ELECTRON INDUCED MODIFICATIONS IN SOME POLYMERS

BY

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Dedicated to my

PARENTS

NORTH-EASTERN HILL UNIVERSITY
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CERTIFICATE

I, Rosaline Mishra, hereby, declare that the subject matter of this thesis entitled "ELECTRON INDUCED MODIFICATIONS IN SOME POLYMERS" is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University / Institute.

This is being submitted to the North-Eastern Hill University for the degree of DOCTOR IN PHILOSOPHY in Physics.

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CHAPTER 1

INTRODUCTION

1.1. POLYMERS

Polymers, also known as macromolecules, are built up of a large number of molecular units, which are linked together by covalent bonds, while separate segments of the same molecule are attracted to each other by intermolecular van der Waals forces. The covalent bonds involved are characterised by high energies (146 to 628 $kJ.mole^{-1}$), short inter-atomic distances (0.11 to 0.16 nm) and relatively constant angles between successive bonds. Covalent bonds govern the thermal and photochemical stability of the polymers. Due to a high strength to weight ratio, their lower cost, ease of moulding and lightness, polymers have diverse and extensive applications.

The structural organisation of polymers comprises of three distinct levels:

- The first level is the monomer chemical structure (primary structure) characterised by the presence of given functional groups and related electronic structure.
- The second level chain configuration (secondary structure) is characterised by spatial arrangement of the repetitive units in the polymer chains.
- The third level is the global form of macromolecule (tertiary structure) as determined by van der Waals forces, hydrogen bonds and the sum up of the conformational constraints.

A polymer single crystal looks as though it consists of many platelets (lamella) kept one over the other in decreasing order of size. The chain folding of the macromolecular chain takes place during polymerisation and then the long chain is accommodated into a narrow lamella. For a standard polymer, lamellar thickness is around 100 Å and the molecular chain length is around 100 to 1000 nm (Gowariker et al., 1996).

Polymers can exist only in solid and liquid states. Polymers in solid state can be completely amorphous, partially crystalline or

almost completely crystalline. Extension of X-ray crystallographic techniques to polymeric solids reveals that polymers do not have perfectly ordered crystal lattice and are not perfectly crystalline. Amorphous polymers are noncrystallisable and exist as glassy solids. The temperature at which the amorphous polymer changes from the glassy state to a rubbery state (glass transition temperature), a segmental mobility is observed. At flow temperature the molecular mobility sets in, the amorphous polymer changes from rubbery state to liquid state and the polymer starts flowing (Gowariker et al., 1996). Due to absence of any crystal lattice in amorphous polymer, no true melting takes place and there is no melting point associated with it. In a crystalline polymer, the segments are firmly held in crystallites by intermolecular forces. On heating the crystalline polymer at higher temperatures, the molecular mobility associated with segmental mobility abruptly sets in and the polymer starts melting. The degree of crystallinity in polymers is based on the premise that crystalline and amorphous components co-exist. Polymers in practical use are partially crystalline and consist of both crystalline and amorphous regions.

The thermal stability of a polymer is evaluated by its softening and degradation temperatures. Aromatic or heterocyclic polymers are generally known to show excellent thermal characteristics. They do not soften and retain their rigidity up to high temperatures. Stereoregular i.e. isotactic and syndiotactic polymers are found to crystallise, whereas atactic ones are unable to do so.

On one hand, polymers offer flexibility, easy processing and good insulating properties. On the other hand, the same properties limit the further applications of polymers. Ion irradiation provides a unique way to modify the polymer properties. Ion beam techniques are more and more popular as a very flexible technique to induce special properties in a large number of materials, including metals, semiconductors, ceramics, inorganic compounds and polymers.

1.2. ION INTERACTION WITH POLYMERS

Energy deposition by an impinging ion beam occurs discretely, not continuously. Electronic excitation is controlled by quantised energy levels and ionisation is restricted by a potential energy barrier, which has to be overcome for electrons to be released from the orbit. In addition to this, an atomic displacement also requires certain

threshold energy to break the bonds and move the atom over a certain potential barrier due to surrounding atoms.

The interaction steps of an ion with the polymer chains are as follows:

STEP 1: Energy is deposited by a series of adiabatic ionisation and/or excitation events and characteristic reaction sites (excited precursors) are formed according to two basic energy-loss mechanisms.

- ***Collisional energy-loss*** mechanism mainly produces a random fragmentation of polymer chains (Non-thermodynamic mechanism).

- ***Electronic energy-loss*** mechanism produces conventional ionised species by adiabatic ionisation of electronically excited species (Thermodynamic mechanism).

The characteristic interaction time, time for ionisation events and collisionaly induced bond breaking is of the order of 10^{-17} to 10^{-16} seconds.

STEP 2: Unstable species ions, radicals, recoiling atoms, excited species, created in the first step, relax through available reaction channels (Thermodynamic mechanisms). Relaxation

time for ionised species is of the order of 10^{-15} to 10^{-14} seconds and that for excited species is 10^{-16} to 10^{-12} seconds.

STEP 3: After a relatively long time, all long term rearrangements and thermalisation occur. This step affects the chain motion, de-excitation of long time radicals and decomposition of unstable bonds.

In polymers, with relatively long electronic relaxation times, part of the energy deposited by penetrating ions may be converted into atomic motion, producing defects and chemical modification in the bulk and material ejection at the surface. Ion tracks in polymers have been applied to engineer materials properties and surface morphology (Papaléo et al., 1999).

A full mechanism interpretation of the very complex beam-polymer interaction still needs a much larger amount of experimental data on suitable chemical systems and the realisation of new experiments pointing to elucidation of primarily induced chemical species with in situ measurements during irradiation. Polymers are characterised in general by a very high and very persistent reactivity. In particular, particle irradiation generates excited species or radicals, which, according to the chemical structure of polymer, can be

extremely resistant, having life-times of the order of days or months for some kind of radicals.

1.3. SPATIAL RESPONSE OF POLYMERS TO THE PERTURBATIONS

Polymers have fairly large free volume resulting in low atomic density. The spatial response of polymers to the energy input are both local and mesoscopical types.

Local response: Modification in polymer structure at the level of primary chemical structure of the monomer units. Optical properties are modified. In aliphatic polymers, the refractive index is modified due to formation of relatively high concentration of unsaturated bonds all along the irradiated polymer layer. In aromatic polymers, intrinsic modification of electronic structure takes place.

Mesoscopical response: Expansion and propagation of dynamic response over a much larger region than the primary interaction site. Modification occurs in properties related to chain configuration, as for instance, solubility and thermo-chemical properties.

Radiation damage includes changes in physical properties stable for a time scale essentially longer than the time of the slowing down of

the primary particle. It is a consequence of deposition of energy of the primary particle in the target.

1.4. ION INDUCED MODIFICATION IN POLYMERS

Ion beam treatment provides a unique way to modify the chemical, structural, optical, geometrical and electrical properties of polymer by causing irreversible modifications of structure and chemical composition (Steckenreiter et al., 1999). Ion beam induced scissions of polymeric chains typically produces charge redistribution along the skeletal backbone of a polymer molecule. This gives rise in turn to chemically unsaturated bonds and a variety of topological cross-linking rearrangements of polymer molecular fragments. There is also a simultaneous generation of free radicals. The nuclear stopping causes atomic displacements, while the electronic processes induce collective excitation of atoms and produce delta rays.

Energy deposition by an impinging ion beam occurs discretely because electronic excitation is restricted by quantised energy levels and ionisation is restricted by a certain potential barrier which has to be overcome for the electrons to be released from the orbit. This

discrete energy-loss entity is called a 'spur' (Lee, 1999). The energy-loss occurs as spurs along the ion track. Thus, changing the linear energy transfer (LET) of the impinging ion beams means changing the spur separation or spur density. For low LET ion beams, spurs are widely separated and occur independently often leading to scission. 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 facilitating cross-linking. 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 the mechanical stability while scission degrades mechanical strength.

Some modifications in polymer properties as a result of ion implantation are briefly described below:

- Formation of graphitic islands / clusters takes place as a consequence of very high locally deposited energy density. These are actually the conducting micro-composites that increase the conductivity in polymers (Davenas et al., 1997).

- Phase transition during irradiation has been observed in ferroelectric polymers (Calcagno et al., 1992).
- Ion implantation in polymers can result in drastic increase in electric conductivity (in some cases, by a factor of 10^{15}) of the pristine material (Popok et al., 1997) that opens its way to developing radically new micro-electronic devices.
- The bulk properties of polymers may not change after implantation, but rather the surface can become electrically conductive (Wang et al., 1997).
- Refractive index is modified due to formation of a relatively high concentration of unsaturated bonds all along the irradiated polymer layer (Darraud-Taupiac et al., 1997).
- Ion implantation causes a remarkable increase in hardness of polymer, increase in wear resistance and decrease in friction coefficient (Lee et al., 1991). Wear is a manifestation of bond breakage and cross-linking is responsible for improving the wear resistance in ion beam treated polymers. Ion beam irradiated polymers were reported to be three times harder than stainless steel.

- Radiation decreases the thermal conductivity of the polymers and can thus lead to higher operating temperatures and larger thermal stresses (Matzke, 1982).
- Molecular weight changes are a critical consequence of polymer irradiation, since a reduction in average molecular weight caused by main chain-scission will result in loss of mechanical strength. On the other hand cross-linking increases the molecular size thus improving the mechanical properties (Spinks and Woods 1990).
- Ion bombardment of polymers by energetic ions produces dramatic changes due to disruption of original chemical bonding as chain-scissions and cross-linking, thus changing the track registration efficiency in most of the polymers (Dwivedi et al., 1999). In general, polymers with only secondary and tertiary carbon atoms in the main chain tend to cross-link, while degradation occurs if chain includes a quaternary carbon atom.
- Disruption of original chemical bonding in polymers by ion bombardment occurs as chain-scission, cross-linking, carbonisation, gas evolution and ejection of polymer fragments with a wide distribution of molecular weights (Beardmore and Smith, 1995).

1.5. APPLICATIONS OF MODIFIED POLYMERS

Modified polymers have a wide range of applications also.

- The recent interest of using polymers as electrically conducting materials, for optical applications, light emitting diodes etc. is increasing (Das et al., 1998).
- Radiation treatment of polymers is employed to cross-link wire and cable insulation in order to improve the abrasion resistance and softening point. It is also used in the production of shrink film, tubing and packaging materials.
- Radiation induced degradation is used to form powdered Teflon which is used as a lubricant. Degradation of Teflon produces Perfluoro intermediates required in production of fluoro surfactants, fluorinated dielectrics and fluorinated finishing agents for textile industry.
- Avoidance of polymer degradation by choice of suitable polymer is utilised for satellite designs, since satellites are exposed to electrons and protons of several MeV energies, with additional stress of UV radiation, temperature fluctuations and high vacuum. The surface dose of satellite is equal to 25 MGy. y^{-1}.

- Automobile products are also irradiated to bring about partial cross-linking to increase their strength prior to conventional vulcanisation.

1.6. ELECTRON INTERACTION PHENOMENA

Heavy particles produce "tracks" densely populated with ions and excited molecules, whereas electrons deposit much of their energy in isolated spurs (micro-zones) containing a relatively small number of ions and excited states. Types of ionic and excited states will be same for both electrons and heavy particles, so that chemical process and radiolysis will be generally same, but different concentrations of reactive species in tracks and spurs will result in the products being formed in different proportions.

Electron interaction differs from heavy ion interaction in the following ways (Tayal, 1992):

1) Because of its small mass, electron, when collides with atomic electrons of the absorber, sustains deflections through much larger angles. The path of the electron is very irregular and not at all straight as the paths of heavy charged particles.

2) A heavy particle loses only a tiny fraction of its energy in each interaction with an atomic electron in its path. Random fluctuations in the amount of energy lost per interaction average out in thousands of interactions that occur during slowing down processes. Therefore, all the members of a mono-energetic beam of such particles have nearly same range. In electrons, large fraction of its energy can be lost in a single interaction. Path-lengths of electrons with same incident energy may differ.

3) Due to identity in character of the two colliding particles, exchange phenomenon must be taken into account in the theoretical investigations of electron-electron collision.

4) High speeds of the β-particles make it necessary to employ a relativistic treatment of the collision mechanism.

The relative importance of these processes vary strongly with energy of the incident electrons and depend to a small extent on the nature of absorbing material.

1.7. PROCESSES OF ENERGY - LOSS BY ELECTRONS

- ***Energy-loss of electrons by Bremsstrahlung emission***

Energetic electrons passing close to the nucleus of an atom, may be decelerated and according to Classical Physics will radiate electromagnetic energy (bremsstrahlung) with a rate, dE/dx (Energy-loss per unit path-length), proportional to z^2Z^2/m^2, where z and Z are the charges of the incident particle and the target nucleus respectively and m is the mass of the incident particle.

Energy-loss by bremsstrahlung will be greatest for light particles and for target materials of high atomic number. Bremsstrahlung emission produces significant changes in the stopping material, when it subsequently interacts with the material.

For electrons, the Bremsstrahlung emission is negligible below 100 keV, but increases rapidly with increasing energy. The energy of Bremsstrahlung radiation ranges from near zero to the maximum energy of the incident electrons, the energy of an individual bremsstrahlung photon depending upon the extent to which the electron, giving rise to it is slowed down. So, the

bremsstrahlung energy spectrum, which extends from zero to the energy of incident electron, is a continuous X-ray spectrum.

- ***Energy-loss of electrons by inelastic collisions:***

  Inelastic scatterings, rather than producing large angle deflections, make electrons lose energy in ionisation and excitation events with atoms. Coulomb interaction of incident electrons with atomic electrons of the stopping material produces ionisation and excitation in the target, thus, slowing down the incident electrons below the energies at which bremsstrahlung emission occurs. Inelastic scattering is relevant in the study of electron penetration through matter.

- ***Energy-loss of electrons by elastic scattering:***

  In elastic scattering with atoms, electrons suffer large angle deflections and negligible energy losses that make electrons traverse matter in tortuous paths, rather than in a rectilinear way (Idoeta, 2000). Owing to its relatively small mass, the electrons can be deflected by Coulomb electrostatic field of the atomic nucleus, which results in the elastic scattering of electrons, i.e.,

only the direction of motion is changed without any conversion of kinetic energy to any other form of energy. This scattering is more pronounced for low energy electrons and for high atomic number materials.

The technological challenges to develop new capabilities in the nanometer scale, tailoring of surfaces and the understanding of the evolution of the energy deposited around the ion path and of the modified region, are fundamental research areas in which interest has recently been aroused. The wide spread application and technological importance of the polymers evoked us to induce some desirable modifications in their properties so as to enhance their applicability. The main challenge was to modify the polymers with the electrons, which do not create tracks of their own and yet change the bulk properties.

So, for the present work five different polymeric materials have been selected on the basis of their applicability and the effect of electron irradiation on them have been studied through different experiments which are described chapter wise, as follows:

- The modification produced in four different types of polymers viz. Polypropylene, Polyethylene terephthalate, Polytetrafluoro ethylene and Polyimide, by a particular dose of 2 MeV electron has been studied by spectroscopic, thermal, track and diffraction techniques and described in **Chapter 2**.
- **Chapter 3** deals with the study of dose dependent variation in optical absorbance, transmittance, structural arrangement, roughness and thermal properties by different characterisation techniques, of a widely used polymer, Polyallyldiglycol carbonate which has been irradiated to 2 MeV electron beam.
- Modifications produced in track registration sensitivity of Polyallyldiglycol carbonate by electron irradiation has been described in **Chapter 4**. The polymer Polyallyldiglycol carbonate pre-irradiated by electrons was further irradiated by heavy ions and the overall etching response of the polymer as a function of electron dose has been investigated.
- **Chapter 5** describes the energy-loss by an electron beam when it traverses the layered metallic targets. The effect of energy-loss on the etching characteristics and thermal stability of Polyallyldiglycol carbonate has been studied. A comparative study has been carried

out to study the effect of metallic targets of different atomic numbers on the energy-loss phenomena.

- Finally in **Chapter 6**, the significant results of the present investigation are highlighted. A brief description on the potentialities and scopes of the work is presented for some future applications.