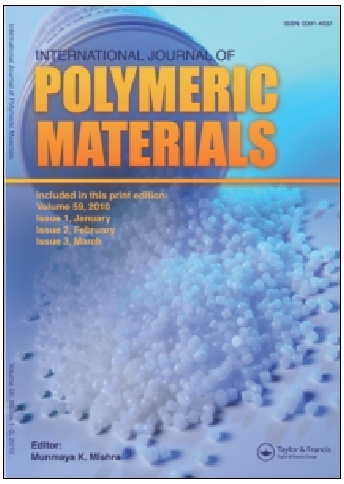

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Optical Energy Estimation of Irradiated Polypropylene

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The optical absorption has been studied under exposure to gamma radiation. Thin films of polypropylene were irradiated with a ^{60}*Co source and doses ranged up to 6 kGy. Analysis of the optical absorption spectra indicated that both direct and indirect electron transitions take place in the polymer. The observed optical energy gap* (E_{opt}) *and energy gap-tail* (ΔE) *for irradiated films were determined from the measured absorption spectra. The average values of* (E_{opt}) *and* (ΔE) *are 5.85 eV and 0.5 eV, respectively. There is no detectable change in the optical energy gaps and tails under the applied gamma-ray doses.*

Keywords: absorption spectra, crosslinking, dose, gamma radiation, gap-tails, optical energy gap, polypropylene

INTRODUCTION

The technological significance of irradiation of polymers appears in several industrial applications: microlithography, aerospace, medical sterilization, biomedical and pharmaceutical items, fabrication of integrated circuits, polymer coatings on metals and substrates, and other high-technology applications [1–3]. Irradiation induces modification of polymers properties, and hence a fundamental understanding of the physics and chemistry involved in irradiation processes occurring in polymers is essential to many industries [4–6].

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When polymeric materials are exposed to ionizing radiation produced by radioactive sources or linear accelerators, their physical and mechanical properties are altered in different ways. For example, the chain backbones may undergo scission and crosslinking. Scission leads to a reduction in the molecular weight, whereas crosslinking increases it.

It was shown by Charlesby [1] and by Dole [7] that polyethylene crosslinked when irradiated by high energy ionizing radiation. The most observed dramatic effect was improvement in thermal behavior and increasing tensile strength. Under long periods of irradiation the polymer becomes brittle. The slow processes of crosslinking occurring step by step depend on the amount and duration of irradiation dose. A high dose irradiation is needed in order to get enough crosslinking. Investigations of the extent of crosslinking in crystalline polymeric samples showed that crosslinking occurs predominantly in the amorphous regions where radiation is absorbed randomly in the polymer. Crosslinking within the crystallites may occur by migration to crystal surfaces or at imperfection. The concentration of crosslinks in the amorphous regions provides an explanation of the memory effect obtained in irradiated polyethylene [8]. Chain scission occurs in parallel with crosslinking in all polymers. Main chain scission produces a deterioration in physical properties. The extent of both crosslinking and chain scission processes depends on the chemical nature and the structure of the material [8–10].

Absorption of high-energy radiation by polymers produces excitations and ionization. It creates ionized species through intra or intermolecular migration of energy or reactive species such as free radical ions. The molecular changes occurring in polymers as a result of irradiation are: chain crosslinking leading to an increase in molecular weight and formation of a macroscopic network, and chain scission causing a decrease in molecular weight, thus changing polymer physical and mechanical properties as tensile strength, crystal morphology, molecular orientation, crystallinity, crosslinks density, and dielectric constants. The rates and nature of chemical reactions in irradiated polymers are dependent on both chemical and physical factors as the rate of reaction and temperature. Chou et al. [11] observed transition loses in UV-spectrum that increase with gamma-ray dose. Zihlif [12] observed severe deterioration and bulk destruction of POM polymer exposed to electron beam (30 kV). Tincer and Cimen [13] reported that UV-irradiation of HDPE undergoes oxidative degradation. Patel and Keller [10] investigated the effect of γ-rays on the crystallinity and fold surface of grown PE single crystals.

This article deals with the effect of γ-radiation on some optical properties of semicrystalline polypropylene (PP), as absorption coefficient and optical energy gap, as a function of radiation dose.

EXPERIMENTAL

Thin films of polypropylene of ($\sim 7\,\mu$m) thickness were used in the UV-optical measurements. Initially, the polymer was irradiated with γ-rays obtained from ^{60}Co source with doses up to 6 kGy. The irradiation and measurements were carried out at room temperature and at atmospheric pressure.

RESULTS AND DISCUSSION

The optical absorbance spectra of irradiated films were collected at room temperature in the wavelength range of 200–800 nm with UV-visible spectrophotometer. The absorption coefficient $\alpha(\omega)$ was calculated from the absorbance (A), after correction for reflection, using the relation:

$$I = I_o \exp(-\alpha x)x \tag{1}$$

Hence

$$\alpha(\omega) = \frac{2.303}{x}\log\left(\frac{I}{I_o}\right) = \frac{2.303}{x}A(\omega) \tag{2}$$

where I_o and I are incident and transmitted intensities, respectively, and x is the specimen thickness in cm. The absorption coefficient varies with photon energy ($\hbar\omega$) for electron direct transition according to the equation:

$$\begin{aligned} \alpha(\omega)\hbar\omega &= \beta(\hbar\omega - E_{opt})^r \quad \text{for } \hbar\omega > E_{opt} \\ &= 0 \quad \text{for } \hbar\omega < E_{opt} \end{aligned} \tag{3}$$

where β is a constant equals to $(4\pi\sigma_o/nc\,\Delta E)$, σ_o is the d.c. conductivity and ΔE is the tail of energy band-gap, and r values determine the allowed direct and indirect transitions [14–16].

Figure 1 shows the absorption coefficient spectrum $\alpha(\nu)$ for irradiated polypropylene specimens with γ-dose of 6 kGy. Figure 2 shows the parameter $(\alpha h\nu)^2$ plotted versus photon energy ($h\nu$) in accordance to Eq. (3). The best straight line I with the exponent $r=2$ indicates that the electron transitions for irradiated PP film are direct in k-space, whereas the line II indicates the indirect electron transition from

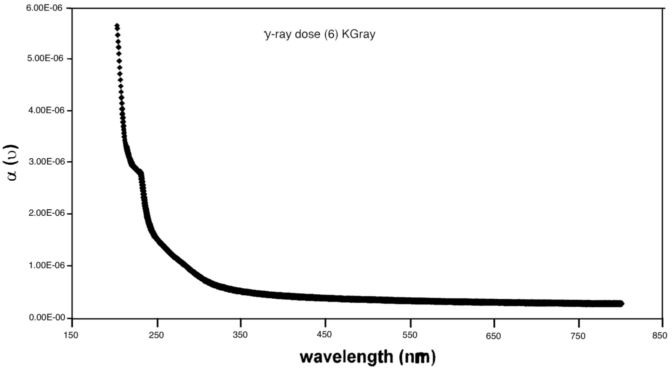

FIGURE 1 The optical absorption coefficient versus the wavelength for irradiated thin film of polypropylene with γ-dose (6 kGy).

band-to-band. The values of the optical energy gap listed in Table 1 for seven PP films at different γ-doses (from 0.25 to 6 kGy) in direct and indirect electron transitions. It can be noticed from the table that the values of the optical energy gap are almost near a value 5.85 ± 0.1 eV for direct transitions, and 5.13 ± 0.1 for indirect transitions. This means that the net irradiation effect on electronic and optical properties of irradiated crystalline polypropylene is not so effective or pronounced inspite of that ionizing radiation causes cross-linking and chain scission in irradiated polymers [1–7].

In the present study two types of radiations were imposed: initially γ-rays with doses upto 6 kGy and later UV-visible rays with

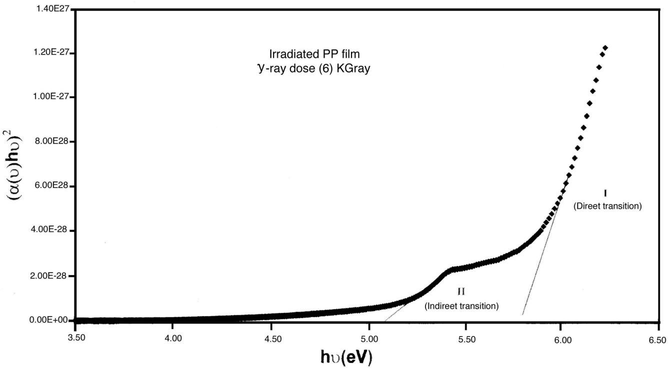

FIGURE 2 The product of optical absorption coefficient and photon energy (hν) versus photon energy for irradiated PP film (6 kGy).

TABLE 1 Irradiated Thin Film of Polypropylene

Sample	Dose (Gy)	E_{opt} (eV) Direct transition	E_{opt} (eV) Indirect transition
1	250	5.88	5.11
2	500	5.89	5.16
3	1000	5.87	5.15
4	1500	5.82	5.15
5	2000	5.87	5.13
6	3000	5.85	5.11
7	6000	5.77	5.12

wavelength of range 200 to 800 nm. Polypropylene has a relatively high degree of crystallinity, where the crystalline regions are much larger than the amorphous ones. It is reported by Sangster [8] that investigations of the extent of γ-ray crosslinking in samples covering a range of crystallinities showed that crosslinking occurs predominantly in the amorphous regions. Also he reported that a memory effect could be obtained in irradiated polyethylene. So relying on these ideas, the undetectable effect of γ-rays on the crystalline PP samples can be explained as: the γ-irradiation leads to small crosslinks concentration in amorphous regions, and by subsequent warming by UV-radiation the chemical nature of the amorphous regions pull back or relief into its original shape as memory effect. Thus the two effects of γ-ray and UV-visible radiations work opposite to each other, and hence the net irradiation process occurring in PP films does not affect or change the optical energy gap as shown in Table 1.

At low absorption levels, in the range of $1\text{–}10^4\,\text{cm}^{-1}$, the absorption coefficient $\alpha(\omega)$ is described by Urbach formula [16]:

$$\alpha(\omega) = \alpha_0 \exp \hbar\omega/\Delta E \tag{4}$$

where α_0 is a constant and (ΔE) is an energy that is interpreted as the tail-width of localized states [17] in the forbidden band gap (in the sub-gap region). Urbach plot was obtained by plotting ln α versus photon energy ($h\nu$) according to Eq. (4). Extrapolating the Urbach plot to low absorption levels gives values of (ΔE) as listed in Table 1. The average value of the energy tail is about 0.5 eV.

CONCLUSION

Polypropylene thin films were exposed to γ-rays radiation whose effect on optical properties is investigated. Two conclusions can be drawn from the results obtained:

1. The effect of gamma radiation on the optical energy gap of polypropylene films is not pronounced. No detectable changes in the physical structure are induced within the imposed doses level.
2. The determined values of optical energy gap and energy tails are about 5.85 eV and 0.5 eV, respectively.

REFERENCES

[1] Charlesby, A. (1960). *Atomic Radiation and Polymers* (Pergamon: New York); *Radiat. Phys. Chem.* **10**, 177 (1977).
[2] Reichmanis, E. and Donnel, J. O., "Irradiation of Polymeric Materials," and "The Effect of Radiation on High-Technology Polymers," ACS Symposium Series **381** (1983), **527** (1993), Washington, DC.
[3] Tabata, Y., *Radiat. Phys. Chem.* **14**, 235 (1979).
[4] Muisenser, P., Sikder, A., and Cassel, A., *J. Mater. Res.* **17**, 2507 (2002).
[5] Lue, K.-P., Lee, S., and Han, C., *J. Mater. Res.* **17**, 2260 (2002).
[6] Siegmann, A. and Shkolnik, S., *Polym. Eng. Sci.* **25**, 318 (1985).
[7] Dole, M. (1973). *The Radiation Chemistry of Macromolecules*, Vol. 2, Academic Press, New York.
[8] Sangster, D. F. (1993). In *Irradiation of Polymeric Materials*. E. Reichmanis, Eds., ACS Symp. Series, 527, Chapter 7, p. 97.
[9] Delides, C. and Shepherd, I., *Radiat. Chem. Phys.* **10**, 379 (1977).
[10] Patel, G. and Keller, A., *J. Polym. Sci. Polym. Phys. Edition* **13**, 303 (1975).
[11] Chou, K., Han, C., and Lee, S., *J. Polym. Sci. Polym. Phys.* **38**, 659 (2000).
[12] Zihlif, A., *Mater. Chem. Phys.* **13**, 21 (1985).
[13] Tincer, T. and Cimen, I., *Polym. Sci. Eng.* **26**, 479 (1986).
[14] Davis, E. and Mott, N., *Phil. Mag.* **22**, 903 (1970).
[15] Saq'an, S., Ayesh, A., and Zihlif, A., *Optical Materials* **24**, 629 (2004).
[16] Urbach, F., *Phys. Rev.* **92**, 1324 (1953).
[17] Elliott, S. (1998). *The Physics and Chemistry of Solids*, John Wiley, Chichester, UK, p. 392.