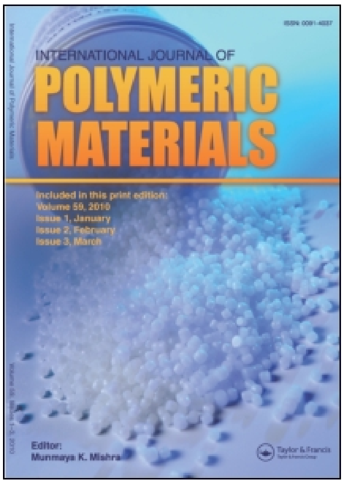


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Optical Properties of Gamma-Irradiated ST/MMA Copolymer

A. F. Mansour[a]; R. M. Ahmed[a]; A. H. Bassyouni[a]; G. M. Nasr[b]
[a] Physics Department, Faculty of Science, Zagazig University, Zagazig, Egypt [b] Physics Department, Faculty of Science, Cairo University, Giza, Egypt

To cite this Article Mansour, A. F. , Ahmed, R. M. , Bassyouni, A. H. and Nasr, G. M.(2007) 'Optical Properties of Gamma-Irradiated ST/MMA Copolymer', International Journal of Polymeric Materials, 56: 3, 207 — 226
To link to this Article: DOI: 10.1080/00914030600812467
URL: http://dx.doi.org/10.1080/00914030600812467

International Journal of Polymeric Materials, 56:207–226, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600812467

Optical Properties of Gamma-Irradiated ST/MMA Copolymer

A. F. Mansour
R. M. Ahmed
A. H. Bassyouni
Physics Department, Faculty of Science, Zagazig University,
Zagazig, Egypt

G. M. Nasr
Physics Department, Faculty of Science, Cairo University, Giza, Egypt

Copolymer films, with various concentrations of styrene (ST) and methyl-methacrylate (MMA), were prepared by thermal polymerization. The films were exposed to different doses of gamma rays up to 10 Mrad. The optical absorption α *and the optical parameters, including the energy band gap* E_g *and band tail width* E_w*, were estimated for the films before and after irradiation by gamma rays. Furthermore, the effect of UV radiation on un-irradiated films was investigated. The specular reflection of PS, PMMA, and copolymer has been measured. The refractive index and Cauchy's constants were evaluated for the films before and after irradiation by gamma rays. The structure–property behavior of the films was scrutinized by DSC and FT-IR.*

Keywords: absorption, copolymer, gamma ray, PMMA, PS, refractive index

INTRODUCTION

Recent research and development of polymer materials have been directed to blends or copolymers of different polymers in order to have new products having some of the desired properties of each component [1]. *PMMA* is characterized by its own crystal-clear light transparency, unexcelled weatherability and its outstanding optical properties combined with excellent environmental resistance. This recommended it for applications requiring light transmission and outdoor exposure. Similarly, *PS* is a versatile polymer whose principal characteristics

Received 11 April 2006; in final form 11 May 2006.

Address correspondence to Rania Mohammed Ahmed, Faculty of Science, Physics Department, Zagazig University, Zagazig, Egypt. E-mail: ranias_7@hotmail.com

include transparency, ease of coloring and processing, and low cost. The excellent optical properties of PS, including high refractive index, make it very useful in optical applications [2]. However, the stability of *PS* to outdoor weathering is poor; it turns yellow and crazes on exposure. Copolymerization of styrene and methylmethacrylate was considered with various concentrations to get the best product whose properties involve those of the individual homopolymers and overcome the weaknesses of both of them. The optical absorption α and the optical parameters E_g and E_w were evaluated for the films after irradiating by gamma rays with various doses and after exposure to direct and filtered *UV* radiation. The refractive index n and Cauchy's constants for the films were calculated before and after irradiating by gamma rays.

EXPERIMENTAL

Materials

From Aldrich, styrene (*ST*) and methyl methacrylate (*MMA*) were purchased to be used in this study. Pure-grade benzoyl peroxide (*BP*) supplied by *BDH* (England) was used as an initiator.

Preparation of the Samples

Films of pure *ST*, *MMA*, and copolymer of *ST*/*MMA* with different concentrations were prepared by thermal polymerization method. The polymerization was performed with *BP* as an initiator (1 wt%) and the mixture was poured into a glass mold. The mold was then immersed in water bath at 80°C for 4 h, then at 60°C for 72 h, followed by a final drying at 80°C for 4 h. The concentrations of the prepared copolymers of *ST*/*MMA* are 100/0, 10/90, 30/70, 50/50, 70/30, 90/10, 0/100 by volume.

UV Radiation

The films were exposed to *UV* and filtered radiation from a 200 W xenon arc lamp.

Reflection Measurements

Specular reflection spectra was recorded with *UV-Vis-NIR* spectrometer (UV-3101 PC) Shimadzu, 200–500 nm.

Absorption Spectra

The absorption spectra was recorded using Perkin-Elmer Lambda 4B spectrophotometer, 200–900 nm.

Gamma Irradiation

A ^{60}Co gamma source model GB150 type B, manufactured by the Atomic Energy Agency of Canada and located at the National Center for Radiation Research and Technology, A.E.A., was used for irradiating the samples at a dose rate of 9.23 kGy/h, and a constant temperature 30°C.

Differential Scanning Calorimeter (DSC)

The DSC thermograms were obtained using a Shimadzu DSC 50 differential scanning calorimeter, for films before and after irradiation by gamma rays with 10 Mrad. A heating rate of 5°C/min was utilized under nitrogen atmosphere, The recorded glass transition temperature was taken at the temperature range from room temperature up to 200°C.

IR Analysis

FT-IR Spectra was measured on Bruker vector 22 spectrometer in the wave number range of 400–4000 cm^{-1}.

RESULTS AND DISCUSSION

Analysis of ST/MMA Copolymer

Glass Transition Temperature T_g

Figure 1 shows the *DSC* scans ot the glass transition temperature of *ST/MMA* copolymer before and after they had been irradiated by gamma ray with 10 Mrad. *DSC* scans illustrate that T_g for *MMA*, *ST*, and 50/50 *ST/MMA* copolymer by volume are 111.49°C, 80.34°C, and 85.3°C, respectively. However, T_g for the same samples after irradiation by gamma radiation for 10 Mrad are 116.97°C, 99.75°C, and 98.84°C, respectively. The value of T_g for 50/50 *ST/MMA* copolymer indicates that it has average properties of the two homopolymers. On the other hand, the increment of the values of the T_g after irradiation can be attributed to crosslinking of chains of the polymer and thereby causes molecular motion restriction.

FT-IR

FT-IR measurements were carried out to detect the influence of gamma rays on *PS*, *PMMA*, and 50/50 *ST/MMA* copolymer. Figure 2 shows the *IR* spectra of all of them before and after irradiation by 10 Mrad of gamma rays. It is obvious that the intensity of the characteristic transmission bands of the films decreased after irradiation by gamma rays. The wave numbers corresponding to characteristic transmission bands for them are summarized in Table 1, which clarified the

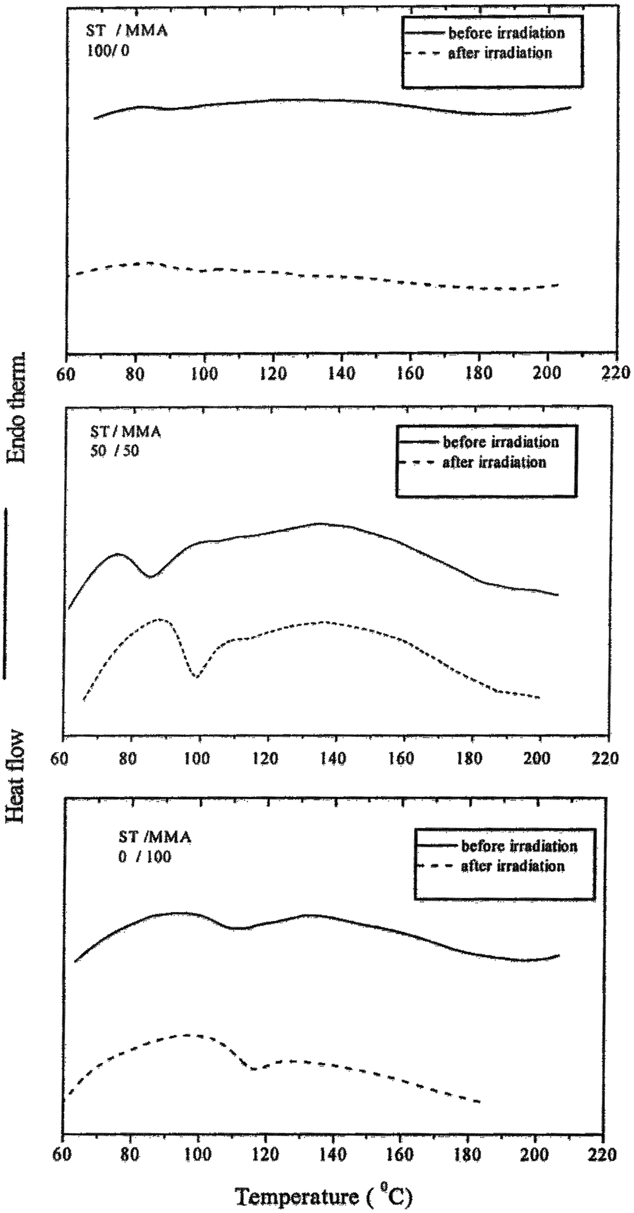


FIGURE 1 DSC of copolymer (ST/MMA) with different concentration before and after irradiation by 10 Mrad of gamma rays.

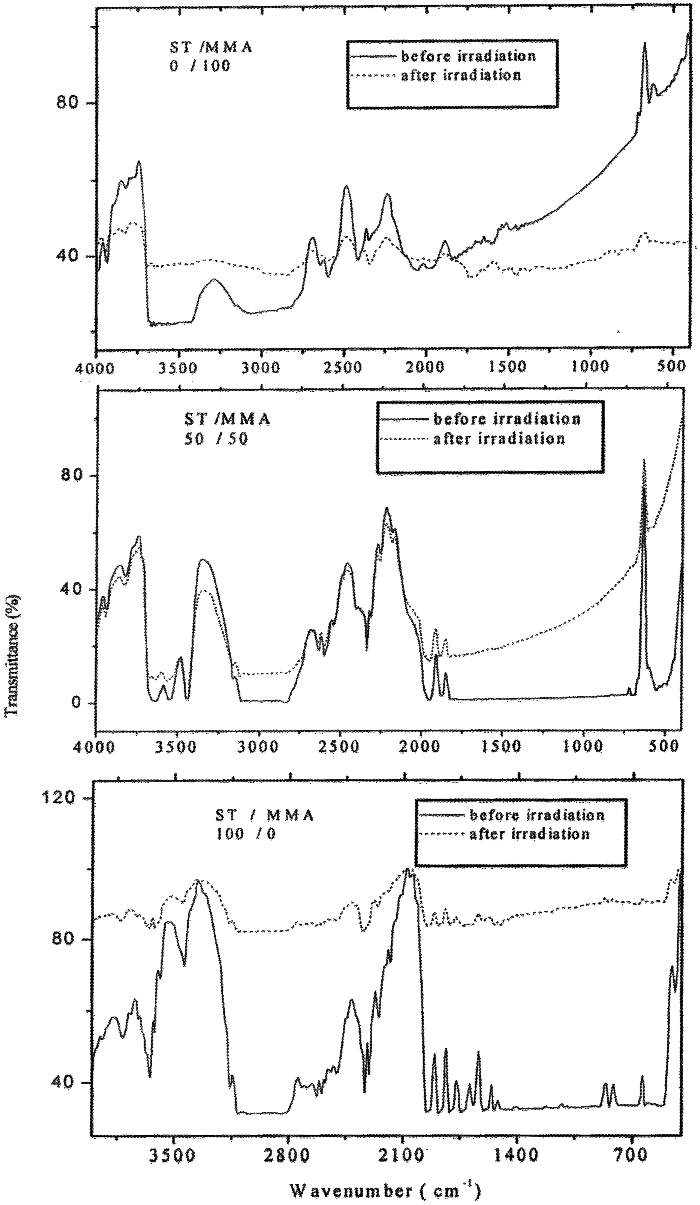


FIGURE 2 FT-IR spectra of copolymer (ST/MMA) with different concentration before and after irradiation by 10 Mrad of gamma rays.

TABLE 1 Wave Number (cm^{-1}) of the Vibrational Transmission Peaks of the Characteristic Groups of the ST/MMA Copolymer Before and After Irradiation by 10 Mard of Gamma Rays

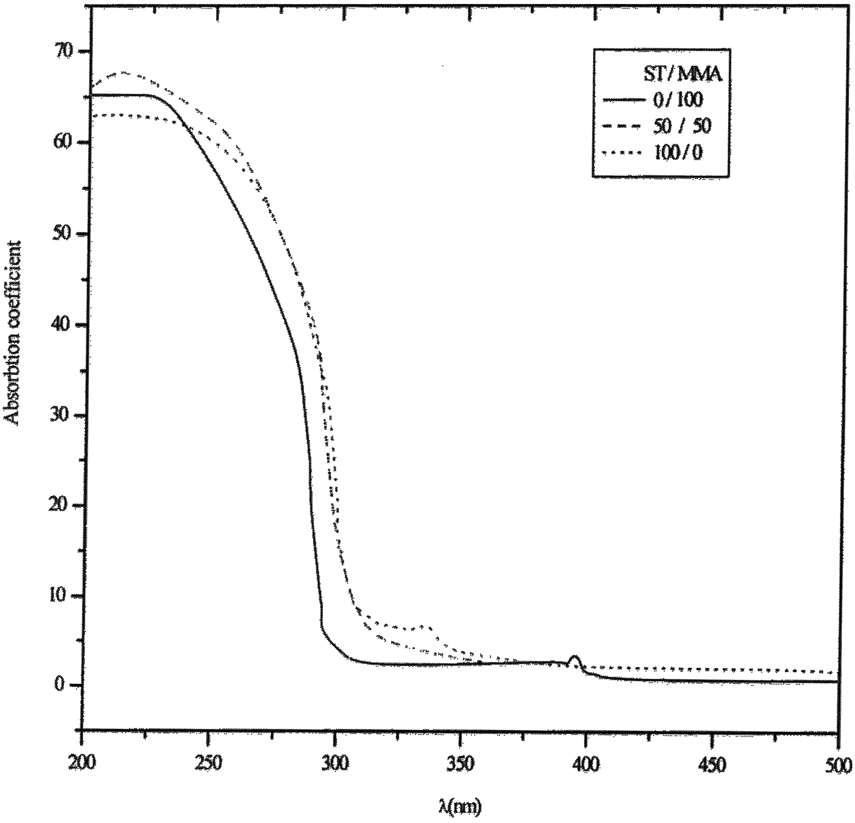
Concentration of (ST/MMA)	Irradiation doses (Mrad)	$-C-CH_2-C-$ bending	C−O−C	C=O (ester)	$O-CH_3$	C−H (CH_2, CH_3)	C−H (Ar-H)	Aromatic ring	C=C aromatic	Phenyl
(0/100)	0	1445.4	1290.3	1784.7	2814.5	2911.3	—	—	—	—
	10	1459.6	1264.7	1740.3	2843.3	2983.8	—	—	—	—
(50/50)	0	—	—	1762.4	2833.5	2983.8	3032	704.7	1645.8	—
	10	—	—	1774	2822.5	2996.8	3064	709.6	1510	—
(100/0)	0	—	—	—	—	2822.5	3048.4	791.2	1610	1510
	10	—	—	—	—	2846.7	3055.9	669.6	1616	1501

disappearance of the aliphatic C=C band at 1680–1600 cm^{-1}, characterizing *MMA* monomers to be evidence of complete polymerization.

Optical Parameters

The variation of the optical bulk absorption coefficient α with wavelength is a unique parameter of the medium. It provides the most valuable optical information available for material identification. The absorption coefficient α can be expressed by the following relation [3]:

$$\alpha(\nu) = 2.3\log(I_0/I)/d = 2.3\,A/d$$



(a)

FIGURE 3 (a) Absorption spectrum of different concentrations of ST/MMA copolymer without exposure to radiation. (b) Absorption spectrum of different concentrations of ST/MMA copolymer after exposure to UV radiation for 10 h.

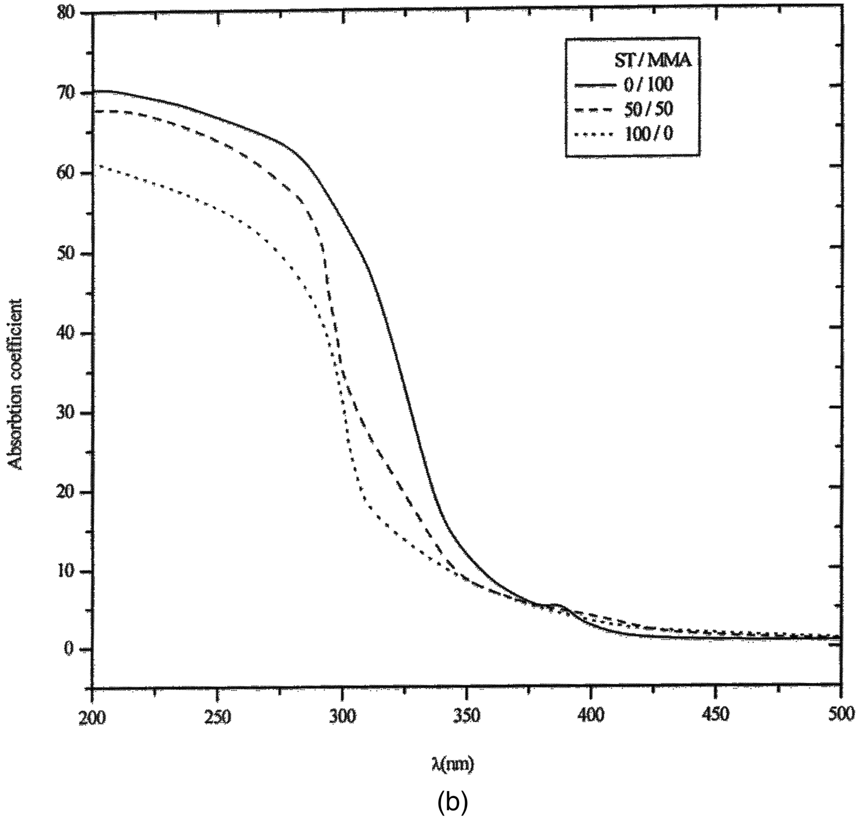


FIGURE 3 Continued.

where I_0 and I are the intensity of the incident and transmitted light; A is the absorbance; and d is the film thickness. The absorption spectra at room temperature for copolymer and homopolymers are measured before and after exposure to *UV* radiation, which is illustrated in Figure 3a and b.

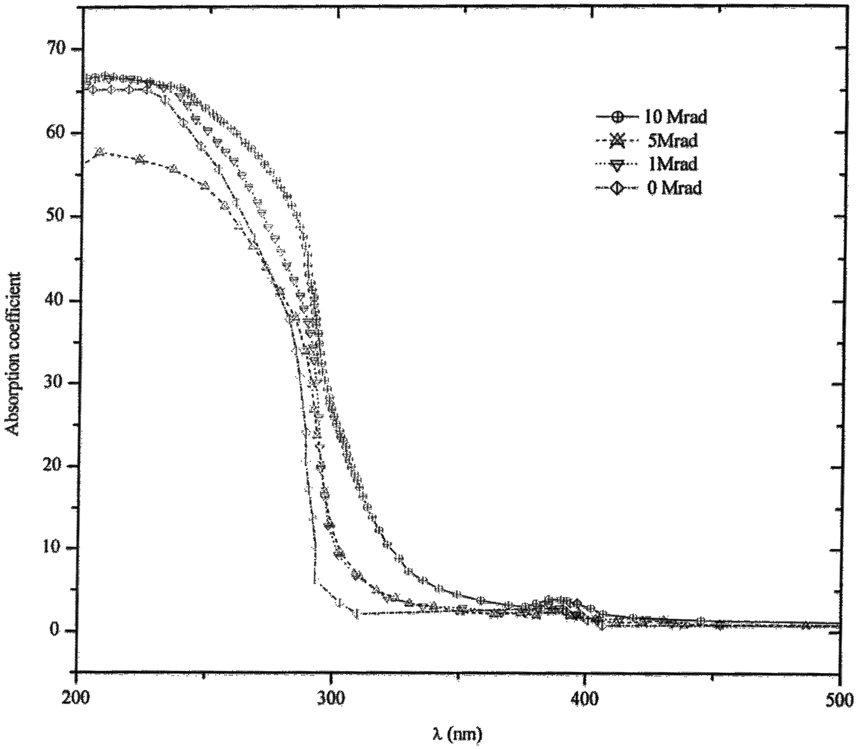
From Figure 3a and b, it can be concluded that the 50/50 *ST/MMA* copolymer controls the spectral breadth of *PMMA* after exposure to *UV* radiation in agreement with the reference [4]. The breadth of the absorption spectrum of *PMMA* is attributed to the existence of more transitions from higher vibration levels of the ground state to higher sublevels of the first excited singlet state.

On the other hand, the breadth caused by *UV* radiation is more than that of filtered radiation because the absorbed quantum in the first case is higher than the energy of any bond in the molecule. In addition, the *UV* absorption spectra at room temperature for 50/50 *ST/MMA* copolymer and homopolymers before and after irradiation by gamma doses (1, 5, and 10) Mrad are illustrated in Figure 4a–c.

When a quantum of radiation is absorbed by a material, the absorption coefficient as a function of photon energy for simple parabolic band can be expressed by the following relation [5–6]:

$$\alpha\,\mathrm{E} \sim (\mathrm{E} - \mathrm{E_g})^{\mathrm{n}}$$

where (n) depends on the transition type and $\mathrm{E_g}$ is the optical gap. Figure 5a–c illustrate the dependence of $(\alpha\mathrm{E})^2$ on the photon energy *E(eV)*, for 50/50 *ST/MMA* copolymer before and after irradiation by



(a)

FIGURE 4 (a) Absorption spectrum of pure PMMA before and after irradiation by gamma rays with different doses. (b) Absorption spectrum of pure PS before and after irradiation by gamma rays with different doses. (c) Absorption spectrum of 50/50 ST/MMA copolymer before and after irradiation by gamma rays with different doses.

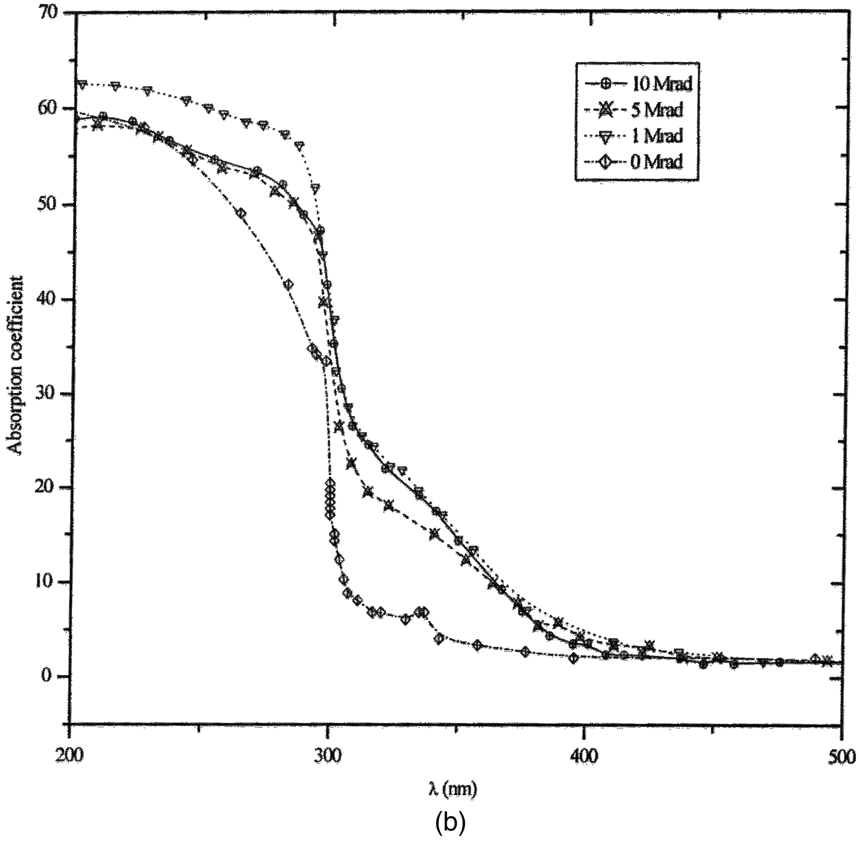


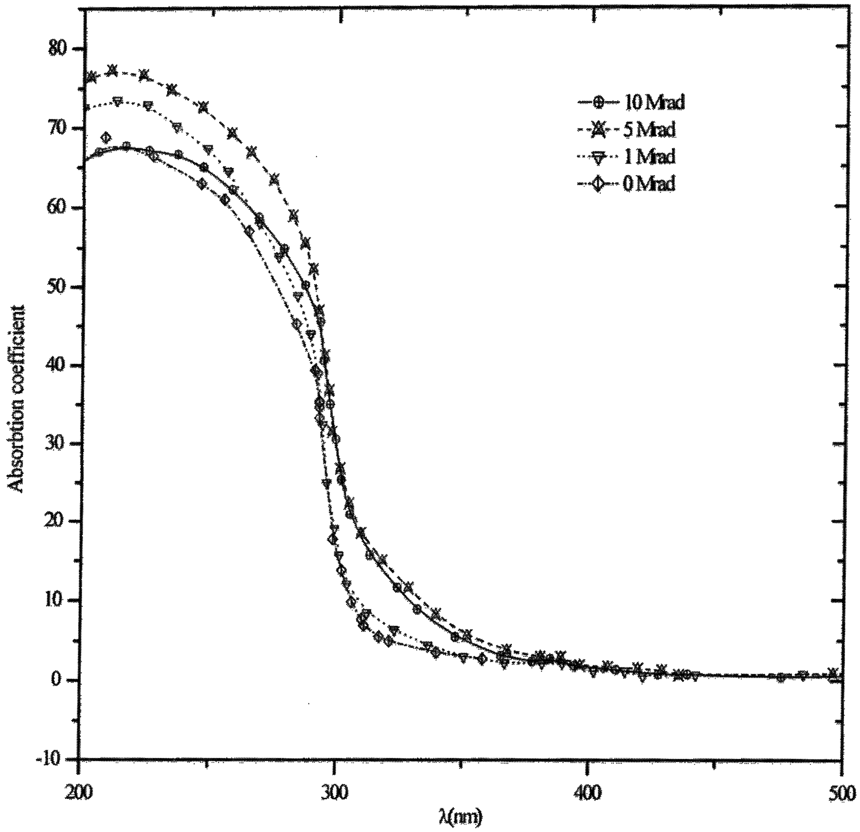
FIGURE 4 Continued.

gamma rays and *UV* radiation, which brought into view a linear behavior that can be considered as evidence of a direct transition (i.e., for n = 1/2) [7–8]. The optical gap was estimated from the intercept on the energy axis of the linear fit of the high energy data of the plot [9–10].

The absorption spectra show an extending tail for lower photon energies below the edge, which can be described by the formula of Urbach [11]:

$$\alpha = \alpha_0 \exp(E/E_u)$$

where E_u is the energy of Urbach corresponding to the width of the band tails of localized states in the band gap. The values of E_u were calculated as the reciprocal gradient of the linear portion of the plot.

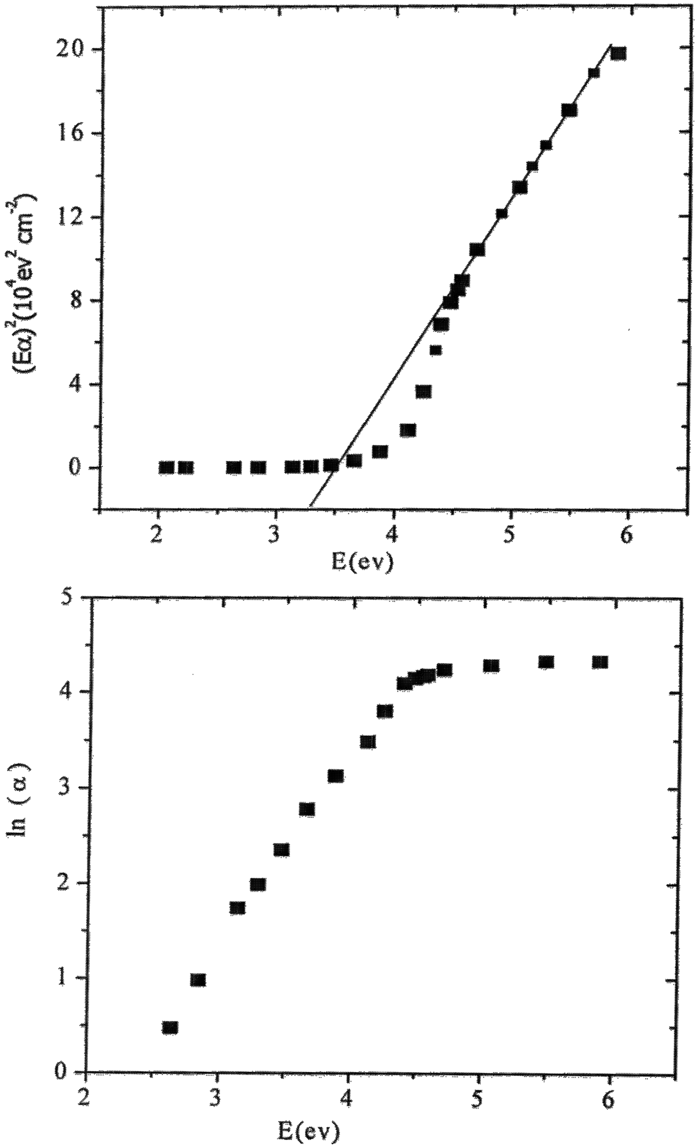


(c)

FIGURE 4 Continued.

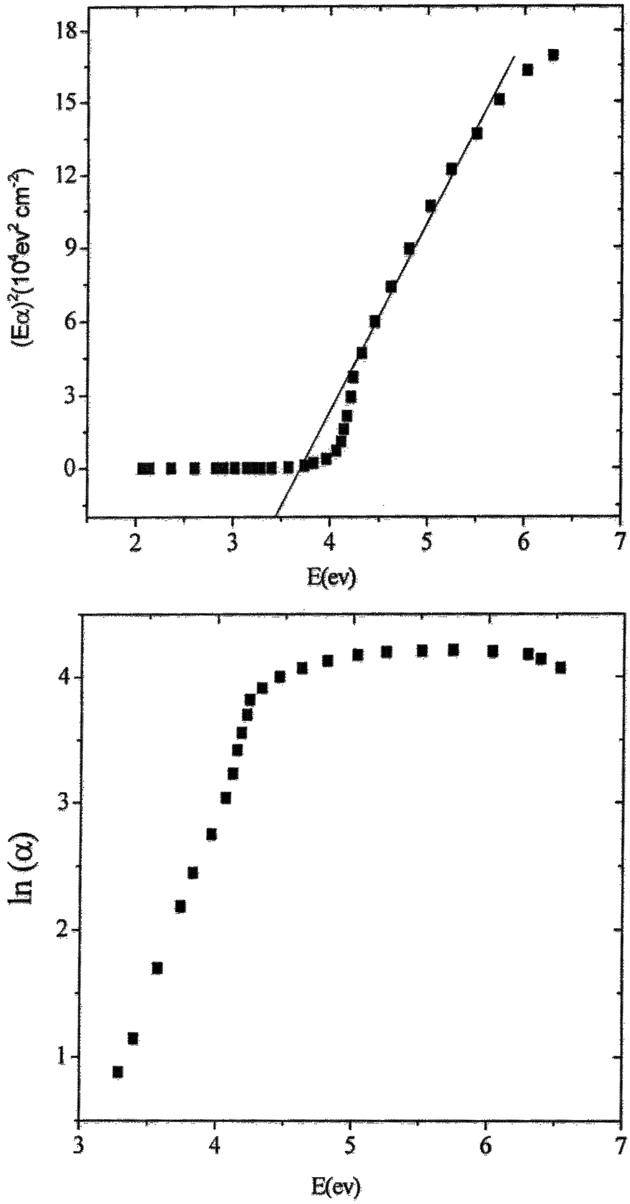
Figures 5 show the plot of ln α versus photon energy *E* (*eV*), for 50/50 *ST/MMA* copolymer before and after irradiation by gamma radiation for 10 Mrad and also after irradiation by UV radiation for 10 h.

Tables 2 and 3 summarize the optical parameters (E_u and E_g) of *ST/MMA* copolymers of various concentration. From Table 2 it was observed that the values of E_g decrease after the sample are exposed to *UV* radiation for 10 h with a percentage of 8.14% for *PS* and 21.85% for *PMMA*. This explains that the *UV* spectrum of *PMMA* was broadened after exposure to *UV* radiation. The 50/50 *ST/MMA* copolymer modifies the breadth of *PMMA* spectrum after exposure to *UV* radiation. The values of E_u are increased by increasing the exposure time. Table 3 shows that the reduction in the values of E_g



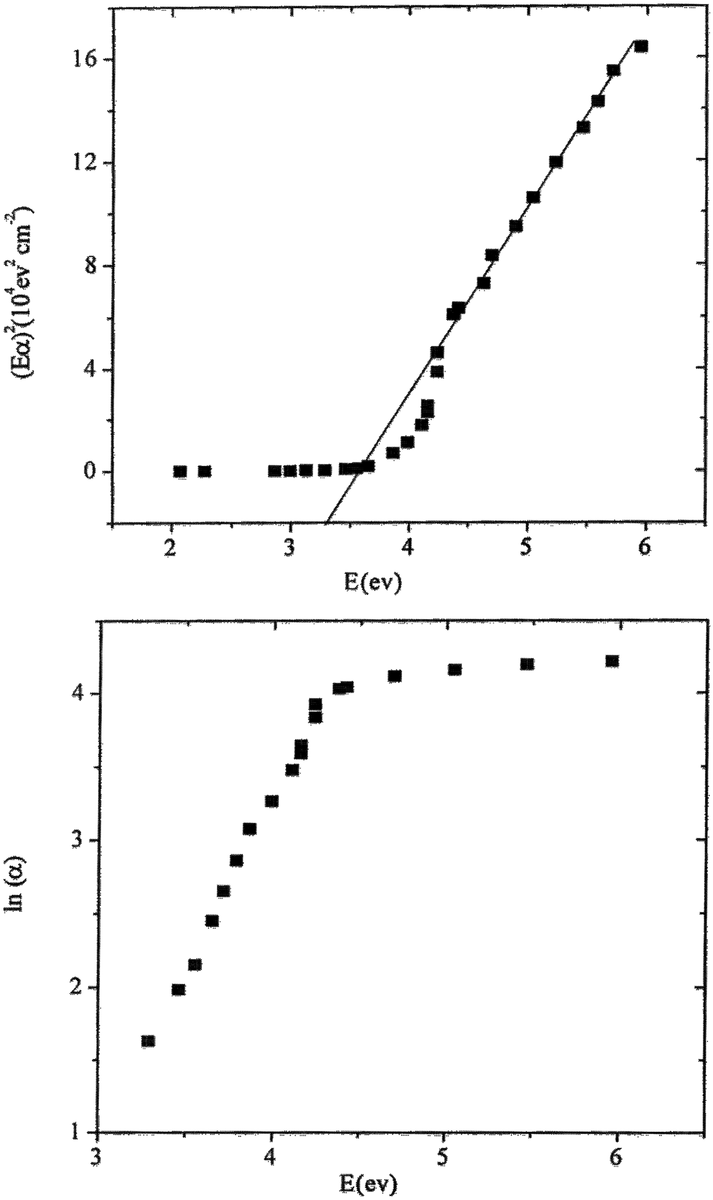
(a)

FIGURE 5 (a) The dependence of $(\alpha E)^2$ and ln α on photon energy E (eV) for 50/50 ST/MMA copolymer without exposure to radiation. (b) The dependence of $(\alpha E)^2$ and ln α on photon energy E (eV) for 50/50 ST/MMA copolymer irradiated by gamma rays with 10 Mrad. (c) The dependence of $(\alpha E)^2$ and ln α on photon energy E (eV) for 50/50 ST/MMA copolymer after exposure to UV radiation for 10 h.



(b)

FIGURE 5 Continued.



(c)

FIGURE 5 Continued.

TABLE 2 The Band Tail Width (E_u) and the Energy Gap (E_g) for the Samples of the ST/MMA Copolymers after Exposure to UV Radiation and Filtered Radiation for 10 h

Concentration of (ST/MMA)	Before exposure to the radiation		After exposed to filtered radiation for 10 h			After exposed UV radiation for 10 h		
	E_u	E_g	E_u	E_g	Percentage of decrease of E_g	E_u	E_g	Percentage of decrease of E_g
(0/100)	0.140	3.98	0.270	3.70	7.04	0.300	3.11	21.85
(10/90)	0.160	3.90	0.420	3.647	6.49	0.300	3.22	17.43
(30/70)	0.170	3.89	0.375	3.64	6.43	0.490	3.28	15.68
(50/50)	0.176	3.89	0.430	3.689	5.17	0.430	3.29	15.42
(70/30)	0.165	3.86	0.344	3.68	4.66	0.430	3.35	13.20
(90/10)	0.400	3.84	0.550	3.64	5.21	0.470	3.20	16.66
(100/0)	0.210	3.81	0.400	3.68	3.41	0.485	3.50	8.14

for the samples irradiated by gamma rays with different doses (1,5, and 10) Mrad, are less than those in the case of exposure to *UV* radiation, except for those of *PS*. Also, there is a random reduction in the values of E_g of *PMMA* that is attributed to *PMMA* being a typical degradable polymer and its main chain suffers random degradation as a result of exposure to irradiation [12]. The presence of gamma ray modifies the stability of the 50/50 *ST/MMA* copolymer. On the other hand, the reduction of the values of E_g for *PS* was more than that of *PMMA*.

TABLE 3 The Band Tail Width (E_u) and the Energy Gap (E_g) for the Samples of the ST/MMA Copolymer after Irradiation by Gamma Rays with Different Doses

Concentration of (ST/MMA)	Doses of gamma ray (Mrad)	E_u	E_g
(0/100)	0	0.140	3.98
	1	0.200	3.69
	5	0.200	3.78
	10	0.328	3.38
(50/50)	0	0.176	3.89
	1	0.255	3.70
	5	0.357	3.41
	10	0.330	3.43
(100/0)	0	0.210	3.81
	1	0.540	2.84
	5	0.377	3.19
	10	0.428	2.85

Optical Constants

The optical absorption coefficient α of the medium provides valuable optical information for material identification. The extinction coefficient k is directly proportional to the absorption coefficient α through [13]:

$$\alpha = \frac{4\pi k}{\lambda}$$

where λ is the free space wavelength of light. For normal incidence, the reflection coefficient is given by [14]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

when $k = 0$, that is, in the transparent range:

$$R = \frac{(n-1)^2}{(n+1)^2}$$

The measurement of specular reflection and the absorbance are used to calculate the optical constants n and k. Figure 6(a) illustrates the spectral distribution of the optical constants for the *ST/MMA* copolymer with various concentrations and Figure 6(b) illustrates the spectral distribution of the optical constants for the 50/50 *ST/MMA* copolymer after irradiation by gamma radiation with different with doses 1, 5, and 10 Mrad. It is observed that the spectral distribution of refractive index n of 50/50 *ST/MMA* copolymer is in the middle of those of the two homopolymers. On the other hand, the values of the refractive indices increase after the films are irradiated by the doses of gamma rays.

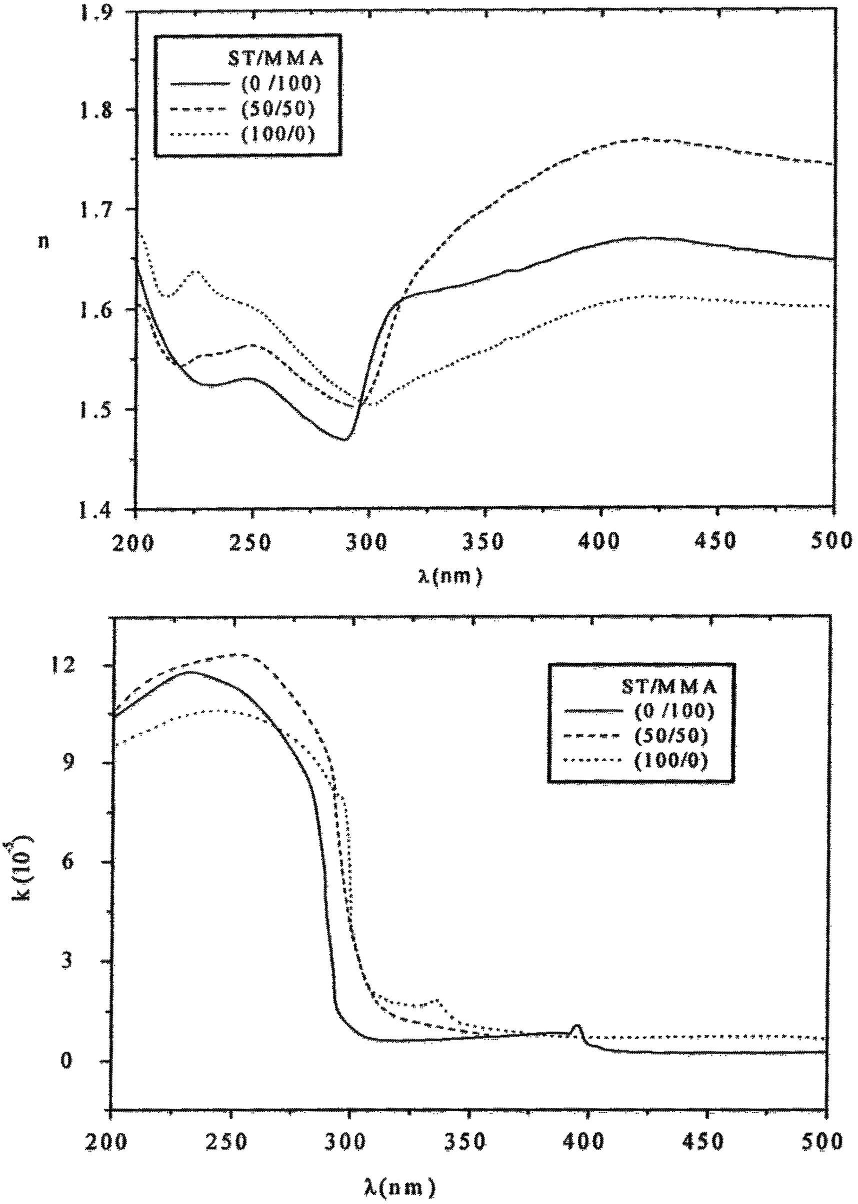
Constants of Cauchy

The first successful attempt to represented the curve of normal dispersion by an equation was made by Cauchy in 1836, which is [15]:

$$n = A + B/\lambda^2 + C/\lambda^4$$

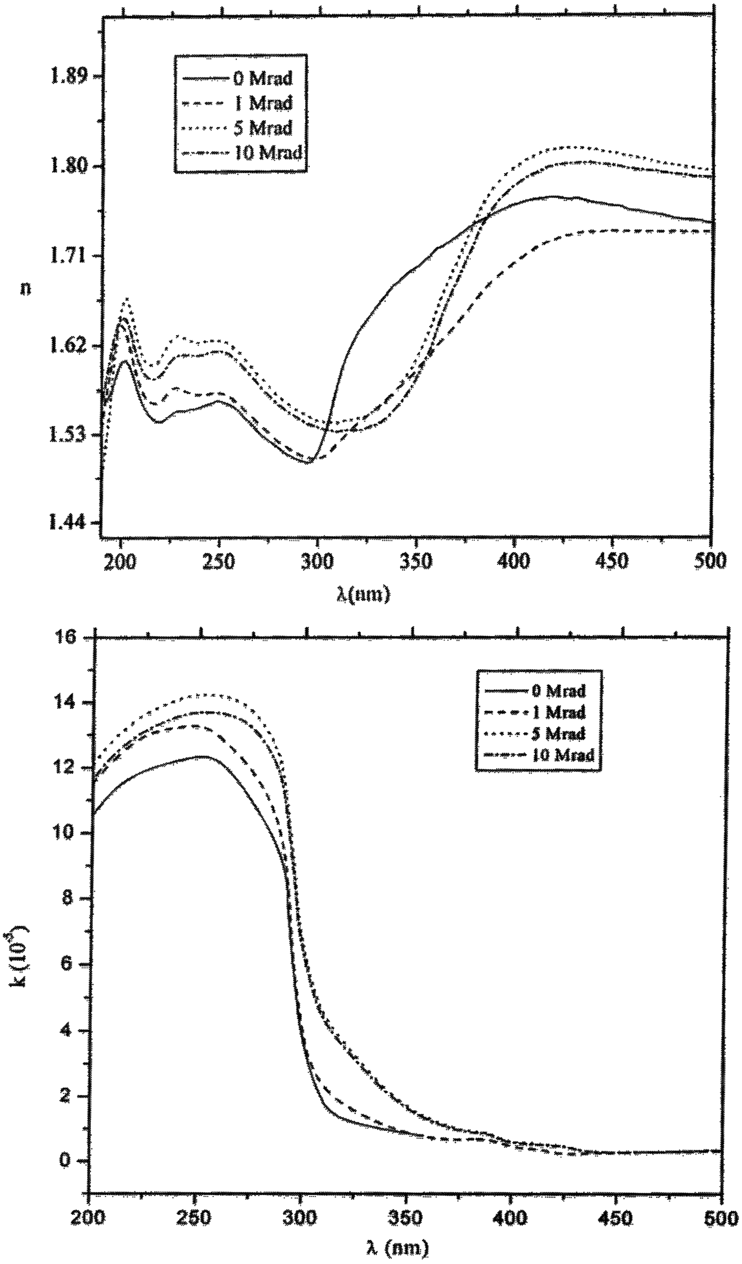
where A, B, and C are constants that are characteristic of any one substance. This equation represents the curve in the visible region. For some purposes, it is sufficiently accurate to include only the first two terms and the two constants can be found form the values of n of two wavelengths:

$$n = A + B/\lambda^2$$



(a)

FIGURE 6 (a) Spectral distribution of n and k for 50/50 ST/MMA copolymer and the homopolymers without exposure to radiation. (b) Spectral distribution of n and k for 50/50 ST/MMA copolymer after irradiation by gamma rays with different doses.



(b)

FIGURE 6 Continued.

TABLE 4(a) The Values of Cauchy's Constants for ST/MMA Copolymers

Concentration of (ST/MMA)	The doses of gamma ray	Before the absorption band		After the absorption band	
		A	B (μm)	A	B (μm)
(0/100)	1	1.060	25.16	1.266	20.22
	5	1.090	23.00	1.260	18.90
	10	0.850	35.70	1.310	17.98
(50/50)	1	0.950	27.80	1.304	17.15
	5	0.804	35.50	1.260	23.30
	10	0.970	27.50	1.290	20.66
(100/0)	1	0.459	55.90	0.927	40.90
	5	0.148	63.80	0.950	33.80
	10	0.488	53.45	0.995	35.00

TABLE 4(b) The Values of Cauchy's Constants for 50/50 ST/MMA Copolymer and the Homopolymers After Irradiation by Gamma Ray

	Before the absorption band		After the absorption band	
Concentration of (ST/MMA)	A	B (μm^{-1})	A	B (μm^{-1})
(0/100)	1.015	25.0	1.15	25.0
(50/50)	1.082	21.2	1.29	17.0
(100/0)	0.950	29.3	1.23	23.3

the values of A and B are tabulated in Tables 4a and b before and after the samples were irradiated by gamma radiation. It is clear that the values of the constant A after the absorption band are greater than those before the absorption band.

CONCLUSIONS

Copolymer films with various concentrations of styrene and methylmethacrylate were prepared by thermal polymerization. The films were irradiated by gamma rays and also exposed to *UV* radiation. The calculated values of the optical parameters illustrate that the reduction in E_g values (by increasing the exposure time) of the films irradiated by gamma rays are less than those that were exposed only to *UV* radiation for *PMMA* and 50/50 *ST/MMA* copolymer. Moreover, the value of the refractive index (n) of 50/50 *ST/MMA* copolymer is in the middle of those of the two homopolymers (*PMMA* and *PS*). On the other hand, the irradiation by gamma rays modifies the values of optical constants. Lastly, from all the investigated results, one can reduce that the 50/50 ST/MMA copolymer modifies the optical properties of the ST and MMA homopolymers.

REFERENCES

[1] EL-Salmawi, K., Abu Zeid, M. M., El-Naggar, A. M., and Mamdouh, M., *J. Applied Polymer Science* **72**, 509 (1999).

[2] Ebewele, R. O. (2000). *Polymer Science and Technology*, CRC Press LLC, Florida.

[3] Sedeek, K., Mahmoud, F. S., Terra, A., and Said, S. M., *J. Phys. D: Applied Phys.* **27**, 156 (1994).

[4] Mansour, A. F., *J. Polymer Testing* **23**, 247 (2004).

[5] El-Shair, H. T. and Bekheet, A. E., *J. Phys. D: Applied Phys.* **25**, 1122 (1992).

[6] Bakr, N. A. and Abdel-Hamid, M. I., *J. Mater. Res.* **10**, 2653 (1995).

[7] Joseph, C. M. and Menon, C. S., *Semiconductor Sci. Technol.* **11**, 1668 (1996).

[8] Bang, T. H., Choe, S. H., Pak, B. N., Jin, M. S., and Kims, W. T., *J. Semiconductor Sci. Technol.* **11**, 1159 (1996).

[9] Swanepoel, R., *J. Phys. E.* **17** 896 (1984).

[10] Marquez, E., Wagner, T., Leal, J. M., Oliva, A. M., Alcon, R. R., and Garay, R. J., *J. Non-Crystalline Solids* **62**, 274 (2000).

[11] Urbach, F., *J. Phys. Rev.* **92**, 1324 (1953).

[12] Bajpai, R., Dhagat, N. B., Katare, R., Agrawal, P., and Datt, S. C., *J. Bull. Mater. Sci.* **26** (4), 401 (2003).

[13] Fax, M. (2001). *Optical Properties of Solids*, Oxford University Press Inc, New York.

[14] Pankove, J. I. (1971). *Optical Processes in Semiconductors*, Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

[15] Jenkins, F. A. and Whit, H. E. (1976). *Fundamentals of Optics*, 4th ed. McGraw-Hill, Kogakusha, Ltd.