Thermal Processing Behaviour.

Polymers can be divided into two major groups based on their thermal processing behaviour: Thermoplastics and Thermosets.

Polymers that can be softened on heating and be processed into a desired form are called thermoplastics. Waste thermoplastics can be recovered and re-fabricated by application of heat and pressure.

Polymers that cannot be softened on heating and be processed into a desired form are called thermosets. Thermosets are polymers whose individual chains have been chemically linked by covalent bonds during polymerization or by subsequent chemical or thermal treatment during fabrication. Once formed, these cross-linked networks resist heat softening, creep and solvent attack, but cannot be thermally processed.

1.3.1 (B)   Classification based on Polymerization Mechanism.

Polymers can also be classified on the basis of mechanism of polymerization: Addition polymers and Condensation polymers.

Addition polymers are polymerized from ethylene based monomers. As an exception a few other polymers that belong to addition class are polymerized, not by addition to an

ethylene double bond, but through a ring-opening polymerization of a sterically strained cyclic monomer.

Condensation polymers are obtained by the random reaction of two molecules. A molecule participating in a polycondensation reaction may be a monomer, oligomer, or higher-molecular-weight intermediate each having complementary, functional end units.

1.3.1 (C)   Classification based on Polymer Structure.

Polymers can be classified on the basis of the chemical structure of their backbones.

Polymers containing only one atom type along their backbone are termed as homochain polymers.

Heterochain polymers are those polymers that contain more than one atom type in their backbone. This type of polymers is grouped according to the types of atoms and chemical groups located along the backbone.

Apart from the classifications mentioned above, polymers can also be classified as natural and synthetic polymers. Owing to the presence of carbon in their backbone structure they can also be classified as organic and in-organic polymers. Polymers can also be classified as crystalline or amorphous depending on their physical structure. This is discussed in detail in the next topic.

1.4 Structure and Morphology of Polymers

Study of polymer structure has been carried out by many scientists [5-13]. The structural details of polymers are closely related with their chemical and physical properties. The micro structural studies have revealed that the basic structural elements of high polymers are linear chain molecules. Russian scientist Lebedev [14], was of the idea that polymers are long chain structures. He polymerized butadiene and assigned to the product a cyclo-octadine structure. Around 1900, one factor inhibiting understanding of the macromolecular nature of polymers, was that the motion of a colloidal state was prevalent in scientific thoughts and the common explanation of the properties of polymer was by an "association" or "misceller" theory. In 1915 Lebedev [15], proposed a chain structure for polybutadine and rubber. In 1920 Staudinger [16], differentiated linear and non-linear or network polymers. A lot of X-ray diffraction analysis of polymers by Sponsor Dore, Mayer, Mark and Freudenberg etc have provided additional evidences for the higher molecular weight theory and long-chain structure.

The description of the morphology and the interpretation of properties of semi-crystalline polymers remained a subject of deep and divisive debate for more than two decades (Geil, 1963; Madelken, 1980) [17,18]. The basic structural elements of high polymer solids, are the chain molecules. The variety of their structures and flexibility permits different modes of organization. The inter-relation between chain parameters (structure and regularity), crystals or super-structural parameters (degree of crystallinity, lattice parameters, nucleation and growth kinetics etc.) and environmental

parameters have been extensively discussed by Geil (1963), Keller (1968) and Wunderlich (1973) [17,19,20].

1.4.1   Crystalline Nature.

Crystallography of natural as well as synthetic high polymers has been known from the beginning of Polymer Science. Analysis of X-ray diffraction patterns has revealed the lattice structure and unit cell dimensions of high polymer crystallites. But the basis of crystallinity in polymers is quite complex. Each atom in the long chain molecule is covalently bonded to its neighbour in the chain, and an atom cannot move independently from one location to another; its neighbour must move in a highly prescribed manner since the nearest neighbour along the chain direction must always be the same atom. This restricted mobility of the bulky long chain of polymer molecules, prevented 100% crystallinity, even if it shows similar results as that observed in metals i.e. increase of crystalline phase with annealing. The basic requirement for crystallinity is chemical regularity along with the polymer chain (tactic), that is why higher crystallinity is not possible in atactic forms.

With the development of X-ray structure analysis, it was found that the diffraction patterns of polymers could be indexed in terms of a unit cell and a structure assigned. The X-ray crystallographic analysis of the unit cell of polyethylene by Bunn (1963) [21], marked an important point in the understanding of polymer science. Up to 1957 it was believed that the crystalline structure is of the fringe miscelle type (Flory, 1953)

[13], and that the chains are frozen into non-equilibrium position due to lack of mobility.
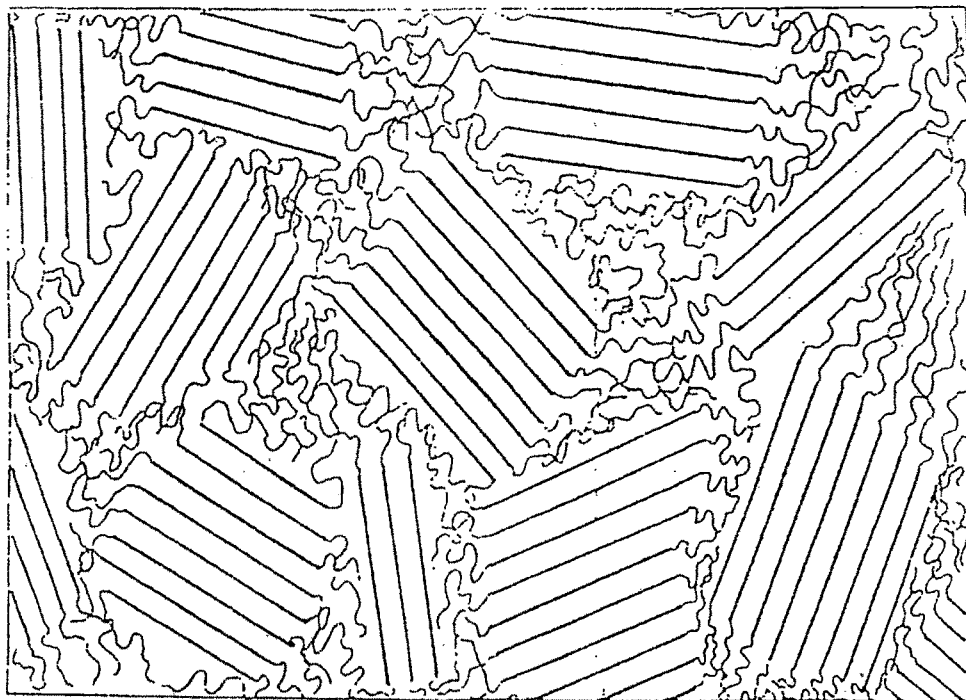
Figure 1.1   Fringed miscella concept of polymer morphology.

A typical miscella (**Figure-1.1**) was supposed to be a bundle of several tens of hundreds of different molecules which after leaving the miscelle and passing through amorphous regions, would randomly join other miscelles. It provides a basis for understanding most of the experimental data such as IR spectroscopy and X-ray diffraction patterns. This two-phase, fringed miscelle model enjoyed widespread recognition and popularity.

One simple experiment, performed independently but nearly simultaneously in 1957, by Fischer (1957), Keller (1957 and Till (1957) [22-24], changed the entire course of

study of the structure of polymers. This simple experiment led subsequently to the conclusion that mechanical properties are much more intimately related to morphology as compared to crystalline properties in single crystals of polyethylene. Polymer crystals are thin sheets with crystal habit called lamella. Their thickness is typically 100-200 A°, with widths extending up to the micron range. Electron diffraction patterns show that the long axes of the chain molecules are perpendicular to the broad surface of the lamella, or are very nearly so. Since the thickness of the lamella is only about one-twentieth of the length of the chain, some sort of chain folding is necessary to create the regularity in the lateral packing of the chains required by the unit cell.
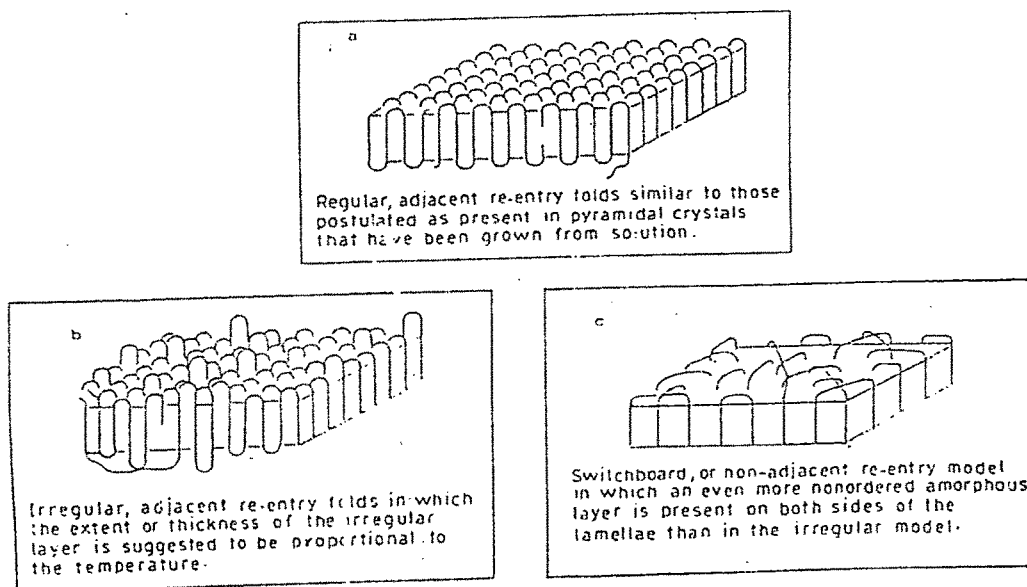
The concept of chain folding in long chain molecules was not new, having been proposed as long ago as 1938 (Lindemeyer, 1963)[25], for gutta-pareha. Although a lot of work on electron microscopy and small angle X-ray scattering regarding chain folding has been done, the chain folding is still debatable and does not have much relevance with experimental and theoretical aspects. The controversies regarding chain folding are divided into following three categories:

1. Regular, adjacent re-entry folds,
2. Irregular, adjacent re-entry folds,
3. Switch board or non-adjacent re-entry model.

The regular, adjacent re-entry model (**Figure–1.2(a)**) appears to be a limiting case which can be realized in practice only under the most carefully controlled conditions

for crystallization environment and for molecular weight uniformity. In the melt crystallized system, where one crystal lamella is developing in very close proximity to another growing lamella, it is simple to envisage a fraction of chain transversing more than one lamella, providing "tie molecules" that contribute strength to the assembly. Such a composite structure of lamella shaped crystals interspread with amorphous regions of loose loops, and tie molecules lends itself to a more realistic interpretation of the dynamic loss phenomenon and other mechanical properties. The various transitions of mechanical loss behaviour can also be interpreted by "irregular adjacent re-entry model" (**Figure –1.2(b)**) which provided both crystalline and amorphous regions in a simple complex "phase". Third model **(Figure-1. 2(c))** is now effectively disregarded. We know that molecules and their trajectories are not observed by electron microscopy. In order to resolve the nature of their interfacial structure, one needs different means and various other logical arguments. The efforts in this direction have been going on for more than 20 years. On tracing the history of this problem, it can be seen (Madelkeru 1980; Yoon and Flory, 1976)[26-27], that many of its aspects are now at the point of resolution.

a

Regular, adjacent re-entry folds similar to those postulated as present in pyramidal crystals that have been grown from solution.

b

Irregular, adjacent re-entry folds in which the extent or thickness of the irregular layer is suggested to be proportional to the temperature.

c

Switchboard, or non-adjacent re-entry model in which an even more nonordered amorphous layer is present on both sides of the lamellae than in the irregular model.

Figure 1.2   Models proposed for chain folding in single crystals of polymers.

The simple single crystals are in fact, structural additives prepared under very specially controlled conditions. Their values lie primarily as objects for the study of the chain folding phenomenon and the lamella crystal habit, which is generally accepted to be the basic structural unit of melt-crystallized polymers. The spiral growth of polymer crystal of polyoxymethylene is one of the very interesting complexities (Geil, 1963) [17]. Multilayer structures with a small fraction of molecules inter-connecting overlapping lamella was observed when a polymer was crystallized from more concentrated solutions. In bulk crystallization, lamella thickness up to the order of 1000 A° or even greater could be observed (Bassett et al., 1980)[28]. The lamella thickness depends on the molecular weight and crystallization conditions under atmospheric pressure.

Despite the observation of larger crystalline dimensions, it was very strongly and vociferously argued through the 1960's and much of the 1970's that the chains were regularly folded in bulk-crystallized polymers, (Geil, 1963; Keller, 1962; Lindemyer, 1962) [17,29,30]. The major principles that were widely enunciated to support regularly folded chain in bulk crystallized polymers were that

1. The chain units in crystalline homopolymers should be assigned to either the interior of the crystallites or to the smooth interface.

2. Chain units connecting crystallites were rare events and, if they existed at all, adopted ordered confrontations and

3. Deviations in properties from those expected from macroscopic crystals were widely known and accepted.

1.4.2   Amorphous Nature

Until about 1960 the general view prevailed that the chain molecules are isotropic, non-crystalline polymers like that in many rubber, glossy polymers, P.V.C., PMMA, PC or quenched "semi-crystalline" polymers such as Teflon, Mylar, which have a random confrontation and random coil. In the years following 1960 the concept of a close range-order of the chain molecules within X-ray amorphous polymers gained growing support.

The evidence for a close range order was thought to be derived from a comparison of segment volume and amorphous density from electron microscopic observation of structural elements from calorimetric investigations, crystallization kinetics and from a

study of network orientation. After 1970 Kirste (1972), Fischer (1976), Cotton (1974) [31-33], and their associates were applying neutron-scattering techniques to amorphous polymers in addition to employing light and small angle X-ray scattering and spectroscopic methods. Flory (1976) [34], summarized his extended observations on polymers in solutions rubbery networks in favour of random coil structure of chain in bulk.

Hosemann (1975), Pechhold (1971) and Yeh (1973)[35-37], proposed that amorphous states and defect rich, originally ordered states are commensurable. They have retained elements of close range order. Their amorphous state is not principally but only gradually different from a well ordered state. The model for amorphous state which is still controversial is now divided in the following four groups shown schematically in **Figure 1.3** respectively.
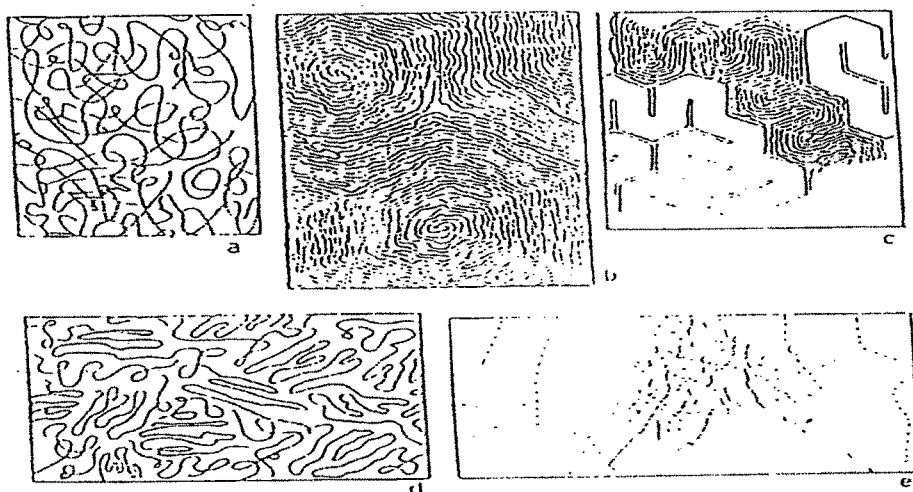

Figure 1.3 **Model representations of the amorphous state**
  (a) interpenetrating coils
  (b) and (c) honeycomb and meander model
  (d) folded chain fringed micellar grains
 **(e) fringed micellar domain structure**

(1) Interpenetrating random coil   [32,3]

(2) Honeycomb and Meander model   [36]

(3) Folded chain fringed misceller grains   [37]

(4) Fringed misceller domain structure   [37]

Further, there is a great variation of crystallinity from more than 90% to less than 5% for a given polymer, although unit cell parameters remain invariant of macroscopic densities over a large range.   The variation of crystallinity, spectroscopic results and melting temperature measurements, can be explained only when there are high interfacial energies. In other words it suggests the presence of a diffuse interfacial zone which is also supported by thermodynamic calculations.

From these results it is concluded that there is a lamella-like crystalline region, which represent the three dimensional ordered structure and a diffused interfacial region (not having sharp boundary). These interfacial regions contain several internal defects of the same order of magnitude as that observed in pure crystalline low molecular weight materials. Details of the structure still need to be worked out, but there must be some type of anisotropic orientation of the chain in the region close to the basel plane of the lamella. On the basis of the existing experimental and theoretical knowledge, the most suitable schematic model can be worked out as shown in the **Figure-1.4** where, crystalline zones are interlinked with amorphous zones irregularly.
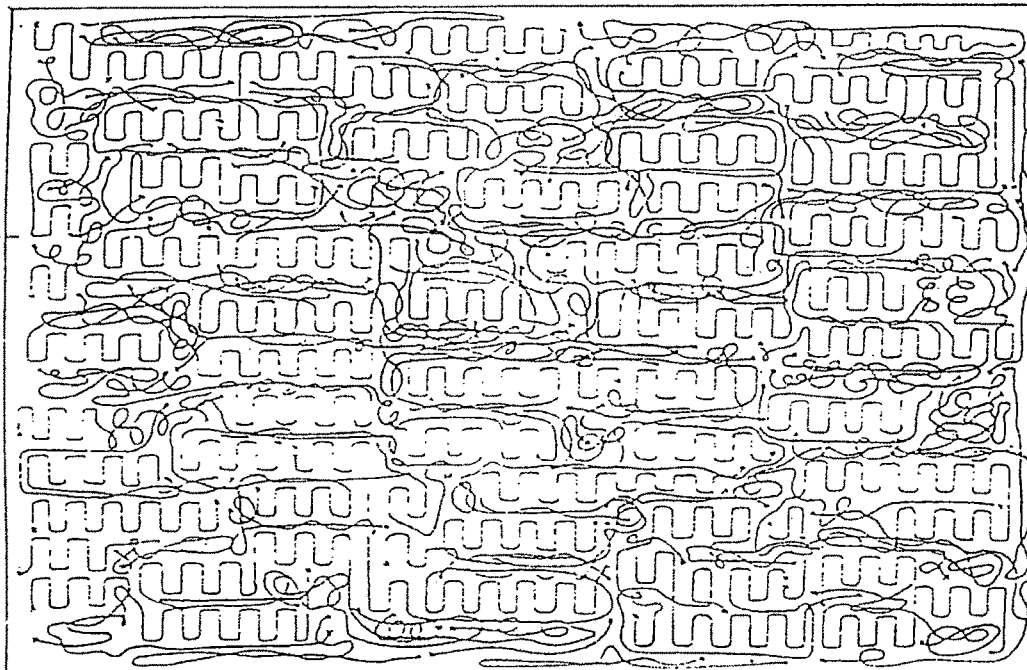
Figure 1.4 (a)   Cross-Sectional view of the structure of semi-crystalline polymers
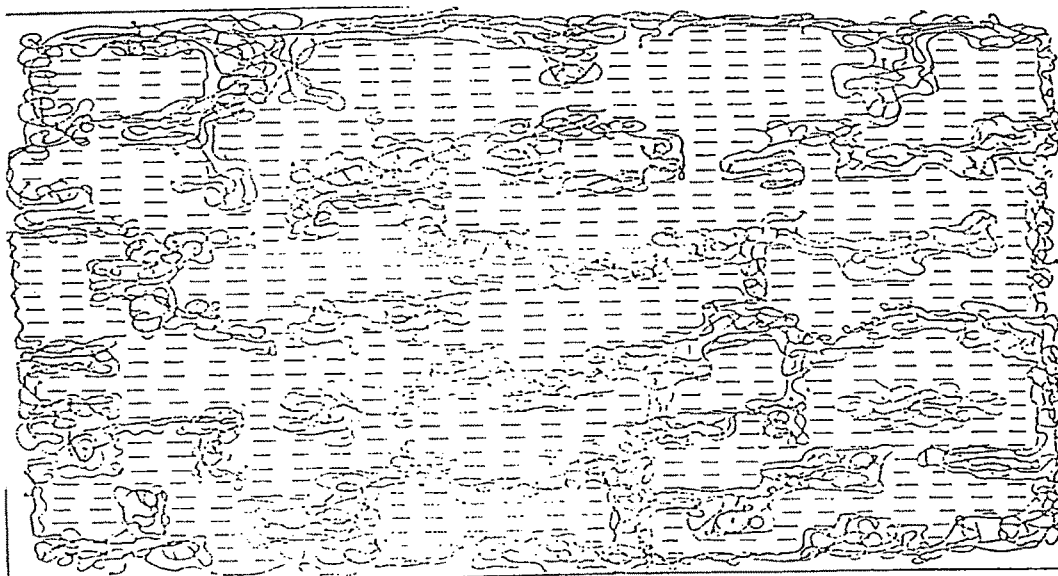
Figure 1.4 (b)   View from parallel to the machine drawing plane of the structure of semi-crystalline polymers.

Another important characteristic of polymer is the crystalline morphology or super-molecular structure, which concerns the relative arrangement of the crystallites to one another. Observations of spherulites in different types of crystalline polymers, lead us to believe that the factor governing the super-molecular structure does not represent a universal mode of polymer crystallization. The most important heterogeneties are derived from the tendency of many polymers to crystallize partially.

More or less well defined crystalline lamellas are found in the form of single crystals i.e. stacked and/or grown upon each other in the form of shearing layer structure, as twisted aggregates in spherulites and in the form of sandwich-like structure in highly oriented fibrils (Geil, 1963; Keller, 1968; Wunderlich, 1973) [17,19,20].

Schelten's (1976) [38], small angle neutron scattering (SANS) observations, Yoon and Flory's (1976) [27], comparison of the intensity distributions for several morphological models with the experimental scattering data, cannot be explained by regularly folded and adjacent re-entry model. The boundary between two spherulites, resembles grain boundaries; these grain boundary zones are enriched in low molecular weight material, impurities, chain ends and defects. Since the cohesion between chains within a crystal's lamella is much stronger than the inter-crystalline interactions. This renders a certain stability to the lamella elements in the samples deformation. Although much remains to be done by neutron scattering, a definite structure can be deduced only when the results for both the radius of gyration and the complete scattering functions are taken into account.

1.5   Effect of Ion Beam Irradiation on Polymers

Since polymer is an important group of materials which are often used in reactor and other radiation environments, it is necessary to know what changes they undergo in composition, structure, physical, mechanical and electrical properties, when subjected to nuclear radiations. These materials are distinctly different from metals or other inorganic solids as they have low melting points and decompose on heating. They are macromolecules built of simple units of covalent bonds of energy 3.5 – 4.0eV, and can be split by heat or high-energy irradiations. These properties depend upon their chemical structure, molecular weight, crystallinity and other materials present like plasticiser, stabilizer and filters. These composites are too complicated for understanding the phenomenon of radiation damage and therefore investigations have to be made on well defined pure polymers and later can be extended to filled systems.

Fortunately or unfortunately polymers are more radiation prone than any other engineering materials, even few M rad is sufficient to cause severe modification in chemical and physical properties of high molecular weight substances, which are used on industrial scale and at an economic cost. Whether radiation effects on polymers are beneficial or harmful depends upon its applications.

Most of the chemical changes in polymers are nearly similar to those in organic substances, both permanent and transient type. In discussing this type of work we may distinguish between:

(1)   Production of polymers by irradiation of monomer (radiation polymerization).

(2)   Modification of polymer where no chain reaction is involved.

(3)   Modification of polymer by a chain reaction (for low molecular weight substance).

The present study is limited with second part i.e. modification of polymers by irradiation or effect of irradiation on polymers. Although the primary chemical effects of irradiation on long chain polymers are not inherently very different from those occurring in low molecular weight compounds, this subject has received a considerable amount of attention for several following reasons.

(1)   Small chemical changes can produce a large physical change readily accessible by a number of techniques developed for polymer research.

(2)   Range of condition under which the material is irradiated can be varied and the effects of condition on the radiation process thereby reduced.

(3)   Many of this reaction take place in the solid state so that the effect of irradiation of organic materials, crystalline, amorphous and oriented can be determined.

(4)   Long chain polymers can serve as a simple model for biological materials and indeed any of the radiation effects observed in radiobiology is closely parallel to those found in simple long chain polymers.

(5)   Several of the processes involved have found large scale industrial use.

(6)   Radiation sterilization of pharmaceuticals.

All the above-mentioned requirements or changes occur in high polymers through two major processes: cross-linking and degradation (scissoning), due to irradiation. In the cross-linking process the two neighboring chains of polymer form bonds with each other which becomes rigid into a three dimensional network; and in the other process i.e. chain scissioning, chain are cleaved into smaller molecules to produce a weaker material. Both may occur at the same time, and over a long range of absorbed dose. The more predominant reaction will control the useful properties of the structure. Cross-linking occurs in the amorphous portion through a number of intermediate processes of energy exchange and free-radical formulation (Compbell, 1981) [39].

1.5.1   Chain – Scissioning

A permanent break in a linear molecular chain can also occur as a result of the radiation interaction, resulting in a more rapid degradation of physical properties. The process known as scission, occurs simultaneously with cross-linking and the predominance of the scission reaction is much dependent on temperature and other conditions during the irradiation (Charlesby, 1960) [40,41].

A more descriptive term for this and the associated processes in which cleavage of an inter or intra-molecular bond occurs is degradation. When the fracturing reaction takes place at random along the polymer chain the average molecular weight decreases rapidly, while the total mass changes very little. This results in a very rapid decrease in hardness, increase in elongation and increase in tensile strength. The formation of

volatile by-products produces out gassing, mass reduction and often-corrosive reactions with adjacent materials in the component. The number of scissions is proportional to dose and they occur at random. In view of these facts radiation furnishes an excellent method of providing polymers of accurately controlled weight and weight distribution, and has in fact been used for this purpose on an industrial scale.
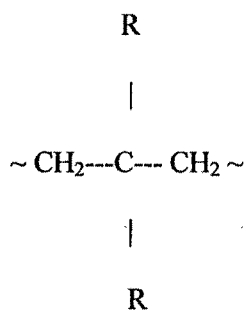
1.5.2   Cross-Linking

This basic phenomenon of radiation induced cross-linking of polymers is a simple reaction. Broadly speaking the main observation can be presented as follows:

(1)   The degree of cross-linking is proportional to radiation dose.

(2)   It depends little on the type of high-energy radiation.

(3)   It depends little on dose rate.

(4)   It does not require unsaturated or other more reactive groupings.

(5)   With some exceptions (aromatic group) it does not vary greatly with chemical structure.

(6)   The efficiency of cross-linking, represented by G value (number of cross-links formed per 100 eV of energy absorbed) is little influenced by molecular weight, however the G value changes by presence of certain additives relatively in small concentration.

(7)   It generally occurs in amorphous portions through a number of intermediate processes of energy exchange and free radical formation.

The types of radiation and their interactions with organic materials, leads to a dosimetry discussion, relative stability of polymer structure and the types of additives that contribute stabilization of the basic polymer matrix. Dosimetry, is an applied and fast growing subject now a days. To approach the objectives, it is necessary to determine the degree of these influences on exact test conditions, and to be familiar with the interaction of various types of radiation with molecules, the mechanism of reactions induced by the radiation and the effects they have on the functional properties of the materials and especially the specific properties, most critical to the service application. An excellent and vast effort in this regard has been made by ASTM (1971) [42].

Tabulations of many studies of polymer materials according to chemical structure versus radiation degradation have been utilized to theorise why scission predominates in some polymers and cross-linking in others. Thus some of these observations have led to the following conclusions (Compbell, 1981) [43].

(1) Scission predominates in polymers, which have the following structure.

$$\sim CH_2---C---CH_2 \sim$$

with R groups attached above and below the central C atom:

R
|
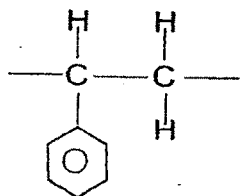$\sim CH_2---C---CH_2 \sim$
|
R

(2) Polymers have low heat of polymerization. If a polymer has a tendency to form monomer, on pyrolysis it normally undergoes scission during irradiation.
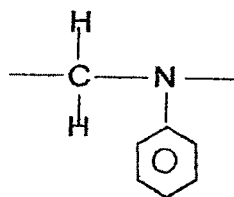
(3) In branched chain hydrocarbons, scission appears to be predominant over cross-linking.

(4) In polymers having a C-O repeating group, the scission occurs very rapidly.

Polymers containing aromatic groups show greater stability in general as compared to polymers containing aliphatic groups, due to energy dissipation by resonance within the ring structure. Bopp and Sissman (1953) [44], have determined a ranking of relative stability of various polymers structure according to their chemical structure from higher radiation tolerance value to radiation prone.
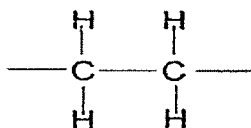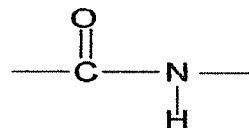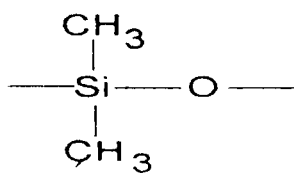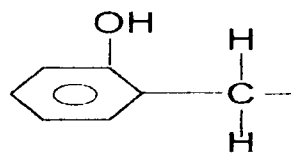
(1)   (2)

(3)   (4)   (5)

$$
\begin{array}{c}
\text{CH}_3 \\
| \\
-\text{Si}-\text{O}- \\
| \\
\text{CH}_3
\end{array}
$$

(6)

$$
\begin{array}{c}
\text{OH} \quad \text{H} \\
| \quad | \\
\bigcirc - \text{C}- \\
| \\
\text{H}
\end{array}
$$

(7)

$$
\begin{array}{c}
\text{H} \\
| \\
-\text{C}-\text{O}- \\
| \\
\text{H}
\end{array}
$$

(8)

$$
\begin{array}{c}
\text{H} \quad \text{S} \\
| \quad \| \\
-\text{C}-\text{S}- \\
| \\
\text{H}
\end{array}
$$

(9)

$$
\begin{array}{c}
\text{O} \\
\| \\
\bigcirc - \text{C}-\text{O}- \\
| \\
\text{H}
\end{array}
$$

(10)

$$
\begin{array}{c}
\text{H} \quad \text{Cl} \\
| \quad | \\
-\text{C}-\text{C}- \\
| \quad | \\
\text{H} \quad \text{H}
\end{array}
$$

(11)

(12)

$$
\begin{array}{c}
\text{F} \quad \text{F} \\
| \quad | \\
--\text{C}-\text{C}- \\
| \quad | \\
\text{F} \quad \text{F}
\end{array}
$$

(13)

$$
\begin{array}{c}
\text{H} \quad \text{R} \\
| \quad | \\
-\text{C}-\text{C}- \\
| \quad | \\
\text{H} \quad \text{R}
\end{array}
$$
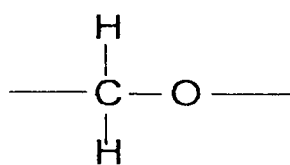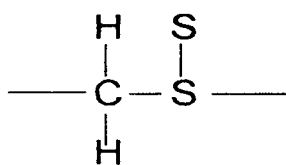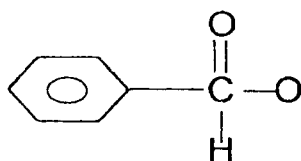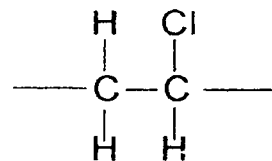
(14)

1.6 Applications of Polymers

As mentioned earlier, during the past one decade or so several polymers started appearing in newer and newer forms with increasingly better properties from various scientific and technological laboratories all over the world. Their rapid growth has been due to various advantages over conventional structural material such as metals, ceramics, wood, leather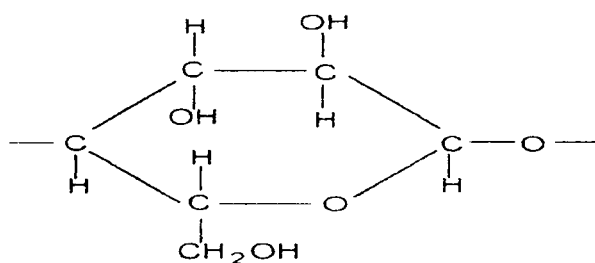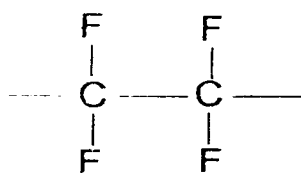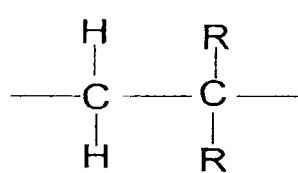, textiles, paper etc., in terms of processability, wide range of rigidity/ flexibility, toughness, wide range of lubricity/ adhesion, thermal and electrical insulation, wide range of clarity/ opacity and colour, resistance to corrosive chemicals as well as over all advantages of economic superiority. The improvement in the qualities of polymers e.g. rigidity, strength, toughness, creep resistance and dimensional stability make plastics to compete or even surpass steel. Finally due to their various remarkable properties, polymers have covered about 75% of the total plastic market in a very short time.

With the commercialization of polytetrafluoroethylene (PTFE) and its family, by Dupont in 1984, the plastic industry gained an important material which is outstanding for self-lubricating bearings and seals, heat and chemically-resistant gasketting, cook-wares and high temperature-high performance electrical insulation (melting point 327°C). The fiber like Nylon 66 (polyhexamethylene adipamide, invented in 1939). Polyacylenitrite fibre (1950), Polyethylene terephthalate (1953, as Terylene and Dacron), Polypropylene (1950) and Polyfluorocarbon (flame resistant fibers), Polybenzimidazole, Aramides (high modulus fibers and strong like graphite and ceramics) have been developed and are used in the textile industry. They have similar

volume compared to cotton and have growing importance in textiles. In 1954, originally ICI developed Polyethylene terephthalate (PET) as fiber which was found to be moisture and crease resistant and superior to cotton. They further prepared it as bi-axially oriented films, having superior mechanical, thermal, electrical, chemical and impermeable qualities as compared to cellulose.

Due to numerous, excellent, physical and chemical properties having wide range of variation and their economical superiority over conventional materials, polymers have assumed great importance in space and nuclear applications. In general, polymers are quite heat sensitive due to which they still have severe limitations for technological applications. The major heat resistive polymers suitable for space and nuclear applications are Polyphenylene (1962, can work upto 550°C) Polyester such as Mylar (1970, can work in N_2 atmosphere upto 380°C) Aromatic polyamides (1974, service temperature up to 370°C) Polyimide e.g. Kapton (1976, service temperature upto 350°C in air), Polypyrrole (1969, service temperature of around 300°C) and their co-polymers. Now a days among the existing polymers three of them namely Kapton, Mylar and Teflon are frequently used in the radiation environments.

The materials used in space and nuclear technologies play a key role in the performance of that particular project. The basic requirements of required materials are that they should be thermally stable (> 300°C) and must have high radiation tolerance limit (>M rad) as they will be exposed to intense radiation's. They are all the more crucial and important when they are used for long service span (several decades). Due to numerous,

excellent, physical and chemical properties having wide range of variation and their economical superiority over conventional materials, polymers have assumed great importance in space and nuclear applications.

1.6.1   Nuclear Applications

As far as nuclear applications are concerned, a number of polymeric materials having much lower resistance for radiation are employed. In recent years, a new class of radiation hardened polymeric material that displays superior "Mylar like mechanical and dielectric properties, has been developed by doping the polyethylene terephthalate (PET) with 2,4,6-trinitro—9-fluorenone (TNF), an electron acceptor molecule. The Mylar and Mylar like materials are quite in use in severe radiation environments such as those encountered in space, fusion and fission reactors.

During the normal operation of a nuclear reactor plant, gamma rays and neutrons that escape through the walls of the reactor core are the major radiations. The energy spectrum of gamma rays, ranges from a few keV to about 8 MeV and for the neutrons from thermal neutron (~0.025 eV) to fission neutrons (>10MeV). The dose rate will vary with location, but is typically found to range from about 10 to 100 rad per hour (rad h^{-1}) with an average rate of 50 rad h^{-1}. This would give an integrated dose of about 2×10^2 rads over 40 years of operation. Such a dose is sufficient to cause catastrophic failure of the plant.

1.6.2   Space Application

Further polymers are extensively used in aerospace applications as radiation resist materials, ablation materials, structural material (in the form of gaskets, O-rings, instruments panel, sealing etc.) and electrical (insulation, cable, transformer bindings etc.) components. Fortunately, polymer is the only material in which the effect of radiation improves some of their physical properties to a certain extent. In fact, in space- crafts, polymers have an edge over metals and wood due to favourable strength to weight ratio of fiber reinforced polymers.

In supersonic aircrafts where heating caused by the air friction, is a serious problem, polymers can be safely used due to their low thermal conductivity, high specific heat and endothermic decomposition, because heating and thermal damages will be limited to their upper surface layer only. Another thermal application of polymer is to maintain the satellite or space vehicle at room temperature. Suitable coating of the polymeric substrate meets this requirement by arranging the ratio of solar energy absorbed (α) and the thermal radiating energy (ε) emitted by the surface at the desired temperature for the payload with small internal power dissipation ~ 1.2. Specially some pigments, paints and polymers show almost negligible change in outer space, in addition to wide ranges of α, ε and α/ε values by varying the thickness of polymer films and the type of metal used as reflecting under coating. Their stability has been tested extensively both in laboratory and in space because of their outstanding α/ε values. It has been found that Ag-coated Teflons are extremely resistant to damage and degradation from UV-irradiation (Heaney, 1974), but has only moderate and some times unsatisfactory

stability to charge particle exposure (Bogdall & Cannady, 1970 Triolo, 1973)[45]. This leads to the conclusion that such a coating is very good for use on satellites in near earth orbit but is doubtful in radiation belts and solar winds. Kapton and Fluorinated ethylene propylene have high electrical resistivity ($>10^{16}$ Ωcm^{-2}) and are used to encapsulate solar cells (Mirtich & Bojeck, 1971) [46], and as reflectors for concentrator arrays and solar panels (Wright & Warmak, 1976) [47]. Their major limitation regarding the application of polymer in deep space is the hazardous radiation threat, which in the long run degrades many properties of the polymer specially that of the outer most layers, which face the maximum exposure.

1.6.3   Sensor Application

Recently, polymers have been increasingly used for sensor applications. Polymer sensor materials are used in the form of thin films coatings, on integrated circuit chips, on optical fibers, or in the form of self-supporting structures such as sheets, cylinders, domes etc. Their versatility allows their use in very small devices of the size of an IC chip, as well as in large area sensors of 10 square inches or more. Several applications are already exploiting the advantages of such materials and the amount of research on the subject is increasing rapidly. A material playing an important role in sensors is polyvinylidene fluoride (PVDF). Similarly, polymer's use will continue to grow in the major sensor developments areas of gas, vapour and humidity devices. In the past their use was limited partly because of incomplete understanding of sensing mechanisms.

1.6.4　Medical Application

In addition to their numerous applications in Engineering Science, Nuclear Science, Aerospace applications and sensor, polymers are not lagging behind for applications in medical science [48-51]. Various polymeric drugs have been developed for the treatment of diseases. A polymeric drug is a polymer that contains a drug unit either as part of the polymer backbone as a terminal group or as a pendant unit of the polymer backbone. In some cases, a polymer can function as drug even though there is no low molecular weight analogous to that polymers.

Finally it would not be too much to say, that at present polymer science has been developed to such an extent that material scientists are in a position to develop an almost limitless range of new polymeric materials which may be useful for housing appliances, clothing, household textiles, sensor development area of gas, vapour and humidity devices, medical science, space and nuclear technological applications.

1.7　Swift Heavy Ion Interaction with Polymeric Materials: Fundamental Principles and Applications

1.7.1　Introduction

The study of the effects induced by energetic heavy ions on polymers has attracted growing attention [52-62] in recent years, both for the fundamental interest in non conventional ion beam effects mainly to understand the radiolysis and polymerization mechanisms (with respect to the conventional photon, electron or neutron effects) and

for potential technological applications. Swift heavy ions (SHI) provide a unique way of material modification, which other wise is not possible by conventional radiations. The reason is very high value of the electron stopping power of the ions $(dE/dx)_e$ or S_e, which induces an unusual high density of electron-hole pairs close to the ion path. As to the technological applications, physical and chemical changes induced by SHI irradiation may lead to large modifications in the macroscopic properties of the polymer.

The modification induced by the high-energy heavy ions in polymeric materials may be understood only if the particularities of the energy transfer from the ion to the target are considered. When an energetic particle passes through a polymeric material, it losses its energy mainly through four processes

1) Electronic stopping "S_e" (inelastic collisions with target atomic electrons resulting in excitation and ionization)

2) Nuclear stopping "S_n" (elastic collision with screened target nuclei, resulting in displacement of the target atoms)

3) Phonon decay and

4) Plasmon decay.

Among the four processes, the first two produce most significant effect in changing the materials properties and the latter two consist mainly of thermal energy losses by atoms and electrons as their energy decay through thermal vibrations and it is assumed that

they do not have any significant impact on material properties. The energy loss by phonons is mostly from recoil atoms and thus its magnitude of loss increases with increasing ion mass because larger ions produce more recoil atoms. Energy losses by plasmons are essentially negligible.

In the case of SHI the first process of energy loss i.e. electronic excitation and ionization as a result of inelastic collision with target electrons, predominates over the other energy loss processes. The electronic processes involve the ejection of electrons and the formation of excited states. The primary products produced during the process are electrons, ions, atoms in excited states, free radicals, and molecules. The energy of an excited molecule may be distributed among its neighbors as phonons or excitons, or it may cause a chemical bond to break, when the excited energy localizes in a particular chemical bond. Thus polymers can break down even by pure ionizing radiation sources such as UV or γ-rays, as in the degradation of polymers in a natural environment.

However, such radiolysis scission frequently causes the loss of side groups, such as hydrogen. This reaction produces unsaturated bonds (-C=C- and -C≡C-) in the polymeric chain, or cross-linking when the cleavage of the C-H bonds occurs on adjacent molecules. The chains can be cross-linked by double bonds also. The important term Linear Energy Transfer (LET), which is generally used to describe the energy deposition per unit path length by one ion (eV/nm/ion), is essentially electronic LET, in case of SHI induced modifications.

Here, we describe the fundamental process involved with energy transfer in polymers by energetic ion beams, distinguishing the effects induced by heavy ion beams from other source of irradiation, specially the contributions of electronic and nuclear stopping on material modifications, the mechanisms involved in cross-linking and scission processes, besides the ion track formation mechanism and applications of track membranes.

1.7.2   Nuclear and Electronic Stopping

When an energetic particle penetrates into a polymer medium, it losses energy by two main processes, namely, by interacting with target nuclei (screened) and by interacting with target electrons. The former process is called nuclear stopping and the later electronic stopping.

Nuclear energy loss arises due to collision between the energetic particle and target nuclei, which cause atomic displacements and phonons. Displacement occurs when the colliding particle imparts an energy greater than certain displacement threshold energy, E_d, to a target atom. Otherwise, knock-on atoms cannot escape their sites and their energy dissipates as atomic vibrations (i.e. phonons). E_d is the energy that a recoil requires to overcome the binding forces and to move more than one atomic spacing away from its original site. Since the nuclear collision occurs between two atoms with electrons around protons and neutrons, the interaction of an ion with a target nucleus is treated as the scattering of two screened particles.

Nuclear stopping is derived with consideration of the momentum transfer from ion to target atom and the inter-atomic potential between two atoms. Thus nuclear stopping varies with ion velocity as well as the charges of two colliding atoms. Nuclear stopping becomes important when an ion slows down to approximately the Bohr velocity (orbital electron velocity). For this reason, the maximum nuclear energy loss occurs near the end of the ion track. For high-energy ions, the Bohr velocity can be varied from the uncertainty principle as:

$$V_b = (1/4 \; \pi\varepsilon_o) \; (e^2/\hbar) \approx 2.2 \times 10^6 \; m/s$$

Where $1/4 \; \pi\varepsilon_o = 9.0 \times 10^9 \; N.m^2/C^2$

ε_o is the permittivity constant

e is a unit charge and

$\hbar$ is plank's constant divided by 2π

The velocity of 1MeV He ion is about 6.9×10^6 m/s.

Electronic stopping is determined mainly by the charge state of the ion and its velocity. When an ion passes through a medium its orbital electrons are stripped off in varying degree depending upon the ion velocity (V_{ion}). The effective charge on a positive ion is given, in terms of ion velocity (V_{ion}) and Bohr (orbital electron) velocity (V_B). By Northcliffe [63] as

$$Z^*_{eff} = Z \; [1 - a \; exp \; \{-b(V_{ion}/V_B) \; Z^{-2/3}\}] \tag{1.1}$$

Where Z is the atomic number

a and b are fitting constants.

There have been scores of proposed empirical formulae such as

$$Z^*_{eff} = Z \left[1 - \exp(-k\beta) / Z^{2/3} \right].$$

Where $\beta = V_{ion} / c$

c is the speed of light.

Somewhat different values have been assigned for coefficient k by various authors. For example: 25 by Pierce and Blann [64] and 130 by Barkas [65]

All expressions give a similar trend. He-ions are almost completely stripped to an average charge of +2 at around 1MeV or ≥0.3 MeV per amu. The higher the Z, the higher the energy required to fully strip an atom.

Electronic energy loss arises from electro magnetic interaction between the positively charged ion and the target electrons. One mechanism is called glancing collision (inelastic scattering, distant resonant collisions with small momentum transfer) and the other is called knock-on collision (elastic scattering, close collision with large momentum transfer). Both glancing and knock-on collision transfer energy in two ways: electronic excitation and ionization. All excited electrons (plasmons) eventually lose energy as they thermalize. Electronic excitation is the process in which an orbital electron is raised to a higher energy level, whereas, in ionization; an orbital electron is ejected from the atom. Glancing collisions are quite frequent but each collision involves a small energy loss (<100eV). On the other hand, knock-collisions are very infrequent but each collision imparts a large energy to target electron (>100eV). These knock-on

electrons are often called δ-rays or secondary electrons. Theoretical and experimental evidence suggested that approximately one half of the electronic energy loss is due to glancing collisions and the other half due to knock-on collisions [66-67]. This phenomenon is often referred to as the equipartition principle and has been confirmed by experiment [68], where two well-defined peaks at low and high energy were observed for protons channeled through mono-crystalline copper. The energy loss ratio for channeled and un-channeled protons was approximately 0.5. The 'best-channeled' particles have a stopping power of the order of one-half the stopping power in the corresponding solid. The half of the energy loss in channeled direction was attributed to glancing collisions.

Nuclear collisions create recoil atoms and these recoil atoms also lose their energy through nuclear and electronic processes until all excited electrons and atoms are thermalized by dissipating energy through phonons and plasmons. For most ion energy ranges of interest, nuclear stopping by small atoms such as H or He is negligible because the Rutherford cross-section and momentum transfer by the low mass atom is small. Nuclear stopping however becomes important for ion species with a large number of nucleons.
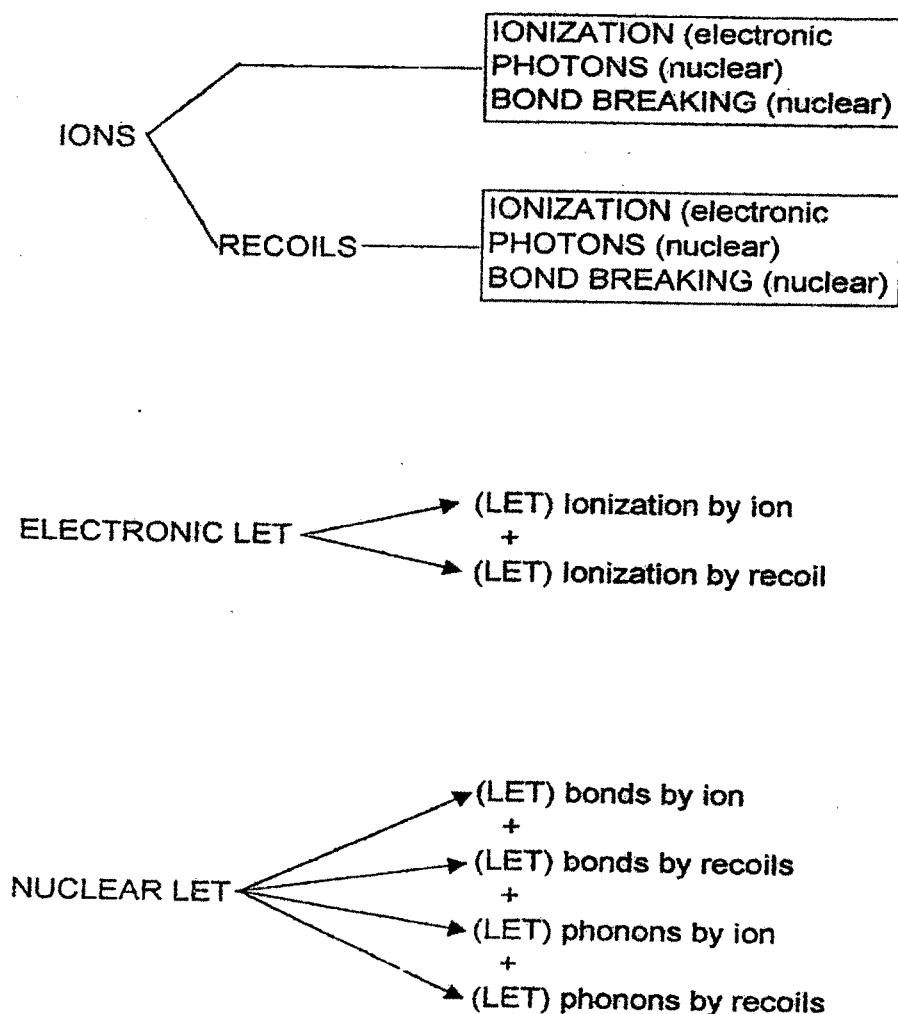
Figure 1.5   Energy partitioning in SRIM

Figure 1.5   Summarizes the energy partitioning in the Monte Carlo simulation program stopping and Range of ions in Matter (SRIM) [69]. The electronic energy loss constitutes the ionization and excitation energy loss by the primary ion as well as by recoil atoms. Binding energies, E_b, of 1-3 eV, are suggested in the TRIM instruction manual, although actual binding energies could be higher due to strong covalent bonds in organic polymers. A usage of a different value of E_b affects the energy partition in

vacancy LET and phonon LET described below but the total nuclear LET remains the same. E_b is the difference in energy for the atom in its site and when removed to an infinite distance. Recoiling target atom losses energy when it leaves its site. In the SRIM calculation, the bond breaking energy (called the vacancy LET, because the number of vacancies that are produced by bond breaking are counted) is treated separately and is derived by multiplying the number of displacements (vacancies plus replacements) by E_b. In the Kinchin-Pease approximation described below, replacements are not calculated and so the displacement number is equal to vacancy number. The minimum or threshold energy required to break the bonds and displace the atom over a lattice potential is called the displacement energy (E_b). Although the values of E_b are not well known for polymers, they are believed to be in the range of 10-30 eV, considering the energy required in breaking strong covalent bonds and placing the released atom over a certain distance. Note that at least two bonds should be broken to release a carbon atom. When a recoil atom does not have sufficient energy to displace another atom, the remaining energy is dissipated in lattice vibration (phonons). The nuclear energy loss is equal to the sum of the phonons LET and (number of vacancies times E_b). The integrated area under the six curves sums up to 100 keV, the energy received by the system. The phonon contribution from the ions is small compared to the recoils, because one ion produces many types of recoil.

In the Kinchin-Pease approximation, the recoils are not individually followed in the Monte Carlo calculation. However, the flight paths of the primary ions are tracked and the energy losses are calculated using ZBL stopping powers [69] S_n and S_e formulas

given below. The defect producing energy or damage energy (E_v) is obtained from the energy transferred (T) from the primary ion to a target atom by taking into consideration electronic losses which arise due to the interaction between overlapping electron shells during nuclear collisions. The electronic losses of the recoils are calculated using an approximation to the LSS theory developed by Norgett et al [70]. The transferred energy and the damage energy are given below. The electronic (ionization and excitation) energy loss by recoils (E_r') is obtained by subtracting E_v from T.

$$T = \frac{4M_1M_2}{(M_1 + M_2)^2} \; E \; Sin^2 (\theta/2) \qquad (1.2)$$

$$E_v = \frac{T}{1 + K_d g (\varepsilon_d)} \qquad (1.3)$$

$$E'_r = T - E_v \qquad (1.4)$$

Where

E is the kinetic energy of the incident atom

θ is the scattering angle in the center of mass system

M_1 and M_2 are the mass number of the colliding and target atoms respectively.

The latter three parameters, which account for the electronic loss, are given by

$$K_d = 0.1337 \, Z_2^{2/3} \, M_2^{-1/2} \qquad (1.5)$$

$$g\left(\varepsilon_{d}\right)=\varepsilon_{d}+0.40244\ \varepsilon_{d}^{\ \frac{3}{4}}+3.4008\ \varepsilon_{d}^{\ 1/6} \qquad (1.6)$$

$$\varepsilon_{d}=0.01014\ Z_{2}^{-7/3}\ T. \qquad (1.7)$$

Where

Z_{2} is the atomic number of the target atom.

From the energy E_v the number of displacements is calculated by employing a modified Kinchin-Pease model (NRT model [70]).

$$V_{NRT}=0 \qquad if\ E_v<E_d \qquad (1.8)$$

$$V_{NRT}=1 \qquad if\ E_d<E_v<2.5\ E_d \qquad (1.9)$$

$$V_{NRT}=0.8\ E_v/2E_d \qquad if\ E_v>2.5\ E_d \qquad (1.10)$$

In the NRT model, the displacement efficiency factor 0.8 is introduced to account for realistic atomic scattering of the hard core approximation where efficiency factor is unity (billard ball type collision), and the number 2 in the denominator is included on the grounds that an atom must have a kinetic energy at least twice the displacement threshold energy in order to cause a net additional displacement. In the full SRIM calculation, total displacements include vacancies and replacement collisions.

As described already, both nuclear and electronic stopping depend upon the kinetic energy or velocity of the colliding atom because the velocity determines the interaction time. In the SRIM full cascade calculation, the ZBL stopping powers are used for both the primary ion and recoils. A mathematical expression for the nuclear stopping cross-section is given by

$$Sn = \int_0^\alpha T(E_o, p)\, 2\pi\, pdp \qquad (1.11)$$

Where

E_o is the initial kinetic energy of the atom,

T the transferred energy defined above, and p is an impact parameter.

p is the distance by which the collision misses being head-on, and is a measure of the directness of the collision or straightness of the flight path, which is determined by the particle velocity and the inter atomic potential between the two colliding particles.

A mathematical expression for the electronic stopping cross-section is given below.

$$S_e = \int I(\upsilon,\rho)\, (z^*,\upsilon)^2\, \rho dv \qquad (1.12)$$

Where $I(\upsilon,\rho)$ ions the stopping interaction function

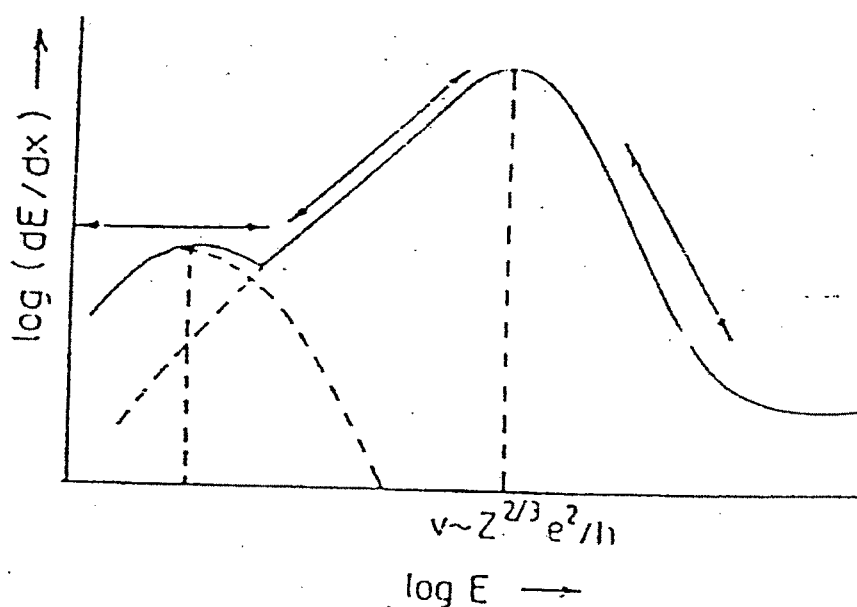υ is the ion velocity

ρ is the target electron density

$z^*$is the effective particle charge and

dV is the volume element.

I(υ,ρ) varies with the particle velocity and plasma oscillation frequencies of the electrons in the stopping medium. Fast particles (v>> Bohr velocity) have little interaction time and so electronic stopping decreases with increasing velocity beyond this velocity. Slow particles (v< Bohr velocity) pickup electrons, so have a lower effective charge. Therefore a maximum in the electronic stopping occurs near Bohr velocity.

The figure shows a curve with the y-axis labeled $\log\left(\frac{dE}{dx}\right)$ and the x-axis labeled $\log E$. A vertical dashed line near the peak is labeled $v \sim Z^{2/3} e^2 / \hbar$.

Figure 1.6   Variation of stopping power (dE/dX) as a function of velocity of the particle.

Figure-1.6 shows, the variation of stopping power or the energy loss per unit path length i.e. dE/dx as a function of energy or velocity of the particle. The curve distinctly shows two regions: one belonging to low energy and the other to high energy of the particles. When the particle's energy is low, (which is the first part of the curve) the ion

losses energy mainly through nuclear collision with nuclei of the target. At higher energies, (> Mev), when the ion velocity ($v \sim z_1^{2/3} e^2/h$, z_1 is the atomic number of the target atom) it becomes comparable to the Bohr velocity, and a maximum in the electronic stopping occurs. Linear energy transfer (LET) is simple given by

$$dE/dx = N \, S(E) \qquad\qquad (1.13)$$

where N is the atomic density of target.

In evaluating the damage produced by irradiation, the unit of displacements per atom (dpa) is often used. The expression of displacement dose in dpa is given by

$$dpa = 0.8/2E_d \, \{dE/dx\}_{nuclear} \text{ (ion fluence/target atomic density)} \qquad (1.14)$$

One dpa is the dose at which, on average, each atom has been displaced from its lattice position once. The term dose is expressed often in terms of the energy deposited per unit mass of material, generally in units of eV/Kg or Gy (=100 Rad), whereas the fluence indicates the number of ions injected per unit area of target material (ions m^{-2}). In the conversion from fluence to dose, the SI unit of gray(Gy) is obtained by multiplying the fluence (ions m^{-2}) by the LET (eV/nm) and dividing by the specific gravity of the target material (Kg/m^3) and finally using a conversion factor of 1Gy = 6.24 x10^{18} eV/Kg.

1.7.3   Ion Track

Although a term "short track" is often used to designate a continuous column of energy

deposit (500-5000 eV) for a high-LET particle, here it simply means a passage of an

ion. When a positively charged ion passes through the medium, orbital electrons in the

stopping medium are pulled of by an electromagnetic force. These charge separations

produce strong restoring forces. Consequently, oscillations of an electrostatic nature are

set up, and the electron density, velocity and electric field all oscillate with the plasma

frequency ω_p [71].

$$\omega_{p = [} 14 \, \pi \, ne^2/4 \, \pi\varepsilon_o \, m_e]^{1/2} \qquad\qquad (1.15)$$

where e (C) and m_e (Kg) are the charge and mass of the electron, $n(m^{-3})$

is the electron number density of the medium.

An expression for the radial extent of energy deposition, proposed by Chatterjee and

Schafer [72], is given below in terms of this plasma oscillation frequency of the

stopping medium as

$$r_c = \beta c/\omega_p \qquad\qquad (1.16)$$

where $\beta = V_{ion}/c$. r_c called the physical core, is the range of fluctuation of electron

density or energy for a period of plasma frequency pulse, or is the range of uncertainty

in energy deposition at the epoch of initial energy deposite ion and can be derived from

the uncertainity principle.

$\Delta t \, \Delta E \approx \hbar r_c$

Or

Δr is given by

$\Delta r \approx \hbar V_{ion} / \Delta E$ in consideration of

$\Delta t \approx \Delta r / V_{ion}$

ΔE is an energy width over which absorption can take place, later we define this energy as "spur". r_c varies with ion velocity and defines the range of energy deposition which occurs at a period of around 10^{-16} s, which is the earliest significant time and can be estimated from $\Delta t \, \Delta E \approx \hbar$ by taking $\Delta E \approx 20eV$ for a relativistic particle (0.99c or ~1000MeV / nucleon).

In this time scale, only electronic processes are possible since the time is too short for molecular motion. Molecular vibration becomes important at around 10^{-14} s. molecular motion and a local temperature rise occurs at ~10^{-13} s. diffusion processes start at ~10^{-12} s [73].

The δ-rays also cause electronic excitation and ionization along the track, mostly outside the r_c. The maximum range of δ-rays can be calculated by the following relationship [74-75]

$r_{max} \, [g/cm^2] = k W^\alpha_{max}$ (1.17)

Where $\qquad K = 6\times10^{-6}\ \text{gcm}^{-2}\ (\text{keV})^{-\alpha}$

$\alpha = 1.097 \quad$ for $\quad W_{max} < 1\text{keV}$ and

$\alpha = 1.677 \quad$ for $\quad W_{max} > 1\ \text{keV}$

W_{max} is the maximum energy of δ-rays, which is desired from the kinematics

consideration for head on collision between ion and electrons in the medium as

$$W_{max} = 4 m_{ion}\, m_e\ /\ {}_{(m_{ion} + m_e)}{}^2\, E_{ion} \qquad\qquad (1.18)$$

$\qquad\qquad$ Or $\quad$ as

$W_{max} = 2 V_{ion}\, m_e\ /\ {}_{(1}\ -\ \beta_{)}{}^2$ with the relativistic correction of mass for fast ions, where

m_e is electron mass. A pictorial description of tracks is illustrated in the **Figure 1.7**

[76].Where the radial range of δ-rays is indicated by the radius, r_p, which is called the

penumbra radius.
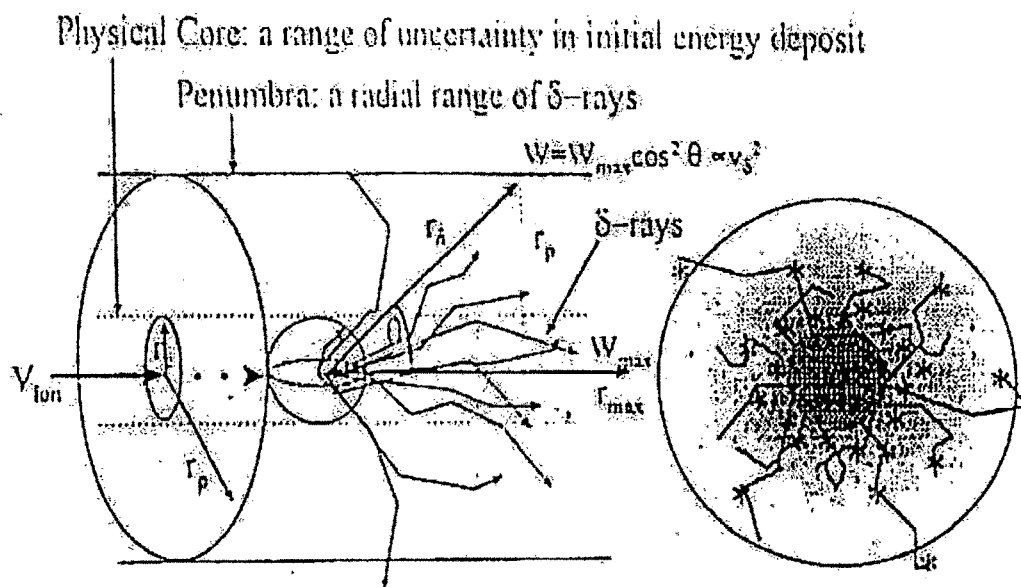
Figure 1.7   Artist's rendition of ion track which shows physical core.

Since a higher knock-on electron energy yields a smaller angle of ejection, r_p (radial) is always smaller than r_{max} (forward direction), r_p can be calculated by considering that the velocity and the energy of δ-rays in a radial direction are $\upsilon_\delta = \upsilon_{max} \cos \theta$ and $W \approx W_{max} \cos^2 \theta$ and that the maximum momentum transferable to electrons in a radial direction occurs at the scattering angle of 45°C ($\pi/4$). Hence for $\alpha = 1$, $r_p \approx r_{max} / (2/\sqrt{2})$ can be derived using $r_\delta = kW$ and $W \approx W_{max} \cos^2 (\pi/4)$ and considering $\qquad r_p \approx r_\delta$

$\sin (\pi/4) = kW \sin (\pi/4) \approx kW_{max} \cos^2 (\pi/4) \sin (\pi/4)$

$\doteq r_{max} \cos^2 \pi/4 \sin (\pi/4)$.

The initial average energy densities within the core r_c and between r_c and r_p are given by Magee and Chatterjee [77-78] below. The energy density with the core is mostly from glancing collisions and a small fraction of low energy knock-on electrons which are trapped inside the core (second term in the first equation below), r is the radial distance from the particle trajectory.

$$\rho_{core} = (LET /2) / [\pi r_c{}^2]_{gl} + (LET /2) / [2 \pi r^2{}_c \ln (e^{1/2} r_p / r_c)]_\delta$$

$$r \leq r_c$$

(1.19)

$$\rho_{pen} (r) = (LET /2) / [2 \pi r^2 \ln (e^{1/2} r_p / r_c)]_\delta$$

$$r_c \leq r \leq r_p \qquad\qquad (1.20)$$

$$(LET /2)_{gl} = [\pi r_c{}^2] (LET /2) / [\pi r_c{}^2]_{gl} \qquad\qquad (1.21)$$

$$(LET /2)_\delta = [\pi r_c{}^2] (LET /2) / [2 \pi r_c{}^2 \ln (e^{1/2} r_p / r_c)]_\delta + \int \rho_{pen} (r) d(\pi r^2) \qquad (1.22)$$

The energy density between r_p and r_c is from δ-rays. The equipartitioning of LET to glancing and knock-on collisions can be confirmed by converting the energy density to LET as shown in equations (1.21) and (1.22). Values of r_p and r_c vary with the specific energy of the particle (energy per nucleon) as mentioned already.

The ion path is thus described by a cylindrical trajectory defined by the physical core with radius r_c (the approximate limiting distance from the particle trajectory at which an electronic excitation occurs initially) and the penumbra with radius r_p (the outermost cylindrical boundary of the δ-rays or secondary electrons) [78]. Another radius used in this model as the radius of the chemical core, lies between the physical core (r_c) and penumbra (r_p) [76]. The chemical radius defines a range where chemical reaction occurs. The chemical radius (r_{ch}) is thus determined by the diffusion and reaction rates of active chemical species such as radicals, cations, anions, electrons and other activated chemical species. Shapes and sizes of track entities are first defined and then followed by the formation of active chemical species, diffusion and their interaction via chemical and coulombic forces. Some chemical species recombine and neutralize in a dense chemical sea, some diffuse out to the penumbra and mingle together with chemical species induced by δ-rays, establishing a fairly large effective radius. Since the chemical radius is difficult to measure or calculate in reality, here, we use a term "effective" radius instead, which defines the extent to which the energy density or radical concentration is significant for a given process. Cross-linking, scission and other chemical reactions occur within this effective radius. Most cross-linking and other chemical reactions occur near r_c where concentrations of radicals and ion pair are high

because of the slow migration of radicals in a viscous medium. In particular, for low LET tracks, δ-rays develop independently and have very little effect on cross-linking. With increasing LET, energy density increases, and so does the effective radius. However, one should be cautioned that, although low Z ions such as H^+ may have large r_c and r_p at high energy (note that r_c and r_p are only ion velocity of low charge state or low LET. This point is examined further by appealing to the concept of spur and its relation to LET.

1.7.4 SPURS

The stopping power formula or the concept of LET is implicitly based on the continuous slowing-down approximation. In reality, energy deposition occurs discretely, not continuously. This is because electronic excitation is restricted by quantised energy levels and ionization is restricted by a certain potential energy barrier, which has to be overcome for electrons to be released from the orbit. In addition, atomic displacement requires certain threshold energy to break the bonds and move the atom over a certain potential barrier due to surrounding atoms. In most cases, a creation of an ion pair involves a removal of two or more electrons, for example one electron from a hydrogen atom and one from the carbon atom. Ionization potentials for the first, second and third electrons of carbon atom are 11.26, 24.38 and 47.89 eV respectively. Ionization of carbon atom to C^{+3} thus requires at least 83.53 eV. This discrete energy loss entity is often called a 'spur' [76]. Most of the energy loss for ionization events or spur energy lies within 100 eV, with an average value of 30-40 eV for polymers [73-79], which is approximately equal to the average energy required to produce one ion or

radical pair. Of course, some of the energy is used for excitation, so the spur energy is larger than the sum of the ionization energy needed to create the ion pairs.

1.7.5 LET and SPUR Distance

As mentioned above energy transfer or loss occurs discretely as spurs along the ion track instead of a continuous decay in energy. Thus changing the LET means changing the spur separation in the track or spur density. The distance between spurs can be calculated by dividing the spur energy by the LET. For example, for spur energy of 40 eV and LET values of 2 eV / nm and 400 eV/nm, the spur distances are 20nm and 0.1 nm respectively. For low LET, spurs are widely separated and occur independently. With increasing LET, more radical pairs are created within the track radius, spurs are connected or overlapped, high radical concentration gradient is established and so the effective radius increases. An effective radius for cross-linking can be estimated in terms of spur density by imposing a condition that at least one radical pair (or spur) is required per nm^3, since the distances between two polymer chains are in the nm range for most polymers and two radicals must be in neighboring chains for cross-linking to occur, (e.g.: LET/ πr^2_{eff} = 40eV/nm^3 for a spur energy of 40 eV). Of course, this approach grossly overestimates the radius because a significant fraction of radicals do not contribute to cross-linking due to recombination. In fact, several thousands of spurs were required per nm^3 to achieve saturation hardness in He and Ar ion irradiated polystyrene [80], suggesting that most radicals were neutralized. It does, however provide a qualitative means to appraise experimental data. On the other hand, the

effective radii may be larger than those defined by the one spur per nm^3 assumption for fluid system where radical and other chemical species can readily diffuse.

1.7.6   Electronic v/s Nuclear LET

An important question is what controls the magnitude of cross-linking and scission.. During irradiation, various physical and chemical processes take place in the polymer. Nuclear collisions cause atomic displacements, which can then lead to chain scission or release of pendent atoms. Superposition of phonon waves can also lead to bond breakage. but the probability of such events is small because phonons have insufficient energy density to start with. Polymers have a fairly large free volume, often larger than 20% and atomic density in such a loose system is relatively small compared to that in a medium with a compact lattice structure. such as metal. Therefore, in polymers, most nuclear displacements occur fairly independently. The probability to cause simultaneous displacement of two atoms from neighboring chains and create two radical pairs for cross-linking is small in nuclear processes. Heavy and low energy ions with less than a few KeV have large nuclear LET and thus generally not desirable for cross-linking. An excellent example for nuclear displacement damage effects, was demonstrated by Hunn and Christensen [81]. They were able to lift free-standing, single crystal diamond layers by causing a maximum damage ~2μm depth below the crystalline diamond surface with 4-5 MeV C-ions and selectively oxidizing diamond layer. An amorphized layer underlying a crystalline diamond surface was also confirmed by Rutherford backscattering spectroscopy in a channeled geometry for 1 MeV Ar irradiated diamond, in that disordering was the least near the surface where the

electronic LET was the highest [82]. An important implication of these results is that the displacement damage followed the nuclear LET profile and that the least damage was observed at the surface where electronic LET was maximum.

On the other hand, when the electronic LET is high, a considerable volume around the ion projectile is influenced because of the coulombic field produced by glancing collisions and ionization (δ-rays) by knock-on collisions. This results in production of active chemical species, cations, anions, radicals and electrons along the polymer chains. Coulombic attraction and repulsion among these active species cause violent bond stretching and segmental motion in the polymer chains, which can then lead to cross-linking as well as bond breakage. Thus, both electronic and nuclear energy transfer can induce cross-linking as well as scission. However, as pointed out above, nuclear stopping causes more scission due to the nature of independent displacement damage and the simultaneous production of two radicals in neighboring chains is low. On the other hand, electronic stopping causes more cross-linking due to collective excitation (plasmons), which produces a large excited volume thereby resulting in coercive interaction among the ions and radical pairs produced within the volume. This trend has been confirmed by G-value and hardness measurement as well as other experiments [83-84]. With increasing ion energy electronic LET increases and nuclear LET decreases. The magnitude of ionization varies with ion velocity and charge state. Thus it is desirable to use atomic species with large atomic number and employ high-energy ions, so long as the velocity of the ion is not too high and so the energy density

(LET) does not become too small due to small stopping power and large r_c and r_p. Note that too fast ion has a short interaction time and yields large r_c and r_p.

17.7 High v/s low LET

As discussed already, the magnitude of ionization depends upon the deposited energy along the ion track or LET. The electronic LET for 1 MeV Ar is about 960 eV/nm for polystyrene, whereas those of e-beam and γ-rays are in the range of 0.2-0.36 eV / nm. Increasing the energy of e-beam or γ-rays does not increase the LET due to the limited effective charge or ionizing capacity, only the depth of penetration increases with increasing energy beyond a certain energy. For 1 MeV Ar ions, about 24 (960 / 40) ion pairs or spurs are created per nm whereas for e-beam, γ-rays, only 0.009 (0.36 / 40) spurs are created per nm. In other words, the average distance between the spurs is 0.042 nm (40 V/960 eV/nm) for 1 MeV Ar and 111 nm (40 eV/ 0.36 eV / nm) for e-beam or γ-rays. In the case of high LET, spurs overlap, the probability for two radical pairs to be in neighboring chains is increased, and cross-linking is facilitated. For low LET, spurs develop far apart and independently, the deposited energy tends to be confined in one chain (not in the neighboring chain) leading to scission. For this reason, low LET e-beams are used in photolithography to make PMMA soluble. However, it should be pointed out that cross-linking is also polymer structure dependent, and even low LET ionizing radiation sources such as e-beam and UV can cause a limited degree of cross-linking for certain polymers.

1.7.8 Ion – Beam Induced Property Changes.

Various gaseous molecular species are released during irradiation. The most prominent emission is hydrogen, followed by less abundant heavier molecular species which are scission products from the pendent side groups and chain-end segments, and their reaction products. The **Figure 1.8** illustrates various functional chemical entities created by irradiation.
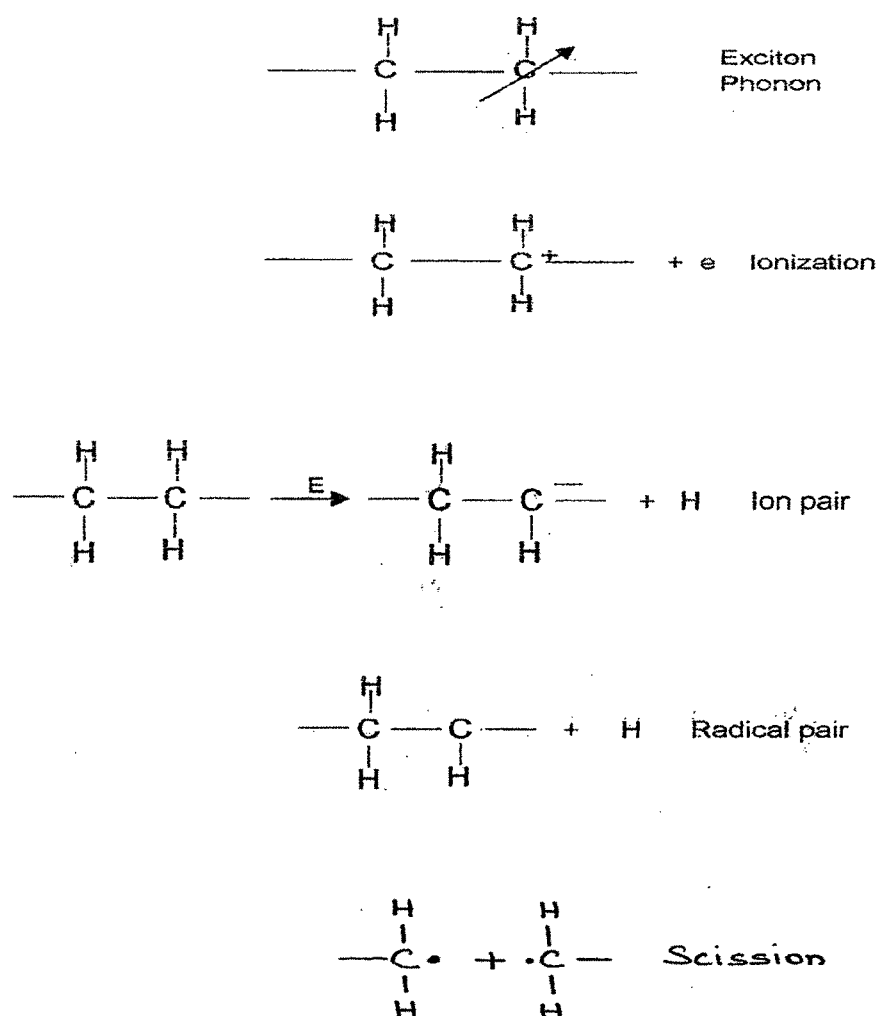
Figure 1.8   Various functional chemical entities created by irradiation.

Cross-linking occurs when two free dangling ion or radical pairs on neighboring chains unite, whereas double or triple bonds are formed if two neighboring radicals in the same chain unite. It has been well established that mechanical, physical and chemical property changes in polymers are determined by the magnitude of cross linking and scission, and that cross-linking enhances mechanical stability while scission degrades mechanical strength [85].

The main features of change in property induced by ion-beam irradiation and potential application areas were described below.

Cross-linking generally increases hardness and slows diffusion, improves wear and scratch resistance, and decreases solubility in chemical solvents. Electrical conductivity and optical density increase due to the formation of cross-links and conjugated double and triple bonds by irradiation. The delocalized π-electrons in the conjugated bonds are loosely bound and thus more mobile than the covalent σ-bond electrons. Furthermore, charge carrier mobility increases by cross-links which facilitate the transport of charge carriers across the chains. Otherwise, charge carriers must hop across the chains for conduction. The loosely bound π-electrons can be excited by the energies of visible light, and thus colour changes occur because light is absorbed when these electrons are excited. Radiation induced defects such as anions and radicles (donars) and cations (acceptors) form a broadened band in the band gap and result in the absorption of light as well. Energetic blue light is absorbed first and the colour changes from pale yellow to reddish brown and eventually to a dark colour with increasing irradiation dose. At very high dose a metallic cluster appears because light is scattered by the abundant π-

electrons similar to the effect of free electrons in metals. On the other hand, scission causes bond breakage and increases dissolution of polymers in solvents. This feature has been used for lithography and positive-resists in electronic industry [86].

1.7.9   Swift Heavy Ion Irradiation Studies on Polymers

Swift heavy ion irradiation of polymers produces significant changes, in the polymer properties such as, solubility, molecular weight, optical, mechanical and thermal properties. These modifications are due to very high value of electronic stopping power, S_e, $(dE/dx)_e$, as already described in the previous sections. Passage of swift heavy ion through the polymer leaves a trail of highly damaged region concentrated along the ion path, known as latent ion track. Heavy ions are a unique tool for manufacturing statistically distributed pores of predictable cross sections and particle density. The track diameter depends on the amount of electronic energy deposited, type of ion and polymer materials properties. The core radius observed is typically in the range of 2-6 nm for ion energy between 1 MeV/amu to few tens of MeV/amu. The latent tracks are discrete entities, which are distributed at random with a negligible overlap. The discreteness condition is restricted to ariel track density below 10^{12} ions/cm^2. Above this limit the distinction between the damaged zones and the unaffected bulk material gradually vanishes.

There are several reports on the study of SHI induced tracks in polymers and the studies mainly confined to use these latent tracks for nuclear particle detectors and micro filter's membranes etc. The effect of ion track can be enhanced, by using suitable

development process (track etching). Therefore, it requires a low dose 10^0 to 10^{12} ions/cm^2. The heavy ions loose their energy in the polymer at a rate of a few 100eV to 2 keV/A which is above the threshold for homogeneous track etching. These etched latent tracks can be utilized in the making of field emitters, micro filters with special shape and size. Ion track membranes can be modified by further processing (grafting).

However, there are very few studies done relating to nature of interaction of SHI with polymer and the processes involved in the formation of latent track [87]. SHI induced radiolysis of polymer i.e. underlying radiation chemistry is not yet understood completely. The interaction of SHI with polymers produces a complexity of phenomenon like chain scissioning, gas evolution, cluster formation, free radials, formation of new and double bonds etc. The new entities may react with each other and with the molecules of the solids. Direct evidence of such processes is the change in the molecular weight distribution and solubility of the polymer [88-90].

(A)   Nature of Ion Track

The mechanism of ion track formation and its detailed structure is also poorly understood, and much more efforts are required in this area. What is known is that on the passage through matter energetic ions lose energy mainly via inelastic collision process and induce a continuous trail of highly excited and ionized target atoms along their path and the associated secondary process leads to permanent radiation damage. The cylindrical zone of damaged material, along the ion path is known as latent ion tracks and has a diameter of a few nanometers. The track core is surrounded by a much

larger halo whose size is determined by the range of the δ-electrons which cause further damage such as chain scission, cross-links, formation of free radicals etc. These chemically activated species undergo reaction in a time scale of milliseconds to hours. Although, we can characterize the size, nature of defects and relative radiation sensitivity of the material but the detailed chemistry of the production of reactive site is still not known.

(B)   Radiation Grafting

Grafting or reactive groups such as enzymes, gels, or catalysts in the latent tracks in the polymer could be used to modify the physical and chemical properties of the polymers. Irradiation and grafting can be simultaneous or consecutive processes [91-92]

(C) Cluster Formation Induced by SHI in Polymers

There are three different concepts on emergence of clusters during ion irradiation.

(1)   For moderate energy transfer, the clusters could be produced along the ion track due to cross-linking and degradation of polymeric chains, so that their linear structures are rearranged in compact 3D-form.

(2)   If the polymer has a grain structure, which gets modified by ion irradiation, the polymeric grains form clusters.

(3)   For very high-energy transfer, highly excited carbon atoms are formed along the track, which tend to condense as clustered objects.

More recently it has been found that SHI irradiation can produce fullerene molecules along the ion track. This adds a new dimension to polymer nanotechnology as the remarkable electronic properties of the fullerene might be exploited. D. Fink et al [93]

have studied in detail the cluster growth along the ion tracks of energetic ions and shown that a threshold energy density is required for cluster growth to set in. The cluster growth was found to scales with the mean transferred electronic energy density of the polymer. They also studied the influence of doping on the cluster size.

1.8   Present Work

In this work, an attempt to characterize the effects of 50MeV, Li^{3+} ion irradiation on the physico-chemical properties of some polymeric materials using various experimental techniques has been made. It is hoped that the findings in this work would be of important relevance to material science and applications of polymers.

Dose dependent modifications in electrical, mechanical, structural, surface morphology, thermal properties of five different polymers at different fluences of 50MeV Li^{3+} ions irradiation have been quantified by various characterization techniques.

Following studies have been made:

(1)   Electrical properties (i.e. conductivity, dielectric constant, dielectric loss) of polypropylene (PP), polyethylene terephthalate (PET), and polymeric blend of polyvinyl chloride (PVC) and polyethylene terephthalate (PET) have been studied in the temperature range 40-150°C and frequency range 0.05 – 100KHz using an LCR meter.

(2) Thermal stability of PP, PET and blended PVC and PET was studied by thermogravimetry analysis (TGA).

(3) Microhardness of PET and polyimide (PI) / Kapton films was also studied at different fluences using Vickers microhardness indenter.

(4) Surface morphology of PI was studied using optical microscope and scanning electron microscope.

(5) Mechanical, thermal and structural properties of PVC and EVA blends were studied using Instron tensile tester, TGA and FTIR spectroscopy.

We have undertaken this investigation with two aims:

(1)   To study the effects of high energy (50MeV) Li^{3+} ion beam irradiation on physical properties of some polymers.

(2)   To explore the possibility of using these irradiated polymers in high tech area.

REFERENCES:

(1) P.J. Flory, Spatial configuration of Macromolecules Chains, The Nobel Lecture Polymer J,8, (1974),1.

(2) P.J. Flory and D.Y. Yonn, Nature 222 (1978), 226.

(3) P.J. Flory, Statistical mechanism of chain molecules (John Wiley & Sons. N.Y.) 1969.

(4) Joel R. Fried, Polymer Science and Technology, Prentice- Hall of India, New Delhi,(2000).

(5) P.H. Geil, Polymer Single Crystals (Inter Science, New York) 1963.

(6) A. Keller, Report. Prog. Phys. 31 (1968), 623.

(7) B. Winderlich, "Macromolecular Physics", Vol. 1, Crystal Structure, Morphology, Defect and Vol. 2 Crystal Nucleation, Growth, Annealing. (Academic Press, New York, 1973).

(8) D.T. Grubb, J. Microsc. Spectrosc., Electron (1976), 671.

(9) D.T. Grubb, in "Development in crystalline Polymer-1 (Applied Science, London, 1982) 1.

(10) D.R. Uhlmann and A.G. Kolbeck, Sci. Am. 233 (1975), 96.

(11) D.C. Bassett, Principles of Polymer morphology (Cambridge University Press, Cambridge, 1981).

(12) D.C. Bassett, CRC Crit. Rev. Solid State Matter. Sci. 12 (2) (1984) 97.

(13) P.J. Flory, "Principles of Polymer Chemistry" (Cornell University Press) (1953).

(14) S.V. Lebedev, and N.A. Shikavronskalya, J. Russ. Phys. Chem. Soc., 43 (1911), 1124.

(15) S.V. Lebedev, Chem. Abs., 9, (1915), 798.

(16) H. Staudinger, Augew Chem., 42 (1929), 67.

(17) P.H. Geil, "Polymer Single Crystals" (Interscience, N.Y.) (1963).

(18) L. Madelkern, Condensed state of macromolecules, Discuss. Faraday Soc., 68, (1980), Paper 19.

(19) A. Keller, Polymer Crystals, Rep. Progr. Phys., 31, (1968), 623.

(20) B. Wunderlich, Macromolecular Phys., (Academic Press)(1973).

(21) C. W. Bunn, Trans. Faraday's Soc., 35,(1963), 428.

(22) E. W. Fischer, Z. Naturforsch, 12a, (1957), 753.

(23) A. Keller, Phil. Mag., 2, (1957), 1171

(24) P.H. Till, J. Polymer Science, 24, (1957), 301.

(25) P. H. Lindemeyer, J. Polymer Science, Cl, (1963), 5.

(26) L. Madelkern, Condensed State of Macromolecules, Discuss. Faraday Soc., 68, (1980), Paper 19.

(27) D. Y. Yoon, and P. J. Flory, Polymer, 18,(1976), 509.

(28) D. C. Bassett, A. M. Hodge, and R. H. Olley, Faraday Soc., 68, (1980),10.

(29) A. Keller, Polymer, 3, (1962), 393.

(30) P.H. Lindemyer, Science, 147 (1962) 12566.

(31) R. G. Kriste, W. A. Fruse and J. Schelter, Macromolecular Chain 162 (1972) 299.

(32) E.W Fischer, Structure of Amorphous organic Polymers in Bulk (Proc. Conf. Non-Crystalline Solids, Claus that Zellerfeld Sept. 1976).

(33) J.P Cotton, D. Decker et al., Macromolecules 7 (1972) 863.

(34) P.J Flory, Spatial Configuration of Macromolecular Chains, The 1974 Nobel Lecture, polymer J., 8 (1976) 1.

(35) R. Hosemann, Macromol. Chem. Suppl. 1 (1975) 559.

(36) W. Pechhold, J. Polymer Science C32 (1971) 123.

(37) G.S.Y. Yeh, Polymer Prepr. 14/2 (1973) 718.

(38) J. Schelten, D.G.N. Ballard, G.D. Wignall, G.W. Longman and W. Schmatz. Polymer 17 (1976) 75.

(39) F. J. Campbell, Rad. Physics Chem., 18, (1918), 109

(40) A. Charlesby, "Atomic Radiation and Polymers", "Pergamon Press, N.Y.) (1960).

(41) A. Charlesby, "Radiation Chemistry of Polymer System" (Interscience, London) (1960), 426.

(42) ASTM, Designation No. D-2953 "Standard Classification System for Polymeric Materials for Service in Ionizing Radiation"(1971).

(43) F. J. Campbell, Rad. Physics Chem., 18,(1981), 109

(44) C. D. Bopp, and O. Sissman, ORNL-1373, Oak Ridge National Lab. Report (1953).

(45) J. J. Triolo, Int. Seminar on Space Simulation, CERT, Toulsouse, France (1973).

(46) M. J. Mirtich, and J. M. Bozek, Spacer Rock, 8, (1971), 1164.

(47) J. Wright, and J. Warmke, Solar Sail Mission Application, AIAA Paper, (1976), 76.

(48) C.G. Gebelein, R.M. Morgan, R. Glawackey, W. Baig. Biomedical and Dental Application of Polymers, Gebelin, C.G. Koblitz, F.F. Ed., Plenum Press, New York, (1981).

(49) C. M. Samour, Chemtech 8 (1978) 494.

(50) L.D. Donaruma and O. Vog 1, Polymeric Drug, Academic Press, New York, 1977.

(51) S. Yoller, Polymers in medicine and O. Surgery, P.L. Kronenthal, Z. Oser, E. Martin, Ed., Plenum Press, New York, (1975), 245.

(52) E. H. Lee Nuclear Inst. And Method, B 151 (1999) 29.

(53) S. Bouffard, E. Balanzat, C. Leroy, J.P. Busnel, G. Guevelou, Nucl. Inst. and Method, B 131 (1997) 79.

(54) T. Steckenreiter, E. Balanzat, H. Fuess, C. Trautmann, Nucl. Inst. and Meth., B 131 (1997), 159

(55) Nobuyuki Nishimiya, Keiji Ueno, Mistsuru Noshiro, Mamoru Satou, Nucl Inst and Meth., B 59/60 (1991) 1276.

(56) L. Torrisi, R. Percolla, Nucl. Inst. and Meth., B117 (1996) 387.

(57) D. Fink, R. Klett, H.J. Mockel, F. Hosoi, H. Omichi, T. Sasuga, L.T. Chadderton, L. Wang, G S I annual report, 94,190

(58) D. Fink, R. Klett, Xuanwen Hu, M. Muller, G. Schiwietz, G. Xiao, L.T Chadderton, L. Wang, C. Mathis, V. Hnatowicz, J. Vacik, Nucl. Inst. and Meth. B 116 (1996) 66.

(59) Natacha Betz, Elenora Petersohn, Alain Le Moel, Nucl. Inst. and Meth., B 116 (1996) 207.

(60) D. Fink, L.T. Chadderton, F. Hosoi, H. Omichi, T. Sasuga, A. Schmoldt, L. Wang, R. Klett, J. Hillenbrand, Nucl. Inst. and Meth., B 91 (1994) 146.

(61) E. Ferain, R. Legras, Nucl. Inst. and Meth., B 83 (1993) 163.

(62) E. Balanzat, N. Betz, S. Bouffard, Nucl. Inst. and Meth., B, 105 (1995) 46.

(63) L.C. Northcliffe, Phys. Rev. 120 (1960) 1744.

(64) E. Pierce and M. Blann, Phys. Rev.173 (1968) 990

(65) H. Barkas, "Nuclear Research Emulsions," Vil. Chap. 9, Academic Press, New York (1963) 371.

(66) A. Chatterjee, H.D. Maccabee and C.A. Tobias, Radiat. Res. 54 (1973) 479.

(67) L.C. Feldman, J.W. Mayer and S.T. Picraux, "Materials Analysis by Ion Channeling," Chapter 2, Academic Press, New York (1982).

(68) M. Kaminsky, Bull. Amer. Phys. Soc., 12 (1967) 635.

(69) J.F. Ziegler, J.P. Biersack, and U. Littmark, "The stopping and range of Ions in Solids," Vol. 1, Pergamon Press, (1985).

(70) M.J. Norgett, M.T. Robinson, and I. M. Torrens, Nucl. Eng. Design 33 (1975) 50.

(71) J.D. Jackson," Classical Electrodynamics," 2nd edition, John Wiley, New York, (1975) 492.

(72) A. Chatterjee and J.J. Schafer, radiat. Environ. Biophys. 13 (1973) 479.

(73) J.L. Magee and A. Chatterjee, Chapter 1,5 and 6 in " Radiation Chemistry, Principles and Applications," Farhataziz and M.A.J. Rodgers, eds., VCH Publishers, New York, (1987).

(74) J.J. Butts and Robert Katz, Radiation Research, 30 (1967) 855.

(75) M.P.R. Waligorski and R.N. Hamm and R. Katz, Nucl. Tracks Radiat. Meas., 11 (1986) 309.

(76) E.H. Lee, "Invited Talk" delivered in the 3rd International Conference on Ionizing Radiation and Polymers (IraP-98), held at Dresden, Germany (19-24 Sep'98). Accepted in Nucl. Inst. and Meth. B (1999).

(77) J.L. Magee and A. Chatterjee, J. Phys. Chem. 84 (1980) 3529.

(78) J.L. Magee and A. Chatterjee, Chapter 4 in Kinetics of Nonhomogeneous Processes," G.R. Freeman, ed. John Wiley & Sons, New York, (1987).

(79) G.D. Zesis, W.J. Meath, J.C.F. Mac Donald and D.J. Dawson, Radiat. Res., 63 (1975) 64.

(80) E.H. Lee, G.R. Rao, and L.K. Mansur, Materials Science Forum, 248, (1996) 135.

(81) J.D. Hunn and C. Paul Christensen, Solid State Technology, 37 (1994), 57.

(82) W.R. Allen and E.H. Lee, Mat. Res. Soc. Sypm. Proc. 279 (1993) 333.

(83) E.H. Lee, G.R. Rao, M.B. Lewis and L.K. Mansur, L. Mat. Res., 9, (1994), 1043.

(84) M. B. Lewis, e.H. Lee and G.R. Rao, J. Nucl. Mater., 211, (1994), 46.

(85) J.M. Cowie, Polymers: Chemistry & Physics of Modern Materials, Intertext Books, Billings, Worcester, Great Britain, (1973), 283

(86) T. M. Hall, A. Wagner, L. F. Thompson, J. Appl. Phys. 53 (1982) 3997.

(87) D.K. Avasthi, J.P. Singh, A. Biswas, S.K. Bose, Nucl. Inst. and Meth., B 146 (1998) 504.

(88) E. Balanzat, S. Bouffard, A. Le Moel, . Betz, Nucl Inst. and Meth., B, 91 (1994) 140.

(89) S. Bouffard, B. Gervais, C. Leroy, Nucl. Inst and Meth., B, 105 (1995)1.

(90) L. Calcagno, R. Percola, G. Foti, Nucl. Inst. and Meth., B, 95 (1995) 59.

(91) R. Percola, P. Musumeci, L. Calcagno, G. Foti, G. Ciavola, Nucl Inst and Meth. B, 105 (1995) 181.

(92) E. Petersohn, N. Betz and A. Le Moel, Nucl. Inst. and Meth., B, 105 (1995) 267.

(93) D. Fink, R. Klett, L.T. Chadderton, J. Cardoso, R. Montiel, H. Vazquez, A.A. Karanovich, Nucl. Inst. and Meth., B, 111 (1996) 303.