Gamma irradiation effect on the optical properties and refractive index dispersion of dye doped polystyrene films

Tariq J. ALWAN

Al-Mustansiriyah University, College of Education, Physics Department, Baghdad-IRAQ
e-mail: tariqjaffer2000@yahoo.com

Abstract

In this work, we have studied the effect of the gamma irradiation on the optical properties and optical constants of Polystyrene doped by methylene blue (mb) with thickness in the range 0.11 + 5 mm. The samples have been investigated via transmittance and reflectance spectra, and characterized in the wavelength range 300–900 nm. The optical band gap E_g was determined while the optical absorption spectra showed that the absorption mechanism is an indirect allowed transition, which found that optical energy gap E_g decreases after irradiation. The optical constants (refractive index, extinction coefficient, and real and imaginary parts of the dielectric constant) showed clear changes with irradiation. The oscillator energy E_o, dispersion energy E_d and other parameters have been determined by the Wemple-DiDomenico method. The most significant result of the present study is to determine the optical constants and optical band gap of the film.

Key Words: Polymer, polystyrene, gamma irradiation, optical constants, optical band gap

1. Introduction

Research in polymer science continues to mushroom, producing a plethora of new elastomers, plastics, adhesives, coatings, and fibers. All of this new information is gradually being codified and unified with important new theories about the interrelationships among polymer structure, physical properties, and useful behavior. Thus the ideas of thermodynamics, kinetics, and polymer chain structure work together to strengthen the field of polymer science [1].

Irradiation in polymers destroys the initial structure by way of cross linking, free radical formation, irreversible bond cleavages, etc., resulting in the fragmentation of molecules and formation of saturated and unsaturated groups. All these processes introduce so-called defects inside the material that are responsible for change in the optical, electrical, mechanical and chemical properties of the material [2].

Polystyrene (PS) is an amorphous polymer with bulky side groups.

General purposes of polystyrene are hard, rigid, and transparent at room temperature and glass like thermoplastic material which can be soften and distort under heat. It is soluble in aromatic hydrocarbon solvents, cyclohexane and chlorinated hydrocarbons [3].

The effect of gamma radiation on the optical properties of PS thin films doped by anthraquinone copolymer has been studied by Al-Ramadhann [4].

Many researchers have succeeded in preparing PS films deposited on various substrates such as glass or silicon wafer [5, 6], in the interest of exploring the technological importance of film stability (e.g. toys and novelties, rigid packaging, refrigerator trays , boxes, cosmetic packs and costume jewelers, lighting diffusers, audio cassette and CD cases) [7]. Several dyed polymers blends containing chlorine have been investigated for possible use in γ-ray dosimetry in and electron beam facilities [8]. Other researchers have worked to modify the styrene ring to reduce or enhance radiation-induced discoloration. Such work is used to help in interpreting the behavior of polymeric scintillator exposed to gamma radiation [9]. While Kojima et al. have studied the response of alanine-polystyrene dosimeter at an absorbed dose of 5 kGy over the low temperature range 196-30 $^\circ$C [10].

The purpose of this paper is to report some of our results on the effect of gamma irradiation on optical constants of doped PS films with methylene blue (MB) dye. This is done in order to find an irradiation polymer that will result in enhancing optical properties. It has been suggested that PS films doped with such types of dye may be used as dosimeters.

2. Experimental

Polystyrene (PS) supplied by ICI with $M_w = 300,000$ g.mol^{-1}, Mw/Mn = 1.06 and 99.995% purity was used as the matrix. Chloroform (ChCl$_3$) of 99.998% purity, used as a solvent, was supplied by BDH (VWR) Chemicals Ltd., Poole, England. Methylene blue (MB), C$_{16}$H$_{18}$ClN$_3$S, $M_W = 319.85$ g.mol^{-1}, supplied by BDH (VWR), was used as dopant. PS grains of weight 0.27 g were dissolved in 5 ml of Chloroform (CHCl$_3$) to obtain solution of 5.4% wt./vol. Dopant was fabricated by dissolving MB in Chloroform of concentration 0.02 w/w. The mixture was mixed well by stirring for about 30 min., to obtain a homogenous solution. 5 ml of the prepared solution was transferred into a clean cm diameter glass Petri dish and dried at temperature 50 $^\circ$C in oven for at least 2 hours, then left to cool slowly to room temperature. The dried films removed easily using tweezers. Other similar films were cast in order to ensure dried samples without bubbles and thermal damage. The thicknesses of prepared films were measured between 0.11 mm to 0.5 mm) by using digital vernier caliper.

^{60}Co served as the irradiation source. For each dose the film samples were placed simultaneously at the centre of the chamber surrounded for radiation equilibrium purposes. Samples were irradiated with various doses, ranging 1000 and 2000 Rad, at room temperature.

The measurements of absorbance and transmittance spectra in the wavelength range 300–900 nm were carried out by using a UV-160A UV-VIS Recording Spectrophotometer.

The optical absorption and reflectance spectra were analyzed to determine optical constants such as refractive index n, extinction coefficient k, and absorption coefficient α. Analysis of the absorption coefficient was also carried out to determine the optical band gap and nature of transitions.

3. Results and discussion

3.1. Optical energy gap

The relation between the optical band gap, absorption coefficient and energy hv of the incident photon is given by [11, 12]:

$$\alpha h\nu = B(h\nu - E_g)^r \tag{1}$$

where E_g is the optical energy gap; α is the absorption coefficient; B is a constant; and r is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption. $r = 1/2$ for allowed direct transition, $r = 3/2$ for forbidden direct transition and $r = 3$ for forbidden indirect transition, and $r = 2$ refers to indirect allowed transitions. The absorption coefficient for direct transition takes the values from 10^4 to 10^5 cm^{-1}, while the absorption coefficient for indirect transition takes the values from 10 to 10^3 cm^{-1}.

The present results were found to obey equation (1) with $r = 2$ for all films, which indicates indirect allowed transitions. Values of the absorption coefficient was taken between 10 to 10^3 cm^{-1}. And, $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ were plotted as functions of photon energy hv to determine the type of transition. The former, $(\alpha h\nu)^{1/2}$, yielded a linear dependence which describes the allowed indirect transition [11–13].

Figure 1 shows $(\alpha h\nu)^{1/2}$ as a function hv the calculation of optical energy gap of dyed PS sample for un-irradiated and irradiated films in different dose.
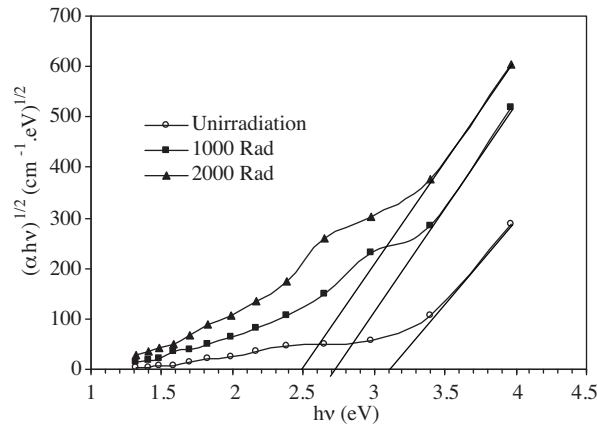

Figure 1. Variation of $(\alpha h\nu p^{1/2}$ as a function of $(h\nu)$ for dyed polystyrene films at different levels of irradiation.

The indirect allowed optical band gap can be evaluated from the linear plots of $(ahv)^{1/2}$ as a function of energy at different doses, as shown in Figure 1. Extrapolations of these plots to the point at which they cross the abscissa give the indirect allowed optical band gap. The plots show E_g decreases with increasing amounts of irradiation. It was found that E_g decreases from 3.1 eV for unradiated, to 2.5 eV for 2000 Rad. Further data is found in Table 1.

The decrease in the band gap energy with increasing dose may be attributed to an increase in structural disorder of the irradiated dyed Polystyrene. Irradiation of the dyed Polystyrene induces methylene blue, $C_{16}H_{18}ClN_3S$, causing the loss of Cl and induce the detachment of ions and unsaturated groups $(-C = C-)$. These contributed to the structural defects, which reduce the band gap with increasing dose [14, 15]. The decrease in E_g implies an increase in the conductivity of irradiated dyed Polystyrene [8, 14–16].

Table 1. Optical parameters of dyed polystyrenes at different Doses irradiation.

Dose	E_o (eV)	E_{Ed} (eV)	E_{Eg} (eV)	n_∞	λ_o, nm	S_o (m^{-2})	E_o/S_o (eVm^{-2})
0 Ra	4.62	3.82	3.	1.12	551.35	2.605×10^{-1}	1.77×10^{17}
1000 Rad	4.61	4.25	2.75	1.23	553.	2.34×10^{-1}	1.97×10^{17}
2000 Rad	4.58	5.06	2.	1.09	554.21	1.969×10^{-1}	2.32×10^{17}

3.2. Refractive index and dispersion

The transmittance, reflectance and absorption spectra of the films are shown in Figure 2.

The extinction coefficient can be calculated by the relation [17]

$$k = \frac{\alpha\lambda}{4\pi}, \tag{2}$$

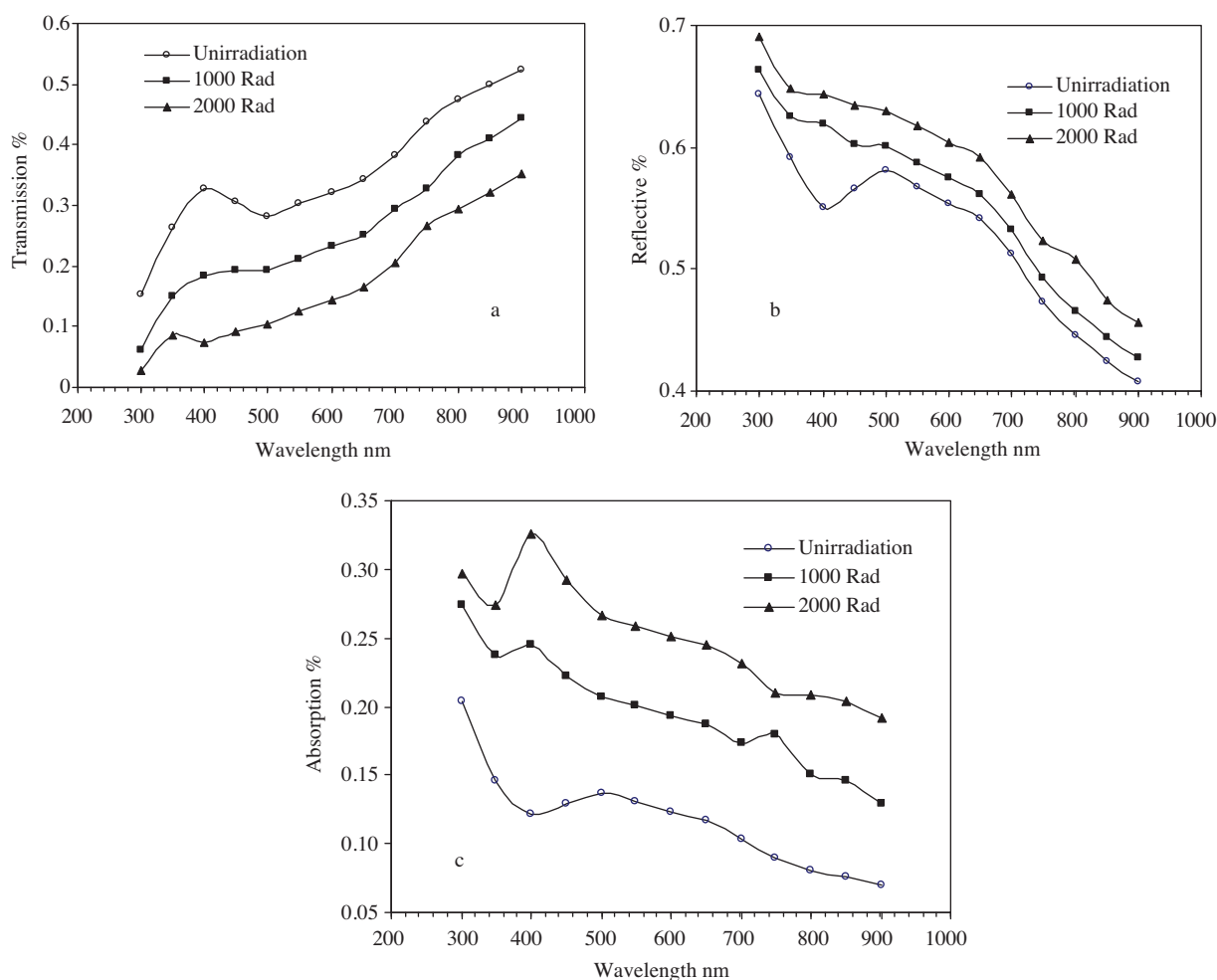where λ is the wavelength, α is the absorption coefficient.

Figure 2. The variation of (a) transmission in percent, (b) coefficient reflection and (c) absorption spectra with as a function of Wavelength, for dyed polystyrene films at different doses of irradiation.

The refractive index of the films was calculated by the following equation [17]:

$$n = \sqrt{\frac{4R}{(R-1)^2 - k^2} - \frac{(R-1)}{(R-1)}},$$ (3)

where R the reflectance and k the extinction coefficient.

Figure 3 shows the variation of refractive index n and extinction coefficient of dyed PS films, with wavelength for different irradiation doses. Figure 3 shows the refractive index increases with doses irradiation; indeed, n changes from 3.82 to 4.41 at $\lambda = 600$ nm, when doses irradiation increases from 0.0 to 2000 Rad. The dependence of extinction coefficient k on the wavelength is shown in Figure 3 for dyed PS samples. The extinction coefficient k exhibits clear changes with increasing doses; indeed, k changes from 1.23×10^{-6} to 2.51×10^{-6} at $\lambda = 600$ nm for increase in irradiation from 0.0 to 2000 Rad.
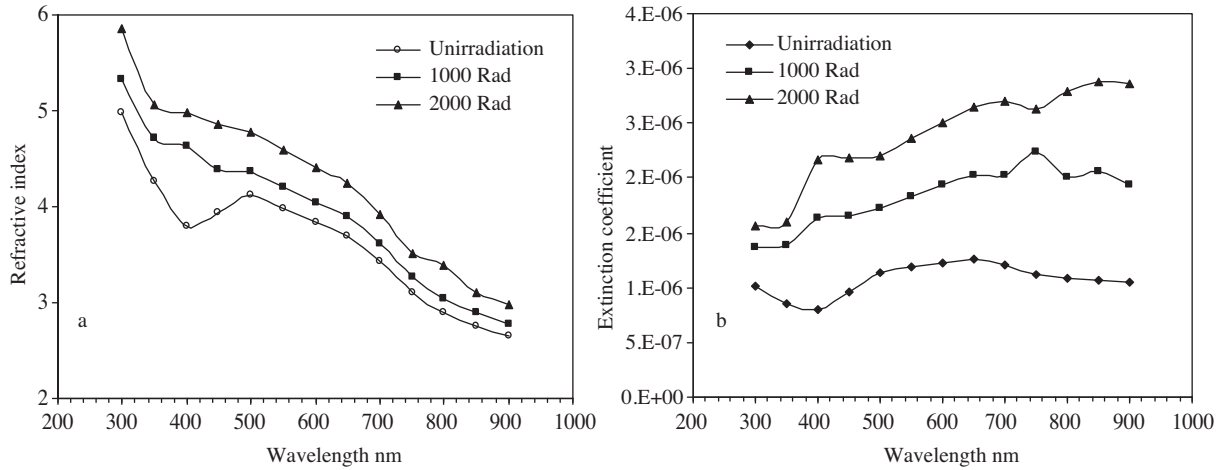

Figure 3. The variation of (a) index of refraction n and (b) extinction coefficient k as function of wavelength, for dyed polystyrene films at different doses of irradiation.

This change in refractive index and extinction coefficient with increasing irradiation is attributed to same reasons that were discussed for the change in the optical energy gap.

The refractive index dispersion of the thin film is expressed as per Didomenico [18]:

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2}$$ (4)

where n is the refractive index, h is Planck's constant, ν is the frequency, $h\nu$ is the photon energy, E_o is the average excitation energy for electronic transitions and E_d is the dispersion energy which is the measure of the strength of interband optical transitions. The dielectric response for transitions below the optical gap is described by this model. Values E_o and E_d were calculated from the slope and intercept on the vertical axis of plot of $1/(n^2 - 1)$ versus $(h\nu)^2$ in Figure 4 and with values given in the Table 1.

The refractive index can also be analyzed to determine the long wavelength refractive index n_∞ and average oscillator wave length λ_o and oscillator length strength S_o of the thin film. These values can be obtained by using the single term Sellmeier oscillator [19]:

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2$$ (5)

From Figure 5 we obtained n_∞ and λ_o values from the linear portion of $1/(n^2-1)$ versus λ^{-2}, and are given in the Table. Equation (4) can be rewritten as [20]

$$(n_\infty^2 = 1 + S_o\lambda_o^2) \tag{6}$$

$$n^2 - 1 = \frac{S_o\lambda_o^2}{1 - \lambda_o^2/\lambda^2} \tag{7}$$

The S_o value for the thin film was calculated and is given in Table 1. The value of E_o/S_o was found on order to 10^{17} eVm^2 for the films and this value is approximately the same order as that obtained by DiDomenico and Wemple [18] and Fahrettin Y. [21] for a number of materials.
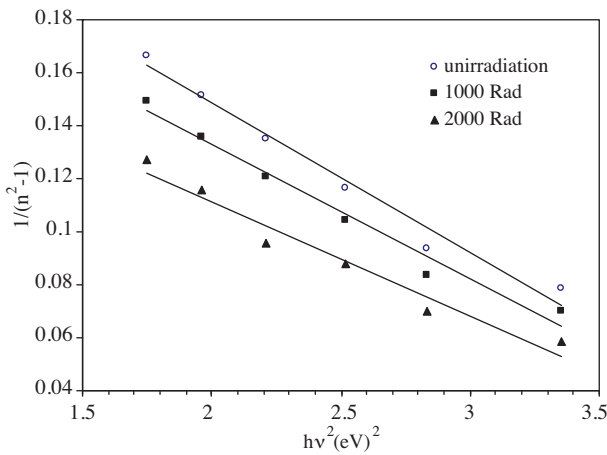

Figure 4. The variation of $(1/n^2\text{-}1)$ with hv^2 $(eV)^2$ of dyed polystyrene films different doses of irradiation.
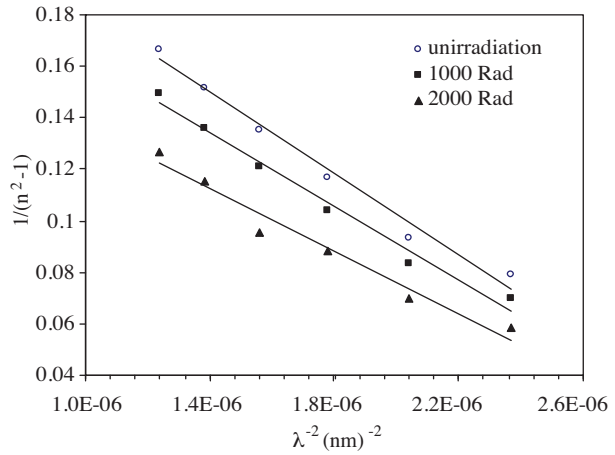
Figure 5. The variation of $(1/n^2\text{-}1)$ with λ^{-2} $(nm)^{-2}$ of dyed polystyrene films at different doses of irradiation.

3.3.   Complex dielectric function

The complex dielectric constant $(\varepsilon^* = \varepsilon_r + i\varepsilon_i)$ characterizes the optical properties of the solid material. The real and imaginary parts of dielectric constant of dyed PS films at different doses of irradiation were also determined by the following relations [22]:

$$\varepsilon_r = n^2 - k^2 \tag{8}$$

$$\varepsilon_i = 2nk \tag{9}$$

Figure 6 shows the real and imaginary parts of the dielectric constant increase with increasing wavelength.

It is concluded that the variation of ε_r mainly depends on n^2 because of small values of k^2, while ε_i mainly depends on the k values which are related to the variation of absorption coefficients.
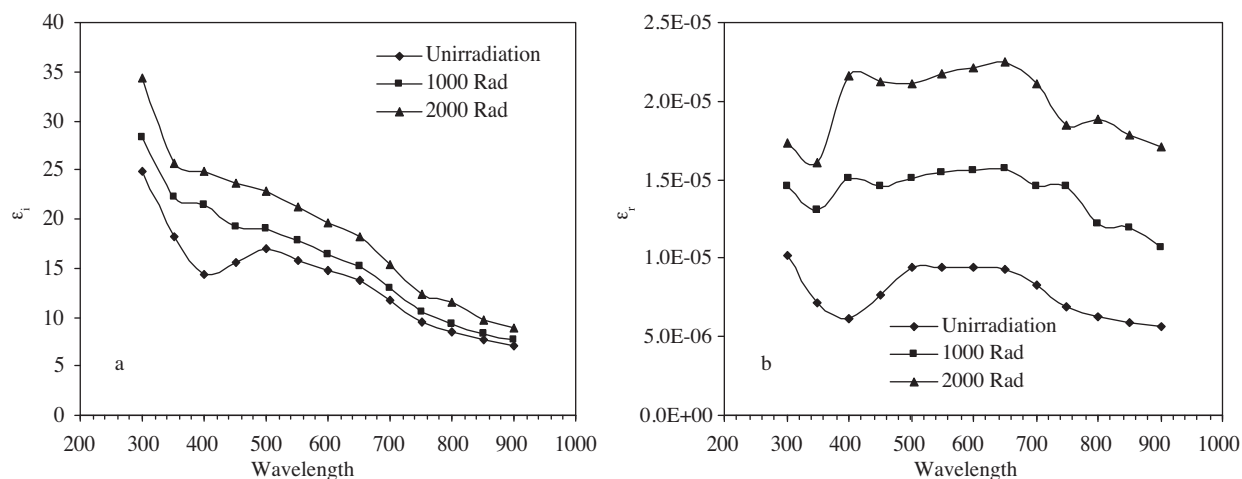
Figure 6. The variation of $\varepsilon_r, \varepsilon_i$ with wavelength (nm) of dyed polystyrene films at different doses of irradiation.

4. Conclusions

UV-VIS Spectrophotometric studies of non-irradiated and irradiated dyed PS films reveals the indirect allow band gap. The decrease in the energy band gaps with increasing dose may be attributed to an increase in structural disorder of the polymer blends when the dose is increased. At the same time, the energy band gap E_g was found to increase towards lower energy with increasing dose.

The optical constants such as the real n and imaginary k are parts of the complex refractive index, the real and imaginary parts of the dielectric constant were also determined. The oscillator energy E_o, the dispersion energy E_d and other parameters have been determined by the Wemple-DiDomenico method. The optical band gap was determined and the optical absorption spectra showed that the absorption mechanism is an indirect allowed transition.

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