In this chapter, the summary and important conclusions of the present study have been highlighted.
Summary

5.1 OVERVIEW OF THE PRESENT STUDY

Polymer science is one of the growing fields of research and development in the modern age of science and technology. Polymers have emerged as the most promising materials in the modern era by virtue of their outstanding inherent properties with a possibility to modify these to the desired extent through various means like chemical doping, irradiation, implantation [Chapiro 1962; Young & Lovell 2002; Fink 2004; Billmeyer 2005] etc. It is well documented that the polymers with the improved properties find extensive applications in various fields such as electronic and opto-electronic devices (solar cells, LEDs, LCDs, optical switches, optical waveguides etc), automobile parts, aerospace technologies, medical applications [Hioki et al. 1983; Darraud et al. 1994; Ruck et al. 1997; Hong 2001; Lee et al. 2001; Singh 2001; Hong et al. 2002; Liu et al. 2002; Fink 2004; Singh et al. 2005; Kondyurin et al. 2008; Hadjichristov et al. 2009] etc.

Among the various available techniques, ion-implantation has proven to be a potential means to improve the surface, near surface and deeper layer properties of polymers depending upon the related external parameters [Fink 1996; Lee 1999; Fink 2004; Sharma et al. 2007; Kondyurin 2008; Abdul-Kader et al. 2010; Kumar et al. 2011]. Similarly, gamma irradiation attracts special attention in improving the bulk properties of the polymers [Chapiro 1962; Durrani & Bull 1987; Ichikawa & Yoshida 1990; Rosenberg et al. 1992; Sinha et al. 2001; Saad et al. 2005; Saqan 2007]. Motivated with these, in the present work, our endeavor is to carry out a systematic study on the change in the optical, thermal, electrical and structural properties of an important polymer Poly(methyl methacrylate) (PMMA) through ion implantation and gamma irradiation.

PMMA is a special polymer possessing exceptional surface properties owing to its unique chemical composition. It is a linear, amorphous, thermoplastic, light weight, low cost polymer. Its optical transparency from near UV to near IR region
Summary

makes it appropriate in many optical and opto-electronic devices. Ion implantation as well as gamma irradiation studies in PMMA are of immense importance because of its usability in various fields such as fabrication of optical waveguides, lithography, bio-medical applications [Leontyev 2003; Kulish 2003; Kuo 2003; Koval 2004; Sousa 2007; Abdelrazek 2010; Fawzy 2011] etc.

The present study is devoted to the optical, thermal and electrical response of PMMA polymer after implantation to 100 keV Ar⁺ and N⁺ ions and irradiation to gamma rays.

From the recorded transmission and absorption spectra in UV-Visible range, the change in the optical parameters like absorption, optical energy gap and refractive index of PMMA polymer after ion implantation and gamma irradiation has been investigated. Further, in order to study the thermal degradation behaviour of the ion implanted and gamma irradiated PMMA, change in activation energy of the thermal degradation process of the treated samples as compared to virgin PMMA has been deduced. The modifications produced in electrical conductivity as an effect of ion implantation and gamma irradiation have been discussed. Such changes in optical, thermal and electrical behaviour of PMMA have been tried to be understood in terms of the induced structural changes revealed through FTIR and Raman spectroscopy. Further, the observed changes in the properties of the polymer after implantation have been tried to be correlated with the linear energy transfer by the implanted ions.

5.2 Broad Objectives of the Present Study

The broad objectives of the present study were:

1. To irradiate the samples of PMMA at different gamma doses with maximum up to ~1600 kGy.
Summary

2. To implant the PMMA samples to 100 keV N$^+$ and Ar$^+$ ions at various fluences with maximum upto $5 \times 10^{16}$ ions/cm$^2$.

3. To study the optical response, thermal stability and DC electrical conduction behaviour of ion implanted PMMA polymeric samples.

4. To study the optical response, thermal stability and DC electrical conduction behaviour of gamma irradiated PMMA polymer.

5. To reveal the induced structural changes in these polymers as a result of ion implantation and gamma irradiation through FTIR and Raman spectroscopic techniques.

6. To understand the mechanism involved in the observed changes in optical, thermal and electrical response of PMMA due to ion implantation in terms of the Linear Energy Transfer (LET) by the implanted ions.

5.3 MAJOR OUTCOMES OF THE PRESENT STUDY

a) Optical Behaviour

In comparison to virgin PMMA, the ion implantation as well as gamma irradiation provoked drastic modifications in the optical behaviour of the treated samples of PMMA. The important results drawn from the present study in this context may be summed up as:

- A considerable reduction in the transmittance of the implanted samples for both Ar$^+$ as well as N$^+$ ions has been observed in comparison to the virgin sample of PMMA. A similar decreasing trend in transmittance with increasing gamma dose was observed for the gamma irradiated samples of PMMA also.

- A significant increment for the reflectance has been noticed for both Ar$^+$ as well as N$^+$ ion implanted samples of PMMA as compared to the virgin
Summary

sample. Similarly, for the gamma irradiated samples also, an increase in reflectance with increasing gamma dose has been observed.

- A continuous red shift in the absorption spectra of the irradiated samples in comparison to virgin PMMA has been observed for both the ion implanted as well as gamma irradiated samples.

- The optical energy gap has been found to decrease from 3.17 eV for virgin PMMA to 2.23 and 0.71 eV for 100 keV Ar$^+$ and N$^+$ ions respectively at the common implantation dose of 5x10$^{16}$ ions/cm$^2$. On the same lines, the value of optical energy gap was found to be reduced to 2.80 eV for the gamma irradiated sample at 800 kGy.

- The values of refractive index were found to increase from 1.54 for virgin PMMA to 2.30 and 2.71 for 100 keV Ar$^+$ and N$^+$ ions respectively at the common implantation dose of 5x10$^{16}$ ions/cm$^2$. For the gamma irradiated sample, the corresponding increment in refractive index was shown by the value which became 1.88 at 800 kGy.

b) Thermal Behaviour

- The TGA thermograms of the ion implanted samples of PMMA clearly indicate an increase in the thermal stability for both Ar$^+$ as well as N$^+$ ions in comparison to the virgin sample of PMMA. But, for the case of gamma irradiated samples of PMMA, the respective thermograms depicts a clear cut decrease in the thermal stability as an effect of gamma irradiation.

- The values of activation energy of thermal degradation were found to increase from 224 kJ/mol to 254 and 262 kJ/mol for 100 keV Ar$^+$ and N$^+$ ions respectively at the common implantation dose of 2x10$^{16}$ ions/cm$^2$. On the contrary, the value of activation energy was found to be reduced to 92 kJ/mol for the gamma irradiated sample at 1600 kGy. Corresponding alterations were observed in the values of frequency factor for both the ion implanted as well as gamma irradiated samples.
Summary

c) Electrical Behaviour

- The I-V measurements of both the ion implanted as well as gamma irradiated samples of PMMA clearly show a significant increase in the current with increasing irradiation parameters (ion fluence and gamma dose for ion implantation and gamma irradiation respectively).
- The DC surface conductivity of ion implanted samples has been found to be increased by approximately five orders and six orders of magnitude after implantation to 100 keV Ar$^+$ and N$^+$ ions, respectively at the common fluence of 5x10$^{16}$ ions/cm$^2$ as compared to the virgin PMMA.
- The bulk (DC) conductivity of gamma irradiated samples has been found to be increased by approximately two orders of magnitude after irradiation at 1600 kGy as compared to the virgin PMMA.

d) Structural Behaviour

- The induced structural changes as a result of ion implantation clearly indicate the formation of a cross-linked carbonaceous structure, the extent of which is more prominent for N$^+$ ions than for Ar$^+$ ions, in the implanted region of PMMA polymer, as revealed through FTIR and Raman spectroscopic techniques. Such changes in the structure of these polymers are responsible for the observed modifications in the optical, thermal and electrical properties of these polymers after ion implantation.
- The component of linear energy transfer through electronic energy loss by the implanted ions, favouring the formation of a cross-linked carbonaceous network within the implanted region of this polymer, seems to be mainly responsible for the observed changes in the optical, thermal and electrical properties of this polymer after implantation. The prominent changes in optical, thermal and electrical parameters after N$^+$ ion implantation, in comparison to Ar$^+$ ion implantation at same energy and same ion fluence, may be due to the deeper penetration depth of N$^+$ ions.
Summary

The observed changes in various optical, thermal and electrical parameters of gamma irradiated samples of PMMA may be due to the fact that the gamma irradiation in polymers leads to chain scissioning resulting in the breaking of various bonds, formation of free radicals, free charge carriers, etc. leading to the formation of disordered structure with extended localized states in the polymers. All these structural changes are in agreement with that as revealed through FTIR and Raman spectra of gamma irradiated PMMA.

5.4 FUTURE PROJECTIONS

The ion implantation related studies in polymers may be extended by choosing the various ion-polymer combinations, to understand the role of linear energy transfer (LET) by the implanted ions, in a quantitative manner, on the change in the optical, thermal, electrical and other properties of polymers. These studies will help in the understanding of the proper mechanism involved in such processes and may lead to the development of a simulated model.