CHAPTER - VII

7.0 CONCLUSION AND FUTURE SCOPE

High energy heavy ions passing inside a material lose their energy mainly through inelastic scattering, producing trail of excited/ionized atoms. The energy deposited produces a high energy density chemistry giving final products which are different from those generated by low energetic ions.

Along the ion trajectory a continuous trail of damage called latent tracks are formed, provided the electronic energy loss exceeds a certain threshold value depending on the material. These tracks consists of atomic displacements, broken molecular chains and free radicals. The formation of these tracks is largely is responsible for the material modification.

The energy deposited by swift heavy ions in materials can be varied by choosing the appropriate ion and their energies. This provides a possibility to create interesting modification in all types of materials. Thus the field of swift heavy ions in materials engineering and characterization offers much possibilities of applications.
In the present work we have therefore tried to characterize and analyze the effect of high energetic heavy ions at high electronic excitation of (2 keV/nm \(\sim\) 11 keV/nm) on polymers and fullerene \((C_{60})\) using different ions and varying doses.

7.1 Polymers:

The present investigation on polymers was undertaken to study:

1. The loss of hydrogen on irradiation with different ions and energies and using the technique of elastic recoil detection analysis (ERDA) for its determination.

2. The effect of swift heavy ion irradiation on the radiochemistry and the melting characteristics of PET at high electronic energy transfer \((\sim 10\) keV/nm) and using the techniques of Fourier transform infrared spectroscopy (FTIR) and Differential scanning calorimetry (DSC).

3. The nature of chemical changes in PVDF by the irradiation of 180 MeV Ag and 95 MeV Ni ions was also studied employing the technique of FTIR.
From the study of hydrogen loss on irradiation by swift heavy ions we come to the conclusion that:

(a) The rate of hydrogen loss from irradiated polymers is proportional to the electronic energy loss.

(b) The loss of hydrogen is dependent on the type of C-H bonds in the polymers. For example PMMA and PP where there are CH$_3$ type bonds, the rate of hydrogen loss is higher than in other polymers.

(c) All hydrogen loss curves can be fitted by two exponential terms. The track radii estimated from the hydrogen release cross section to be 2 - 6 nm.

(d) As the ions pass through an insulating medium like a polymer, hydrogen gets partially released within the volume of the track. At the ion fluence when the track diameters start overlapping, it is observed that the rate of loss of hydrogen loss curve tends to flatten. This fluence also reveals the track radius.

The differential calorimetric(DSC) measurements of swift heavy ion irradiated PET shows significant changes in their melting property. Preliminary studies indicate that the melting temperature of irradiated PET increases with ion fluence and then decreases again. It appears that, whereas the pristine material
requires both the energy to induce oriented chain mobility at $T_{premelt}$ and the energy to enable orientation free chain mobility at $T_{melt}$, the ion irradiation suppresses oriented chain mobility, so that only the melting peak at $T_{melt}$ remains. When ion track overlapping sets in, amorphization overtakes, leading to a reduction in the melting point. FTIR signals indicate a different trend of amorphization from earlier observations, which might support speculation of a transient recrystallization upon swift heavy ion impact. The XRD results show the appearance of a new peak at $2\theta = 37.33^\circ$ on irradiation, probably stemming from the reaction products, along with the decrease in the main peak at $2\theta = 25.62^\circ$.

Studies on the nature of chemical changes in PVDF by the irradiation of energetic ions of 180 MeV Ag ions indicated the formation of $=C=CF_2$ at low fluence which was found to decrease again at higher fluence. The C - H stretching modes sustained their identity even at a fluence of $5\times10^{11}$ ions/cm$^2$. However, the 95 MeV Ni ions irradiation at a fluence of $5\times10^{13}$ ions/cm$^2$ suggested substantial modification of the polymer leading to simpler structural units.

7.2 Fullerene ($C_{60}$):

(1) Thin films of $C_{60}$ were subjected to swift heavy ion irradiation of 189 MeV Ag, 110 MeV Ni and 50 MeV Si ions, spanning the region from 2 to 11keV/nm of electronic excitation at doses ranging from $1\times10^{10}$ to $1.8\times10^{12}$.
ions/cm². The irradiated thin films were studied using Raman and Photoluminescence spectroscopy.

(2) To obtain more information on the effect of high energetic heavy ions on C₆₀, characterization on the irradiated films of fullerene by 180 MeV Ag at doses ranging from 1x10¹⁰ to 5x10¹² ions/cm² were also performed using the techniques of Atomic force microscopy (AFM), X-ray diffraction (XRD) and Fourier transform infra-red spectroscopy (FTIR).

The Raman scattering and Photoluminescence observations indicated structural transformations of C₆₀. Raman spectra indicated polymerization and damage of the film with ion fluence arising from high electronic loss deposition. The track radii as calculated from the damage cross section are found to be, Tᵣ = 6 nm, Tᵣ = 5 nm and Tᵣ = 4 nm for Ag, Ni and Si whose electronic stopping power (Sₑ), corresponds to 11 keV nm⁻¹, 6 keV nm⁻¹ and 2 keV nm⁻¹ respectively. Photoluminescence spectroscopy of the irradiated film indicated a decrease in C₆₀ phase with dose and increase in the intensity at the 590nm wavelength, which is attributed to increase in oxygen content.

X-ray diffraction studies of C₆₀ powder, pellet and film gave the characteristic peaks of f. c. c. crystal. On irradiation it was observed that the peak intensities decreased and broadened indicating destruction of C₆₀.
molecules. The film exhibited the crystalline structure even in the highest fluence of $5 \times 10^{12}$ ions/cm$^2$, though the intensities were much reduced.

AFM pictures showed on the average there was a decrease in the grain size on irradiation, suggesting possible sputtering of carbon atoms from the film. The film showed surface roughening at the highest fluence. This is explained as the formation of compact material in the damaged surface layer.

Fourier transform infra-red spectroscopy (FTIR) spectra showed the strong four infrared peaks at 1426, 1179, 573 and 528 cm$^{-1}$ expected for C$_{60}$ in the solid state. The 1426 and 1179 cm$^{-1}$ bands were found to decrease in intensity with fluence without changes in the peak position and widths, suggesting fragmentation/destruction of C$_{60}$ molecules. It also suggests that the contribution of energy loss due to collision to the destruction of C$_{60}$ molecules in the present case is minimum.

7.3 Future Scope:

From the results of the present work it is realized that this area offers a wide scope for further studies. For swift heavy ions the flexibility of varying the electronic energy transfer to the material by choosing appropriate ion and their energies itself offers unlimited area of interesting material modification. A few areas are suggested below in order to gain a deeper understanding on the mechanism of material modification by ion irradiation.
Polymers:

(a) The molecular emission quantification on irradiation at different energies and fluence may throw new insight on the chemical modification of the material.

(b) Electrical conductivity measurement of irradiated polymers in relation to the hydrogen loss may be useful information on hydrogen dependent conductivity.

(c) The concept of MeV heavy ion induced constructive phase transition in polymers is a field of interest, particularly in the light of interesting results obtained in this work at energy transfer ~10 keV/nm. It would be worthwhile to study the radiochemistry and melting behavior of a polymer in the energy transfer region above ~10keV/nm.

(d) High resolution electron microscopy would be very useful for visualizing the tracks generated by the energetic ions, whereby the track areas can be obtained.

(e) For changes in the physical properties like elasticity or chain flexibility of irradiated polymers the use of pulsed T$_2$ NMR would be very valuable.
(f) Hardness measurement for different doses on the irradiated polymers would also be a very important study area.

**Fullerene (**$\text{C}_{60}$**):**

(a) The study of destruction of $\text{C}_{60}$ by comparing fullerene destruction by different projectiles with varying electronic but constant nuclear energy transfer, would be very informative. It would also clearly be useful to make a number of depth profile measurement of fullerene destruction.

(b) High resolution electron microscopy would be very useful to observe the possible track formation in $\text{C}_{60}$ generated by the energetic ions.