As already mentioned in Chapter 1, Section 1.4, inspired with the improved bulk properties of the polymeric systems by gamma irradiation, in this chapter, modifications produced in the optical, thermal and electrical properties of PMMA polymer after gamma irradiation have been discussed. The observed changes in these properties have been tried to be understood with the induced structural changes as revealed through FTIR and Raman spectroscopy.
4.1 Optical Studies

This part of the present study relates to the induced changes in the optical behaviour like transmission, reflection, absorption, optical energy gap and refractive index of PMMA as a result of gamma irradiation up to a dose 800 kGy.

a) Transmission Behaviour

Figure 4.1 presents the recorded UV-Visible transmission spectra of virgin and gamma irradiated samples of PMMA at different doses. It is clearly evident from the figure that the transmission is about 90% in the entire visible range (~400 to 800 nm) for virgin PMMA polymer, confirming its almost transparent nature. After gamma irradiation, the transmission reduces continuously with increasing dose and becomes 53% and 35% at doses 400 and 800 kGy respectively in almost entire visible range. As a consequence of reduced transmission, slight change in the colour of the sample from transparent to yellowish has been observed.

b) Reflection Behaviour

The recorded diffuse reflection spectra of virgin and gamma irradiated PMMA polymer samples at various doses have been presented in figure 4.2. These spectra clearly depict an increase in reflection as an effect of gamma irradiation from ~11% for virgin sample to ~12% and 13.5% for the samples irradiated at the dose of 400 and 800 kGy respectively, at wavelength 600 nm.

The observed changes in the transmission and reflection behaviour of gamma irradiated samples of PMMA may be ascribed to the induced structural rearrangements as a result of gamma irradiation. Such changes are responsible for the alterations in various optical parameters e.g. absorbance, optical energy gap and refractive index.

c) Optical Parameters

Various optical parameters for virgin and gamma irradiated PMMA polymeric samples have been determined using the recorded transmission (T) and reflection (R) spectral data of figures 4.1 & 4.2 respectively. Since these values do not
Figure 4.1: UV-Visible transmission spectra of virgin and gamma irradiated PMMA at different doses.

Figure 4.2: UV-Visible reflection spectra of virgin and gamma irradiated PMMA at different doses.
incorporate for reflection losses from top and bottom air-sample interfaces, therefore, the same are to be corrected for such losses. The corrected values of the transmittance \((t)\) and reflectance \((r)\), as already discussed in detail in Chapter 2, Section 2.3.1, for virgin and gamma irradiated samples of PMMA, in terms of the recorded values of transmission \((T)\) and the reflection \((R)\) can be expressed, in the light of the following relations, as

\[
r = \frac{2R}{1 + t^2 + \sqrt{(1 + t^2)^2 - 4t^2R(2 - R)}} \quad (4.1)
\]

\[
t = \frac{2T}{(1 - r)^2 + \sqrt{(1 - r)^4 + 4T^2r^2}} \quad (4.2)
\]

The values of \(r\) and \(t\) have been determined for virgin and gamma irradiated PMMA, after substituting the recorded values of \(T\) and \(R\) in the above equations, followed by the iterative process, as explained earlier in Chapter 2, Section 2.3.1. These values of \(r\) and \(t\) were finally used to determine the various optical parameters like absorption coefficient, optical energy gap and refractive index of virgin as well as gamma irradiated samples of PMMA.

**i) Absorption Coefficient**

The values of absorption coefficient \((\alpha)\), deduced from the values of transmittance \((t)\), in the light of the equation 3.2 (Chapter 3, Section 3.1.1), for virgin and gamma irradiated PMMA samples, have been presented in figure 4.3, as a function of wavelength. This figure clearly indicates the presence of two peaks in the wavelength region \(\sim 275-375\) nm arising due to \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transitions in the absorption behaviour of virgin PMMA. At the dose of 400 kGy these peaks get broadened with a reduction in their intensities while at the dose of 800 kGy these peaks have completely disappeared. In addition, the continuous red shift in the absorption edge with increasing gamma dose is clearly observable from the figure.
Figure 4.3: Absorption spectra of virgin and gamma irradiated PMMA polymer.
ii) Optical Energy Gap

In order to determine the optical energy gap ($E_{\text{OPT}}$) of virgin and gamma irradiated samples of PMMA, the absorption data (figure 4.3) corresponding to the fundamental absorption edge as a function of wavelength ($\lambda$) have been considered [El-Shahawy 1997; Fink 2004; Migahed & Zidan 2006; Sharma et al. 2007] and plotted in the form of $(\alpha h\nu)^{1/2}$ as a function of photon energy ($h\nu$). Figure 4.4 presents such plots for virgin and gamma irradiated samples of PMMA. From the intercepts of these plots on $h\nu$ axis, the values of optical energy gap have been determined in the light of Tauc’s relation [Tauc 1974; Fink 2004] and are presented along with their standard errors in Table 4.1. The table clearly depicts that the optical energy gap of PMMA decreases from 3.17 eV in virgin sample to 2.80 eV after gamma irradiation to the dose 800 kGy.

iii) Refractive Index

The refractive index ($n$) values for virgin and gamma irradiated PMMA samples have been determined at different wavelengths using the expression (3.5), as already presented in Chapter 3, Section 3.1.1 and reproduced here again for continuity

$$n = \left[\frac{4r}{(r-1)^2-K^2}\right]^{1/2} - \frac{r+1}{r-1} \quad (4.3)$$

The variation of the refractive index as a function of wavelength has been presented in Figure 4.5. From this figure, it is clear that the values of refractive index increase gradually with the increase in gamma dose. These values at $\lambda = 632$ nm are presented in Table 4.1 with their standard errors.

The induced changes in optical behaviour of PMMA as a result of gamma
Figure 4.4: Plots of $(\alpha h\nu)^{1/2}$ versus energy $(h\nu)$ to determine the optical energy gap for virgin and gamma irradiated PMMA samples.

Figure 4.5: Refractive index behaviour of virgin and gamma irradiated PMMA polymer with respect to wavelength at different doses.
irradiation can be explained on the basis of the fact that the interaction of these radiations with the polymeric material leads to breaking of polymeric chains, formation of free radicals, escape of low molecular weight volatile species, trapping of high molecular weight fragments, etc. within the polymer matrix [Chapiro 1962; Ichikawa & Yoshida 1990; Rosenberg et al. 1992; Darraud-Taupiac at al. 1997; El- Shahawy 1997; Lee 1999; Sinha et al. 2001; Saad et al. 2005; Sagan 2007]. All such processes are governed simultaneously as a consequence of irradiation and lead to the formation of disordered structure with extended localized states [Rizzatti 1995; Fink 2004; Winder & Sariciftci 2004; Enemchukwu 2005], responsible for the observed changes in the optical behaviour of PMMA as a result of gamma irradiation.

Table 3.1: The various optical parameters (optical energy gap and refractive index) for gamma irradiated PMMA.

<table>
<thead>
<tr>
<th>Gamma Dose (kGy)</th>
<th>$E_{OPT}$ (eV)</th>
<th>Refractive index ($\lambda = 632$ nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>3.17 ± 0.01</td>
<td>1.54 ± 0.02</td>
</tr>
<tr>
<td>400</td>
<td>2.95 ± 0.02</td>
<td>1.72 ± 0.01</td>
</tr>
<tr>
<td>800</td>
<td>2.80 ± 0.01</td>
<td>1.88 ± 0.02</td>
</tr>
</tbody>
</table>

4.2 THERMAL STUDIES

Figure 4.6 presents the TGA thermogram for virgin PMMA while the corresponding DTG thermogram, deduced by differentiating the TGA data, has been presented in figure 4.7. These thermograms after irradiating PMMA at different gamma doses are presented in figures 4.8 and 4.9 respectively.

Figure 4.6 clearly indicates that the major degradation of virgin PMMA initiates at ~ 390°C and continues upto a temperature of ~ 460°C. The same is quite apparent
Figure 4.6: TGA plot of virgin PMMA.

Figure 4.7: DTG plot of virgin PMMA.
Figure 4.8: TGA thermograms of virgin and gamma irradiated PMMA at different doses.

Figure 4.9: DTG thermograms of virgin and gamma irradiated PMMA at different doses.
from the DTG thermogram (figure 4.7) with the appearance of a major peak in this range of temperature. Figure 4.8 clearly depicts that after irradiation to gamma rays at 800 kGy, this degradation step shifts from ~390°C (virgin sample of PMMA) to a lower temperature i.e. at 346°C, which further reduces to ~260°C at higher gamma doses, without any appreciable change in the final temperature up to which the degradation occurs. The same is confirmed from the respective DTG thermograms also (figure 4.8) through the observed broadening of the respective peaks. Such behaviour clearly indicates that the temperature range of the degradation step broadens continuously with the increasing gamma dose. Thus, there is a clear cut indication that the thermal stability of PMMA decreases continuously with increase in gamma dose. The same is further confirmed by the kinetic analysis.

Kinetic Analysis
From the TGA thermograms (figure 4.8) various kinetic parameters like activation energy and frequency factor related to the thermal degradation process were determined for the virgin and gamma irradiated samples of PMMA following the Horowitz –Metzger method [Kalsi et al 1995; Rizzatti et al 2001; Ferriol 2003; Mallikarjun 2004; Zaki 2008; Singh et al 2009].

a) Activation energy
The activation energies of virgin and gamma irradiated samples of PMMA corresponding to the main step of degradation process have been evaluated using the expression (3.6) as already mentioned in Chapter 3, Section 3.1.2, reproduced below for continuity

\[ \ln \left( \frac{w_o - w_f}{w - w_f} \right) = \frac{E_a \theta}{R} \frac{1}{T^2} \]  \hspace{1cm} (4.4)
In the light of this equation, the plots between $\ln(\ln(W_0 - W_f / W - W_f))$ and $\theta$ for virgin and gamma irradiated samples of PMMA have been deduced and presented in figure 4.10. The values of activation energy $E_a$, as determined from the slope of the linear fitted lines (Chapter 3, Section 3.1.2) from these plots are tabulated in Table 4.2 along with their standard errors. A clear cut reduction in the values of activation energy with the increasing gamma irradiation dose has been clearly observed from the table.

b) Frequency factor

The values of frequency factor for the virgin and the gamma irradiated samples of PMMA have been determined by substituting the respective values of activation energies in the expression (3.7) as already described in Chapter 3, Section 3.1.2, reproduced below

$$1 = -\frac{A R \beta}{E_a} x e^{(E_a / R \theta)} \ldots \ldots \ldots \ldots \ldots (4.5)$$

These values of frequency factor, so determined for virgin as well as gamma irradiated samples of PMMA have been enlisted in Table 4.2. A decreasing trend has been observed in the values of the frequency factor with the increasing gamma dose.

The observed decrease in the values of kinetic parameters i.e. activation energy and frequency factor after gamma irradiation may be attributed to the reorganization of molecular states, possible evaporation of volatile side groups, reduced packing densities etc resulting in a significant reduction of molecular weight of the polymeric sample. Such a reduction in the molecular weight of the sample, in turn, causes a decrease in the thermal stability of the polymer as an effect of gamma irradiation [Kalsi et al 1995; Nouh et al 2004; Anslyn 2006; Sousa et al 2007].

Corresponding to the decrease in values of activation energy, the values of frequency factor also decreases. Such a reduction in the values of frequency factor...
Figure 4.10: Plots of \(\ln(\ln(W_o - W_t/W_t))\) vs \(\theta\) for virgin and gamma irradiated samples of PMMA.
signifies the reduced rate of reaction. This may be due to the possible destruction of some interstates as a result of decrement in the packing density which further decreases the reaction rate as an effect of gamma irradiation [Flynn 1966; Rizzatti et al 2001; Ferriol 2003; Mallikarjun 2004; Zaki 2008].

Table 4.2: The various kinetic parameters of thermal degradation (activation energy and frequency factor) for virgin and gamma irradiated PMMA.

<table>
<thead>
<tr>
<th>Gamma Dose (kGy)</th>
<th>Activation energy (kJ/mol)</th>
<th>Frequency factor (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>224 ± 2</td>
<td>(5.7± 0.02)x10(^{17})</td>
</tr>
<tr>
<td>800</td>
<td>164 ± 1</td>
<td>(5.3± 0.01)x10(^{11})</td>
</tr>
<tr>
<td>1200</td>
<td>131 ± 2</td>
<td>(5.1± 0.02)x10(^{9})</td>
</tr>
<tr>
<td>1600</td>
<td>92 ± 1</td>
<td>(4.7± 0.02)x10(^{6})</td>
</tr>
</tbody>
</table>

4.3 ELECTRICAL STUDIES

a) I-V Measurements

As already described in Chapter 1, Section 1.4, the bulk properties of the polymers can be suitably modified after irradiation to gamma rays. This section relates to the study of bulk conductivity behaviour of virgin and gamma irradiated samples of PMMA. For this purpose, the bulk I-V measurements were carried out in the voltage range 0-100V. Figure 4.11 presents the I-V plots, so obtained, for virgin and gamma irradiated samples of PMMA at various doses. It is clearly observable from the figure that for the virgin sample, the current is of the order of 10\(^{-11}\)A and remains almost independent of the applied voltage. A continuous increase in current for gamma irradiated samples, with increasing irradiation dose, is clearly evident from the figure.
Figure 4.11: Plots of current vs voltage for virgin and gamma irradiated PMMA at various doses.
b) DC Conductivity Behaviour

From these I-V measurements (figure 4.11), the resistance (R) offered by the virgin and gamma irradiated samples has been determined. From these values of R for virgin and gamma irradiated samples, the corresponding values of bulk conductivity ($\sigma_{\text{bulk}}$) have been deduced using the expression (2.30) already presented in Chapter 2, Section 2.5.1; reproduced below to maintain continuity [Blythe & Bloor 2005]

$$\sigma_{\text{bulk}} = \frac{d}{R A}$$  \hspace{1cm} (4.6)

where d is the thickness of the sample and A is the area of the electrode. The values of bulk conductivity, so obtained, for virgin and gamma irradiated samples of PMMA are enlisted in Table 4.3.

Table 4.3 clearly indicates a significant increase in the bulk conductivity of gamma irradiated PMMA samples with increasing gamma dose. The observed increase in bulk conductivity, as a consequence of gamma irradiation, may be attributed to chain scissioning leading to the dissociation of various bonds, formation of radicals etc in the host polymer matrix. This, in turn, enhances the molecular mobility [Radwan 2007; Nanda et al. 2011] and the number of free charge carriers resulting in the increased conductivity as an effect of gamma irradiation.
### Table 4.3: Values of bulk conductivity for virgin and gamma irradiated samples of PMMA.

<table>
<thead>
<tr>
<th>Gamma Dose (kGy)</th>
<th>Bulk conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>$(2.96 \pm 0.01) \times 10^{-11}$</td>
</tr>
<tr>
<td>400</td>
<td>$(5.64 \pm 0.02) \times 10^{-11}$</td>
</tr>
<tr>
<td>800</td>
<td>$(1.90 \pm 0.01) \times 10^{-10}$</td>
</tr>
<tr>
<td>1200</td>
<td>$(4.48 \pm 0.02) \times 10^{-10}$</td>
</tr>
<tr>
<td>1600</td>
<td>$(5.43 \pm 0.01) \times 10^{-10}$</td>
</tr>
</tbody>
</table>

### 4.4 STRUCTURAL BEHAVIOUR

**a) FTIR Analysis**

Figure 4.12 presents the FTIR spectra of virgin and gamma irradiated samples of PMMA at various doses. The virgin spectrum exhibits various weak and strong peaks at different wavenumbers. The major absorption peak at 1732 cm\(^{-1}\) corresponds to the C=O stretching vibrations owing to free carbonyl group present in PMMA. The peaks lying in the region 1060-1270 cm\(^{-1}\) represent C-O-C stretching vibrations. In particular, the peaks at 1066, 1150 cm\(^{-1}\) exhibit symmetric C-O-C stretching, while those at 1190, 1242, 1270 cm\(^{-1}\) correspond to antisymmetric C-O-C stretching mode. The smaller peaks in the wavenumber range 910-989 cm\(^{-1}\) show O-CH\(_3\) rocking, while the peak at 842 cm\(^{-1}\) is due to CH\(_2\) rocking vibrations. The peak at 752 cm\(^{-1}\) may be attributed to C-O bending. All these peaks [Pavia et al. 1994; Campbell et al. 2000; Choi 2001; Anslyn 2006] confirm the chemical structure of PMMA, as described earlier in Chapter 3, Section 3.1.4.
Figure 4.12: FTIR spectra of virgin and gamma irradiated PMMA at various doses.
The spectrum of gamma irradiated PMMA at the dose 400 kGy shows a reduction in the intensities of the peaks lying in the region 700-1000 cm\(^{-1}\) but the peaks corresponding to the region 1100-1900 cm\(^{-1}\) show no major changes. Further, from the spectrum corresponding to 800 kGy, it is clearly observable that all the peaks in the wavenumber region 700-1000 cm\(^{-1}\) start disappearing, while the peaks lying in the region 1000-1300 cm\(^{-1}\) are observed with reduced intensities. No considerable change is observed in the peaks lying in the region 1400-1900 cm\(^{-1}\). All these changes may be due to the structural rearrangements such as chain scissioning, free radical formation, etc. taking place inside the polymer matrix as a consequence of gamma irradiation.

**b) Raman Analysis**

Figure 4.13 presents the recorded Raman spectrum (Ar\(^+\) laser with \(\lambda = 488\) nm) for virgin and gamma irradiated samples of PMMA at various doses. The spectrum corresponding to virgin PMMA clearly indicates the presence of various peaks and bands, as described earlier in Chapter 3, Section 3.1.4, reproduced below for the sake of continuity.

The most prominent band originated in the wavenumber range ~2800-3100 cm\(^{-1}\) is due to C–H stretching vibrations. The other observed bands are evident at 590, 815, 860, 980, 1454, 1727 cm\(^{-1}\). The band at 590 cm\(^{-1}\) may be assigned to the vibrational stretching of (C–COO) while the bands at 815 and 860 cm\(^{-1}\) arise due to the stretching vibrations of (CH\(_2\)). The band at 980 cm\(^{-1}\) is due to (C–C) skeletal mode whereas the band present at 1454 cm\(^{-1}\) is due to C-H bending and the band at ~1727 cm\(^{-1}\) may be due to O-CH\(_3\) vibrations. All these bands confirm the bonding structure of PMMA [Smith et al 2005; Thomas et al 2008].

The induced structural changes in PMMA after gamma irradiation are clearly depicted from the recorded spectra presented in figure 4.13. It is clearly observable
Figure 4.13: Raman spectra of virgin and gamma irradiated PMMA at various doses.
from figure 4.13 that at the dose of 400 kGy, the intensity of the peaks lying in the wavenumber region ~2800-3100 cm\(^{-1}\) is reduced, while a prominent peak in the region ~1200-1600 cm\(^{-1}\) with two small conjugated peaks appear. The peaks in the region ~700-1000 cm\(^{-1}\) have disappeared completely. The spectrum of PMMA sample irradiated at the dose of 800 kGy clearly shows the disappearance of all the peaks in the region ~1200-2400 cm\(^{-1}\) converting this region in the form of a broad band. All such changes in the Raman spectra of gamma irradiated samples of PMMA confirm the induced structural changes as an effect of gamma irradiation.

The structural changes, revealed through FTIR and Raman spectroscopy, as discussed above, are responsible for the induced modifications in optical, thermal and electrical properties of gamma irradiated PMMA.
4.5 CONCLUSION

It can be concluded that a considerable change has occurred in the optical parameters like absorbance, optical energy gap and refractive index of PMMA polymer as a result of gamma irradiation. A clear cut reduction in the optical energy gap from 3.17 eV for virgin to 2.80 eV for the sample irradiated at 800 kGy has been noticed. In addition, the refractive index of gamma irradiated samples of PMMA has been found to increase from 1.54 (virgin) to 1.88 at the dose of 800 kGy at \( \lambda = 632 \text{ nm} \).

Regarding the thermal behaviour of PMMA, the related TGA thermograms indicate a substantial decrease in thermal stability of this polymer as an effect of gamma irradiation. The same is confirmed from the sharp decrease in the values of activation energy from 224 kJ/mol for virgin sample to 92 kJ/mol for the gamma irradiated sample at the dose of 1600 kGy. Further, a considerable increase in electrical conductivity by \(-2\) orders of magnitude at the dose of 1600 kGy as compared to virgin PMMA has been observed.

All such changes may be attributed to the fact that the gamma irradiation in polymers leads to chain scissioning resulting in the formation of free radicals, free charge carriers etc. As a consequence, the formation of disordered structure with extended localized states may occur in the host polymer matrix. Such structural changes produced in the gamma irradiated samples of PMMA have also been confirmed from FTIR and Raman spectroscopy. Finally, it can be inferred that the bulk properties of PMMA may be tailored as per requirement through gamma irradiation leading to its applications as material for specific requirements.