PREFACE

Polymer research and development is a relatively young discipline that spans the field of physics, chemistry, electrical engineering and beyond. It is one of the most interdisciplinary endeavors of modern science. The finding that ionizing radiations may modify/improve certain properties of materials has become one of the sought after techniques in present day polymer research. This thesis is a comprehensive study of irradiation effects on polymeric materials and is divided into five chapters discussed below.

Chapter 1

This chapter includes a brief introduction to conducting and non-conducting polymers. The arrangement of a large number of structurally similar chemical units into linear or branched chains provides polymers with their unique properties, which cannot be matched by any other class of materials. Polymers, though introduced in the beginning of 19th century, still play a major role in our day to day life. Polymers are generally known for their insulating property and resist the flow of current. However, for more than a decade now, researchers have shown that certain class of polymers which are conjugated (those that possess an extended \(\pi\)-conjugation along the polymer backbone) exhibit semiconducting behavior. In the mid 1970s, the first polymer capable of conducting electricity, polyacetylene, was reportedly prepared accidentally by Shirakawa. The electrically conducting polymers or synthetic metals combine the electrical properties of metals with the advantages of polymers such as light weight, greater workability, resistance to corrosion and chemical attack and the lower cost and have infiltrated our day-to-day life with range of products, extending from most common consumer goods to highly specialized applications in space, aeronautics, electronics and non-linear optics. It is, therefore, no wonder that these polymers are called the Materials of the twenty first century. It has been found that the high conductivities obtained in these polymers are associated with formation of self-localized excitations such as solitons, polarons and bipolarons which may move relatively free through the material.

In the second half of the chapter the effects of irradiation on the materials, in general, is discussed. When radiation passes through the material, it interacts with
material and deposits energy and resultantly causes ionization and excitation of atoms and molecules. After chemical reactions of intermediate species, cross-linking, degradation (scission), unsaturated bonds etc. are induced in the polymers. These events can cause deterioration of properties of polymer materials. The irradiations of polymers produce useful improvements in their physical properties, electrical conductivity and optical transmission properties. Such improved polymers may be used as substitutes for metals, alloys and glasses, while retaining the inherent advantages of polymers. Ionizing radiation is applied in the plastic industry due to its ability to produce cross-linking, a process whereby polymer chains link together in a three-dimensional network, thereby making the material strong. The intentional degradation of polymer materials is another application of ionizing radiation. It results in the decrease of the molecular weight. An overview of the literature studied is given in this chapter. The present research work has been undertaken to investigate the effect of ionizing radiations on physico-chemical properties of polymers. The effect of different ions and gamma irradiation is investigated.

Chapter 2

This chapter provides details of the sample preparation and facility used for exposing the polymeric materials by ionizing radiations. Non conducting polymers namely Polytetrafluoroethylene (PTFE) and Low Density Polyethylene (LDPE) in the form of flat sheets were procured from Good Fellow England and used in as received form without any further treatment. The conducting Polypyrrole (Ppy) is prepared by electrochemical method from pyrrole monomer. In the present work, a 15 UD Pelletron Accelerator located at Inter University Accelerator Centre (IUAC), New Delhi, provided high energy heavy ion beam. IUAC is a UGC centre, dedicated for accelerator-based research in material science, nuclear physics and biological sciences. Two beams viz N$^6+$ with energy 86 MeV and Ni$^{11+}$ with energy 150 MeV are used. The gamma ray source used in the present work is the gamma chamber having Co$^{60}$ gamma rays at Jawaharlal Nehru University (JNU), New Delhi, India. The dose rate was 4.8 Gy/s. Another gamma source with a dose rate of 7.65 Kgy/hr installed at IUAC is also utilized for the present work. The chapter also includes the instrumental techniques and methods employed to study the various aspects of this
research. The techniques i.e. FTIR, UV/Visible and Powder XRD used to characterize the pristine and irradiated polymers are discussed.

Chapter 3

In this chapter, the experimental results in terms of the physico-chemical properties of the pristine and irradiated Polytetrafluoroethylene (PTFE) samples are reported. PTFE is being widely used in the industrial fields due to its unique properties. It is a linear polymer having no branching and highly crystalline having melting point of 328 °C. The effects of radiations on PTFE studied by various researchers have been discussed in brief. FTIR spectra of the pristine and irradiated samples are recorded to investigate the chemical response of the polymer. Significant change in the intensity of characteristic absorption bands of −CF₂ groups evidencing the break of the polymer chain is observed. UV/Vis spectra of the pristine and all the irradiated samples are recorded in the range 200 nm to 800 nm. The UV-Vis spectral studies reveal the decrease in the band gap energy with irradiation. The disturbance in the crystal structure of PTFE is studied with the help of X-ray diffraction in the range of 2θ = 10°-40°. The micro strain developed in the polymer samples is also investigated. The irradiation results in significant change in the chemical, optical and structural properties of PTFE.

Chapter 4

An experimental investigation on ion beam and gamma irradiations on non conducting Low Density Polyethylene (LDPE) is presented in this chapter. LDPE is a highly branched molecule with branches of varying lengths. Structure of LDPE usually contains chains with about thousand of carbon atoms which form about 20-30 branches, and about 40 – 55 % of crystalline structure. Previous investigations on changes in the various properties of irradiated LDPE are briefly discussed in the first half of the chapter. The changes in the various bond strengths and bond angles are investigated with the help of FTIR studies in the range 400-4000 cm⁻¹. Irradiation of LDPE gives a combination of degradation and cross-linking accompanied by the formation of unsaturated products. The optical properties are greatly affected due to irradiation. The UV-Vis spectroscopy is used for the investigation of the optically induced transitions. This provides useful information about the bond structure and
energy gap in pristine and irradiated LDPE. The variations in band gaps with ion fluence or gamma dose are discussed. Further, Urbach energies and number of carbon atoms formed in a cluster are also reported. The XRD analysis is also carried out to investigate the changes in the structure of the polymer samples. Increase or decrease in the peak intensity with irradiation is reported.

Chapter 5

Polypyrrole (PPy) is an especially promising inherently conducting polymer, as it is environmentally stable and relatively easy to synthesize. The changes in the conducting Polypyrrole films subjected to different doses or fluences of irradiation are discussed in this chapter. FTIR spectroscopy has been employed for studying the molecular bonding structure and functional group analysis in the pristine and irradiated PPy samples. The electronic structure and the carrier type in the polymers are visualized by UV–Vis spectra. In order to understand the crystalline or amorphous nature of the material XRD results are discussed.