

Optical Parameters and Absorption Studies of UV-Irradiated Azo Dye-Doped PMMA Films

H. M. Zidan,¹ A. El-Khodary,² I. A. El-Sayed,¹ H. I. El-Bohy¹

¹Department of Physics, Faculty of science, Mansoura University, New Damietta, Damietta, Egypt

²Department of Physics, Faculty of science, Mansoura University, Mansoura, Egypt

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ABSTRACT: PMMA and PMMA films doped with different contents of azo dye have been made by using the casting technique. The absorption spectral analysis showed that the doped films have two absorption bands attributed to the π - π^* and n - π^* transition of chromophore groups. These bands disappear upon UV-irradiation, suggesting that the studied system undergoes a photo degradation process. The absorption coefficient and optical energy gap (E_g) have been obtained from the absorption edge in the 200–900 nm range. It was found that E_g decreases with increasing doping levels, whereas it increases with increasing irradiation time. The width of the tail of localized states in the band

gap (ΔE) was evaluated using the Urbach edge method. Some optical parameters were determined from the reflection and transmission spectra in the spectral range of 200–2500 nm. The dependence of the refractive index on irradiation time and doping level have been discussed. It was found that the photo-induced refractive index changes are very large. These changes suggest the applicability of the studied system in optical devices. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1416–1423, 2010

Key words: PMMA; azo dye; doping; UV-irradiation; optical constants; refractive index changes; degradation

INTRODUCTION

Some materials have been found to exhibit a change in refractive index under the influence of light, which makes it possible to use these materials to record not only the magnitude but also the phase of illumination. The latter is especially important in holographic optical data storage and in the fabrication of various integrated components and devices such as selective optical filters, mixers, couplers, and modulators.^{1,2}

Photo-chemical reactions in polymer films can induce various changes in physical properties of polymer films such as solubility, transparency, thickness, and refractive index.³ The photo-chemically induced refractive index change in polymer films is an important method for controlling optical properties of polymers.⁴ The photo-chemical reaction can induce larger refractive index modulation in polymer films and the modulation remains after the photo-reaction, leading to a permanent change in refractive index. Therefore, photo-chemically induced refractive index changes in polymer films have attracted much attention for various applications, such as optical memories, switching devices,

holographic image recording and waveguide lithography.⁵ Recent publications^{6–12} have discussed photo-induced refractive index changes of organic polymers containing photo-chromic dyes.

Photopolymers were among the first materials used to displace the photographic plate in holography and many variations of these photopolymers have been reported.^{13–15} One important type of photopolymer is that comprising PMMA as the base.¹⁶ This type of polymer is primarily sensitive to UV light but its sensitivity could be extended to some other regions of the visible spectrum with sensitizers or dyes. For the past few decades, photosensitive polymeric systems and mostly azo-dye doped polymers (ADP) have been in the centre of this feverish activity.¹⁷ They have shown their impact on optical storage technology for developing high information density and fast access type memories with a high read-out efficiency. Furthermore, these polymeric systems allow the manufacturing of reusable films yielding many thousands of write / read / erase cycles, involving no chemical or thermal post-recording treatments.

Real-time dynamic holography with polarized and unpolarized lights has been performed involving PMMA-based recording media, doped with five azo-dyes.^{18–20} Pham et al.²¹ studied the characterization of these azo dye doped PMMA samples by means of changing of different parameters (thickness, concentration of PMMA, concentration of azo dye, etc.).

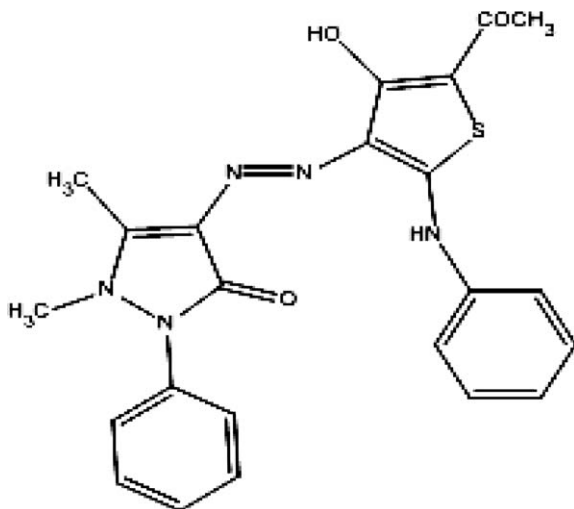
Correspondence to: H. M. Zidan (hmzidan@yahoo.com).

The optical band gap, refractive index and extinction coefficient are the most significant parameters in amorphous films. The optical behavior of a material is utilized to determine its optical constants. In previous studies,^{22,23} the structural modifications and optical constants of polymeric films doped with iodine and metal chlorides were studied. Also, the effect of UV-irradiation on the structure and optical properties of polycarbonate films were investigated.²⁴ The motive of this work is to study the effect of both of the doping level and the UV-irradiation on the optical properties of PMMA films doped with azo dye using optical absorption measurements and the determination of optical constants and energy gap width.

EXPERIMENTAL PROCEDURES

Sample preparation

Poly(methylmethacrylate) (PMMA), an average molecular weight (M_w) of 350,000, used in this study was obtained from Aldrich Chemical Co., USA, and it was used without any further purification. The molecular structure of a novel yellow azo dye is:



The azo dye-doped PMMA films were prepared by the casting technique. Pure chloroform was used as a common solvent for PMMA and azo dye. The solutions were then mixed and left to reach a suitable viscosity. The mixture was casted on a glass plate and kept in a dry atmosphere at 303 K to form transparent films. Samples were transferred to an electric air oven held at 333 K for 48 h to minimize the residual solvent. The thickness of the obtained films ranged from 0.05 to 0.1 mm. All films were stored in desiccators with a dry agent in dark medium to avoid direct exposure to light. Azo dye-doped PMMA films with mass fractions 0, 0.25, 0.50, and 0.75 wt % were prepared.

Physical measurements

UV-vis absorption spectra of unirradiated and irradiated films were carried out at room temperature in the wavelength range 200–900 nm using a Perkin-Elmer UV / VIS spectrophotometer. The samples were irradiated using a monochromatic light of 254 nm wavelength from a low-pressure mercury lamp cole Parmer (100 W). The distance between the light source and the sample was 5.0 cm. The thermal effects of the UV lamp were compensated by regulating the sample temperature to be fixed around $(298 + 1)$ K. The spectrophotometer method was used to determine the optical constants of the studied samples. The transmittance $T(\lambda)$ and the reflectance $R(\lambda)$ of PMMA films and azo dye-doped PMMA films were measured using a double-beam spectrophotometer JASCO model V-570-UV/VIS/NIR. The transmittance and reflectance spectra were measured in the wavelength range 190–2500 nm. A deuterium discharge tube (190–350 nm) is used in the UV region and a tungsten iodine lamp (340–2500 nm) is used in the VIS-NIR region as light sources.

RESULTS AND DISCUSSION

Absorption spectra

The absorption of light energy by polymeric materials in the UV/VIS region involves promotion of electrons in σ , π , and n -orbitals from the ground state to higher energy states which are described by molecular orbitals.²⁵ Many of the optical transitions which result from the presence of impurities have energies in the visible part of the spectrum; consequently, the defects are referred to as color centers.²⁶ Doping the polymers or UV-irradiation leads to the formation of new defects and new charge states.

The absorption spectra with UV/VIS spectrophotometer carried out on pure PMMA and PMMA films doped with different amount of azo dye are present in Figure 1(a). The observed spectrum of pure PMMA film has an absorption band (shoulder) at about 275 nm. This band may be attributed to the $n - \pi^*$ transition of the carbonyl group in the polymeric macromolecule. It is observed that the spectrum of pure azo dye dissolved in chloroform (Common solvents for the studied system) has two absorption peaks at 356 and 461 nm. The positions of the peaks are marked by arrows in Figure 1(a). For the PMMA films doped with different amount of azo dye, the spectra contain two absorption peaks at about 356 and 461 nm. It is reasonable to assign the observed bands to the $\pi - \pi^*$ and $n - \pi^*$ transitions of chromophoric groups (the extended conjugated double bond system including the diazo group). It is found that the position of the peaks is

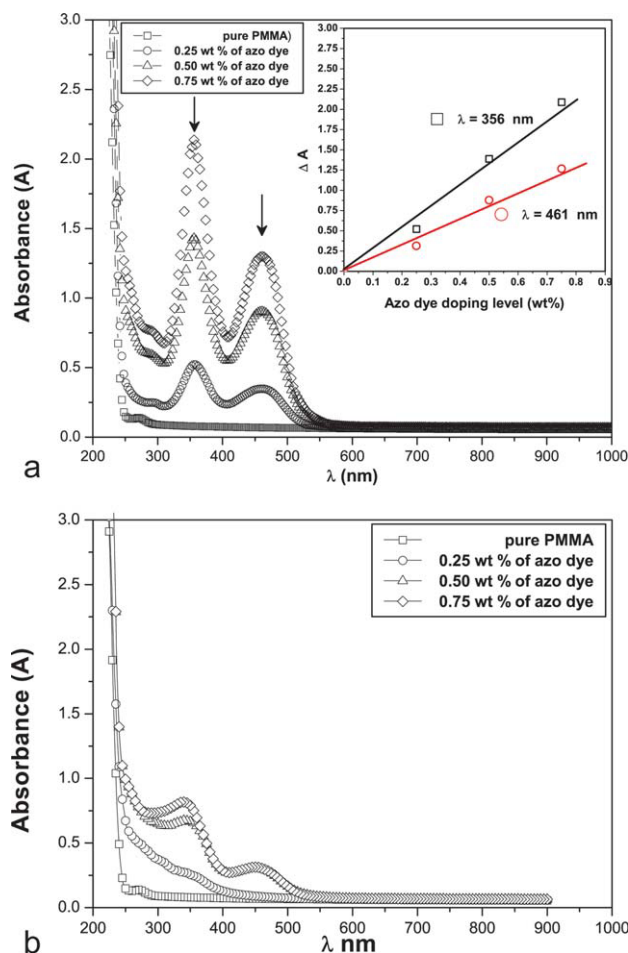


Figure 1 UV/VIS scan for pure PMMA and PMMA films doped with different levels of azo dye (a) before irradiation, (b) after irradiation for 1 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

not altered, while the intensity (A) increases with increasing the doping level. The dependence of the intensity of the bands on the doping level provides an evidence for the incorporation of azo dye into PMMA matrix. Figure 1(b) displays the UV/VIS spectra for irradiated pure PMMA and PMMA films doped with different levels of azo dye for irradiation time (IT) 1 h. It is clear that the exposure of pure PMMA film has no influence on their UV spectral features; therefore, it can be used as a photo stable polymer. On the other hand the spectra of the doped films changed.

Figure 2 represents the spectra of irradiated PMMA films doped with 0.75 wt % azo dye with different irradiation time (IT). It is observed that the intensity of the azo dye peaks decreases and shifted toward lower wavelength (hypsochromic shift). This revealed that the number of conjugated double bonds was decreased due to the bond cleavage. Also it is found that the intensity of the peaks decreases with increasing IT until the peaks vanished. This

explain the visual observation of the change in color of the original plastic films from yellow to transparent upon UV-irradiation, so this dye cannot be used as a photo resistance medium. The results can be interpreted on the basis of photo-degradation of the azo dye. The photo-irradiation of the azo dye causes a bond cleavage of $-N=N-$ group.

Optical energy gap

Significant changes of different amounts have been observed in optical response of the polymers after doping or UV-irradiation. UV/VIS spectroscopy can be used for the investigation of the optically induced transitions and can provide information about the energy gap in crystalline and non-crystalline materials.²⁷ It is clear that the absorption spectra for the present system (Figs. 1 and 2), characterized by a main absorption edge for all curves, are shifted toward longer wavelength as the doping level increases. On the other hand, the absorption edges are shifted towards shorter wavelength upon UV-irradiation. Also, the edges are not sharply defined, signifying the glassy nature of the films. The absorption coefficient (α) can be calculated from the optical absorption spectrum using the relation:

$$\alpha = 2.303 \frac{A}{X} \quad (1)$$

where X is the film thickness in cm and A is defined by $A = \log(I_0/I)$ where I_0 and I are the intensities of the incident and transmitted beams, respectively.

The optical band gap was determined from the analysis of the spectral dependence of the absorption near the absorption edge. The absorption coefficient for noncrystalline materials has the following frequency dependence

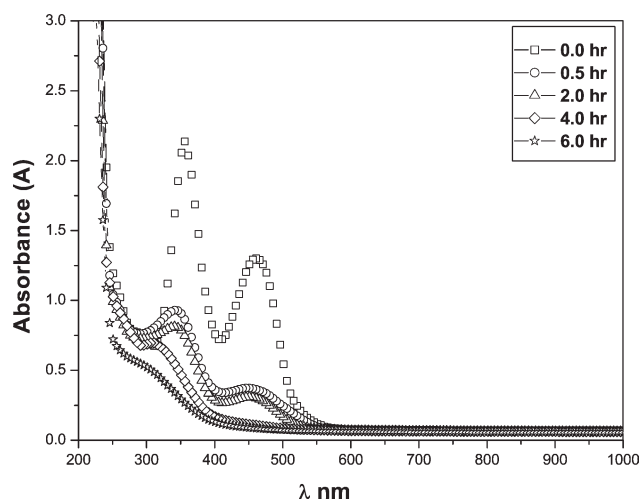


Figure 2 UV/VIS scan for PMMA and PMMA films doped with 0.75 wt % of azo dye irradiated with different IT's.

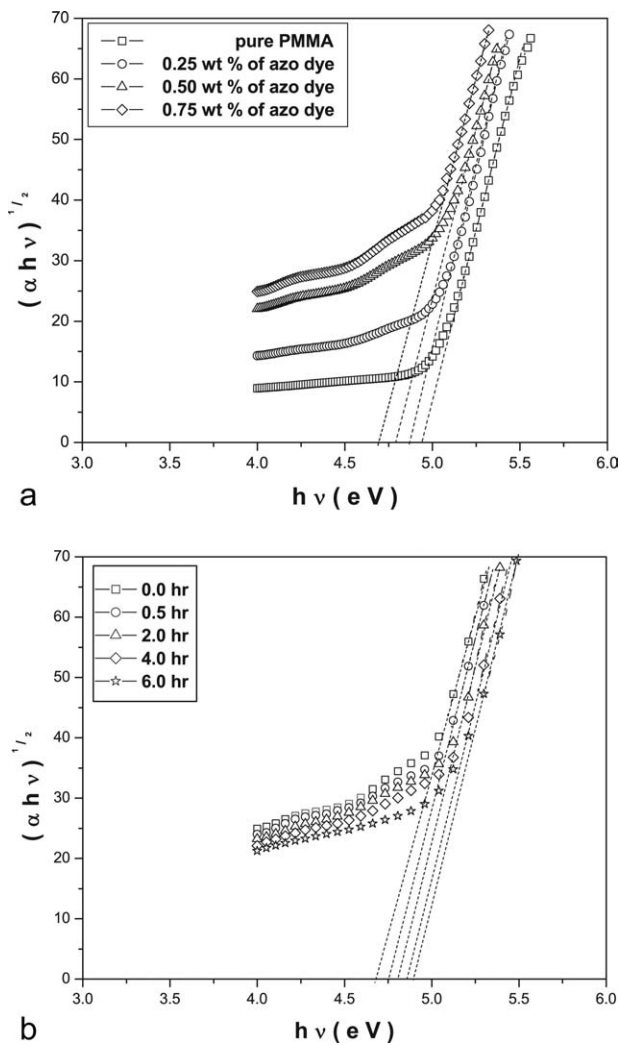


Figure 3 The dependence of $(\alpha h\nu)^{1/2}$ on photon energy for (a) PMMA films doped with different levels of azo dye, (b) PMMA films doped with 0.75 wt % of azo dye for different IT's.

$$\alpha = \frac{B(h\nu - E_g)^r}{h\nu} \quad (2)$$

where $h\nu$ is the energy of the incident photons, B is constant, E_g is the value of the optical energy gap, and r is the power, which characterizes the transition process in the K-space. The usual method for the determination of the value of E_g involves plotting $(\alpha h\nu)^{1/r}$ against $(h\nu)$. The dependence of $(\alpha h\nu)^{1/r}$ on photon energy ($h\nu$) was plotted for the studied films using different values of r , the best fit was obtained for $r = 2$. This indicates that the transition energy for electrons is indirect in K-space and interactions with lattice vibrations (phonons) take place. From the plots of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ near the absorption edge we can determine E_g . The values of E_g for PMMA films doped with different contents of azo dye and those for PMMA films doped with 0.75 wt % of azo dye before and after UV-irradiation

with different IT's are calculated from Figure 3. The dependence of E_g on azo dye content and UV-irradiation with different IT's is shown in Figure 4. It is clear that E_g decreases with increasing azo dye content and increases with increasing IT. The variation of the calculated values of energy gap may reflect the role of azo dye content and UV-irradiation in modifying the electronic structure of the PMMA matrix due to appearance of various polaronic and defect levels. These implications can be explained in the following sense. The decrease of E_g may be attributed to the induced energy states due to azo dye doping, while the increase of E_g evidence the presence of another type of induced states depending on UV-irradiation.

The density of localized state, $N(E)$, was found to be proportional to the concentration of these defects²⁸ and consequently, to azo dye content or IT. Increasing azo dye content or IT may cause the localized states of different color centers to overlap

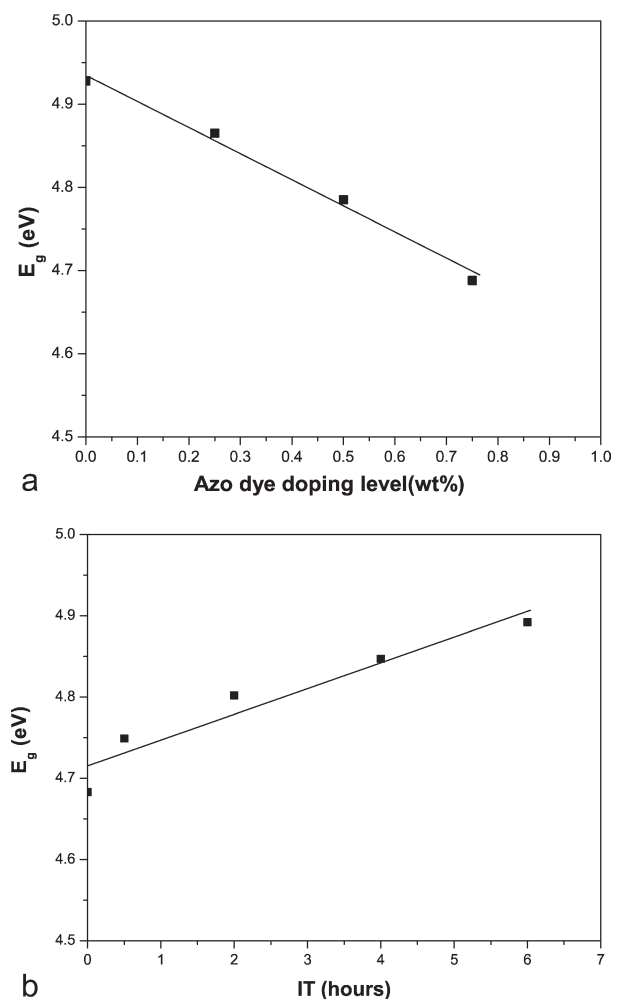


Figure 4 The dependence of E_g on (a) Azo dye doping level, (b) IT(h) for PMMA films doped with 0.75 wt % of azo dye.

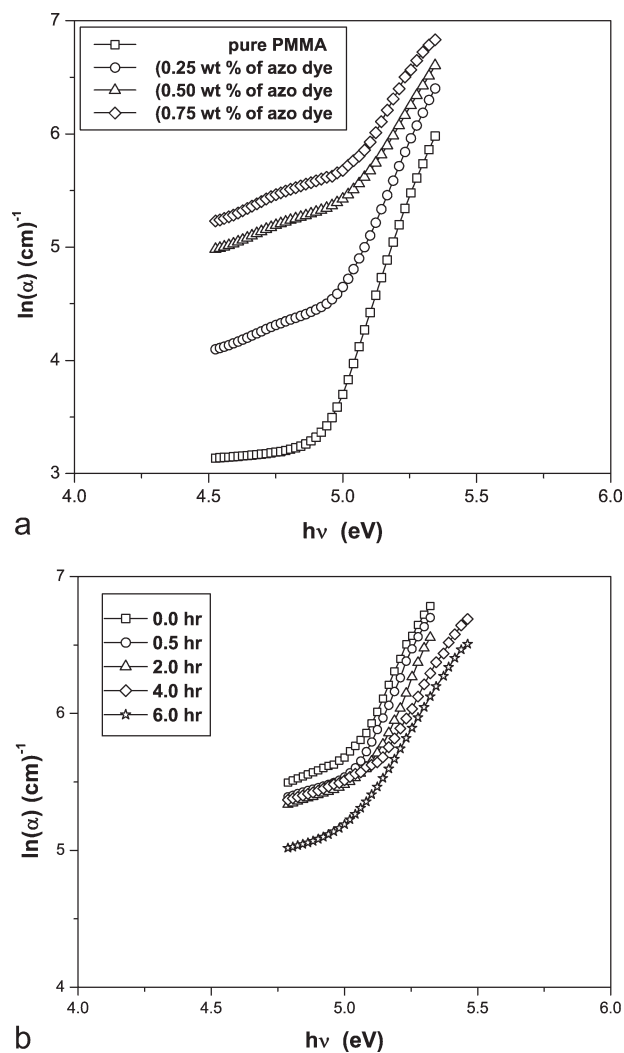


Figure 5 The dependence of $\ln(\alpha)$ versus $h\nu$ for (a) PMMA films doped with different levels of azo dye, (b) PMMA films doped with 0.75 wt % of azo dye irradiated with different IT's.

and extends in the mobility gap.²⁹ This overlap may give us an evidence for decreasing E_g when azo dye content is increased in the polymeric matrix and an evidence for increasing E_g with increasing IT.

The absorption spectra (Figs. 1 and 2) show an extending tail for lower energies below the band edge. It could be corresponding to the transition from the localized states in the valence band tail, which was formed because of the extrinsic origins arising from defects or impurities, to extended states

in the conduction band. The absorption coefficient α (ν) is described by the Urbach formula,³⁰

$$\alpha(\nu) = \alpha_0 \exp(h\nu/\Delta E) \quad (3)$$

where α_0 is a constant and ΔE is an energy which is interpreted as the width of the tail of localized states in the forbidden band gap. The origin of ΔE is considered as thermal vibrations in the lattice.³¹ Figure 5 shows the linear dependence of the $\ln(\alpha)$ versus $h\nu$ for films of PMMA doped with different contents of azo dye and PMMA films doped with 0.75 wt % of azo dye irradiated with different IT's. The reciprocal of the slopes yields the magnitude of ΔE . The values of ΔE for PMMA doped with different contents of azo dye and that for PMMA doped with 0.75 wt % of azo dye irradiated with different IT's are calculated and listed in Table I.

Reflection and transmission spectra

The optical properties obtained from the measurements of reflection and transmission were studied. The spectral distribution of both reflectance $R(\lambda)$ and Transmittance $T(\lambda)$ for the studied system in the wavelength range 200–2500 nm are shown in Figure 6. From the inspection of this figure, it is noticed that the pure PMMA film is transparent, that is, $T \sim 1$, and gives a normal dispersion region. On the other hand, the doped samples become transparent only at $\lambda > 500$ nm [Fig. 6(a)]. The inequality $T + R < 1$ at $\lambda < 500$ nm is due to the existence of absorption. For the irradiated films [Fig. 6(b)], the intensity of absorption peaks decreases with increasing IT's. It vanishes at IT about 6 h and the film become transparent, as undoped samples. The peaks indicating the anomalous dispersion behavior are due to a rapid increase in the absorption mechanism in the fundamental absorption edge due to the presence of absorbing color centers induced as a result of the azo dye group presence in the polymer matrix. This behavior obeys a multioscillator model.

The refractive indices (n) for the studied samples were determined from the measured values of $T(\lambda)$ and $R(\lambda)$ according to the following equations:

$$T(\lambda) = (1 - R) \exp\left(-\frac{4\pi kx}{\lambda}\right) \quad (4)$$

TABLE I
The Values of ΔE for PMMA Films Doped with Different Levels of Azo Dye and Different IT's

Wt % of azo dye	0.0	0.25	0.50	0.75				
IT(h)	–	–	–	0	0.5	2	4	6
ΔE (eV)	0.21	0.185	0.255	0.251	0.23	0.204	0.284	0.305

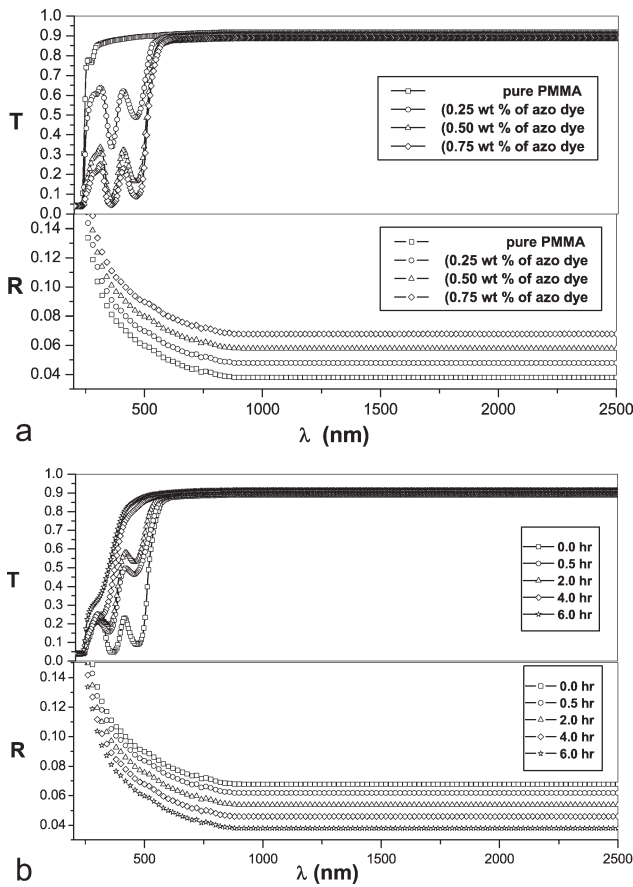


Figure 6 The spectral distribution of $T(\lambda)$ and $R(\lambda)$ for (a) pure PMMA and PMMA films doped with different contents of azo dye, (b) PMMA films doped with 0.75 wt % of azo dye irradiated with different IT's.

$$R(\lambda) = \frac{[(n - 1)^2 + k^2]}{[(n + 1)^2 + k^2]} \quad (5)$$

where k is the absorption index.

Figure 7 shows the dispersion curve $n(\lambda)$ in the wavelength range 500–2500 nm for the studied system. The observed spectra show that the refractive index decreases with increasing wavelength and reaches a nearly constant value at long wave length, suggesting a normal dispersion. Also, it is found that for the doped films, the value of n increases with increasing the azo dye doping level [Fig. 7(a)]. On the other hand, the value of refractive index decreases with increasing IT and reaches nearly to the value of unirradiated pure PMMA film [Fig. 7(b)]. Therefore, we can say that the increase in the value of n for PMMA films due to the effect of azo dye doping can be annihilated by UV-irradiation. The change of n is a criterion of structure change.

The obtained data of n can be analyzed to yield the long wavelength refractive index (n_∞) together

on the average interband oscillator wavelength (λ_o) and the average oscillator strength (S_o) for the present system using the dispersion equation. Using the single term Sellmeier oscillator,³² the relation between the refractive index n and λ is given by

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \quad (6)$$

where λ_o and n_∞ can be evaluated from the plots of $(n^2 - 1)^{-1}$ against λ^{-2} as illustrated in Figure 8.

Equation (6) can also be rewritten as³³

$$n^2 - 1 = \frac{S_o \lambda_o^2}{\left(1 - \frac{\lambda_o^2}{\lambda^2}\right)} \quad (7)$$

where $S_o = \frac{(n_\infty^2 - 1)}{\lambda_o^2}$. The values of $n_\infty^2 = \epsilon_\infty$, λ_o and S_o can be obtained for the studied system and are listed in Table II.

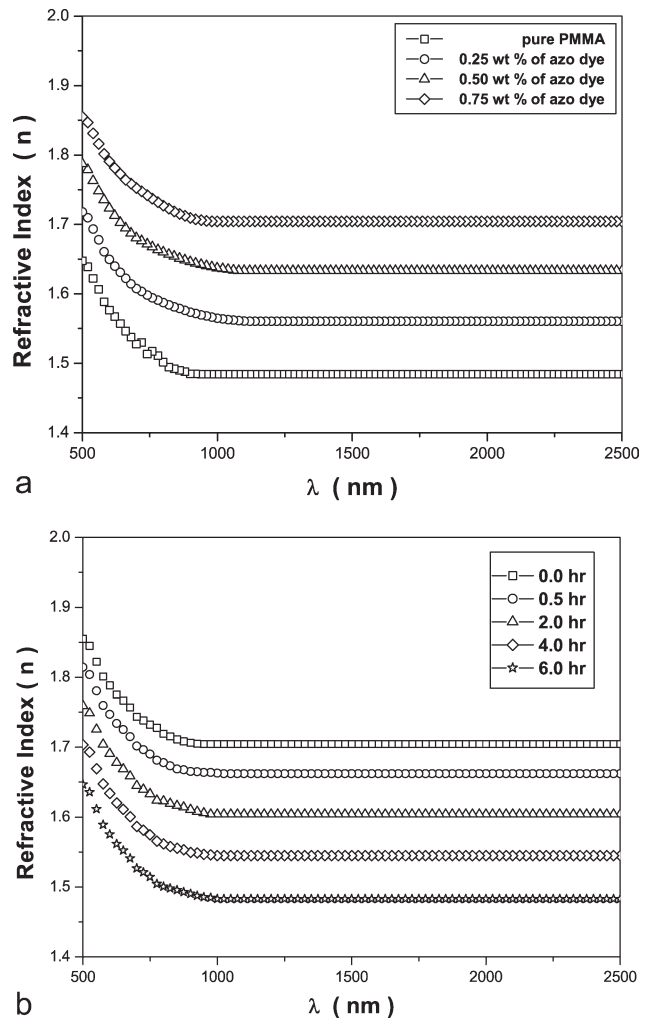


Figure 7 The dispersion curve of $n(\lambda)$ for (a) pure PMMA and PMMA films doped with different contents of azo dye, (b) PMMA films doped with 0.75 wt % of azo dye irradiated with different IT's.

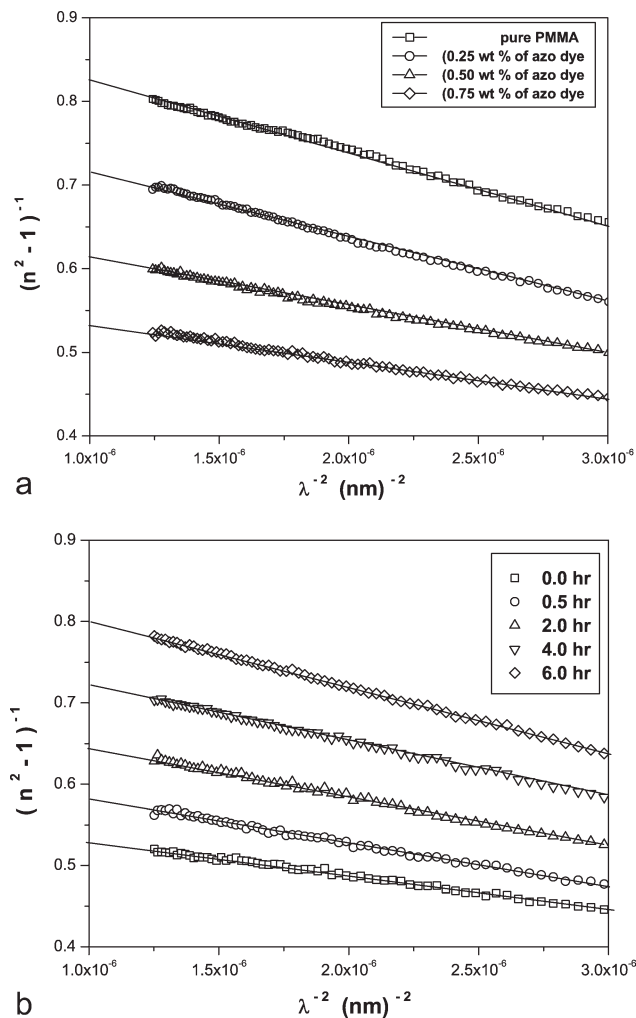


Figure 8 The plots of $(n^2 - 1)^{-1}$ versus λ^{-2} for (a) pure PMMA and PMMA films doped with different levels of azo dye, (b) PMMA films doped with 0.75 wt % of azo dye irradiated with different IT's.

Figure 9 shows the long wavelength refractive index (n_∞) of PMMA films doped with 0.75 wt % of azo dye as a function of IT. It is observed that n_∞ decreases with increasing IT and the photo-induced refractive index changes are very large. These changes show that the azo dye-doped PMMA films

are suitable to change refractive index efficiently by photo-irradiation. It has a potential applicability for optical devices which are based on channel waveguides. The changes in refractive index during photo-irradiation may be due to the following reasons: (1) The specific refraction of the photo-product, which well describe the changes in electronic structure, turned out to have less specific refractions compared to polymer matrix. This leads to the differences in the refractive index. (2) The photo-degradation in the polymer film indicates the density change, which leads to a decrease in the refractive index.

In the normal dispersion region (the transparent region), the refractive index dispersion has been analyzed using the single oscillator model developed by Wemple and DiDomenico.^{34,35} They introduced energy parameters E_d to describe the dispersion of the refractive index. In terms of the dispersion energy E_d and a single oscillator energy E_o , the refractive index at frequency ν can be expressed by the following equation:

$$n^2 - 1 = \frac{E_d E_o}{[E_o^2 - (h\nu)^2]} \quad (8)$$

where $h\nu$ is the photon energy. From this equation, E_o and E_d can be obtained and listed in Table II.

CONCLUSIONS

In this work, the results demonstrated significant modifications in the structure and optical properties in of the studied system. From these results, the following conclusions were drawn:

1. UV/VIS spectra show that: (a) the spectra of doped films contain two absorption peaks assigned to the chromophoric groups of azo dye. The intensity of these peaks increase with increasing the doping level and decreases with increasing IT. This can be interpreted on the

TABLE II
The Values of Some Optical Parameters for PMMA Films Doped with Different Levels of Contents of Azo Dye and Different IT's

Wt % of azo dye	0.0	0.25	0.5	0.75
IT(h)	—	—	—	0.0, 0.5, 2, 4, 6
E_g (eV)	4.492	4.87	4.782	4.683, 4.749, 4.802, 4.847, 4.892
n_∞	1.487	1.547	1.621	1.695, 1.647, 1.596, 1.543, 1.499
ϵ_∞	2.211	3.393	2.627	2.883, 2.713, 2.547, 2.381, 2.247
λ_o (nm)	322	329	300	286, 298, 304, 306, 321
E_o (eV)	3.885	3.762	4.117	4.239, 4.75, 4.492, 4.055, 3.986
E_d (eV)	4.7	5.234	6.707	7.895, 7.881, 6.732, 5.413, 4.814
$S_o \times 10^{15}/m^2$	1.165	1.287	1.805	2.283, 1.865, 1.667, 1.475, 1.2

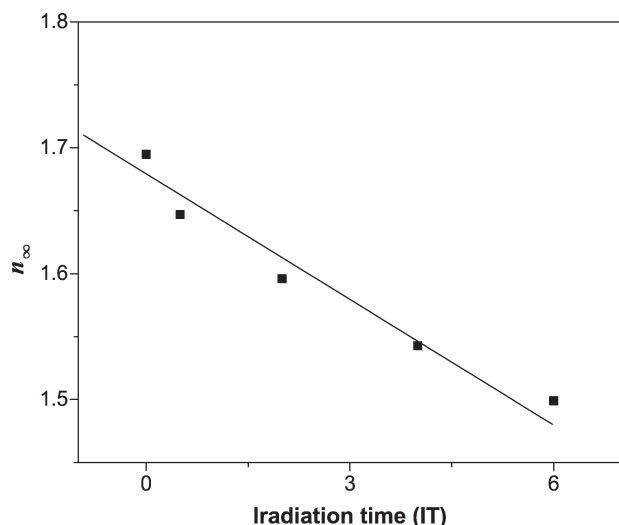


Figure 9 The dependence of n_{∞} on IT for PMMA film doped with 0.75 wt % of azo dye.

basis of photo-degradation of azo dye. (b) The analysis of the calculated values of E_g evidences the presence of induced energy states due to azo dye doping and another type of induced states depending on IT. (c) The width of the tail of localized states in the forbidden band gap for the studied system are calculated.

- The spectral distribution of both $T(\lambda)$ and $R(\lambda)$ in the wavelength range 200–2500 nm evidences the following: (a) The pure PMMA film is transparent and gives the normal dispersion region. On the other hand the doped films become transparent only at $\lambda > 500$ nm due to the presence of induced azo dye color centers in the polymer matrix. (b) For the irradiated films the intensity of absorption peaks decreases and vanishes at IT about 6 h (the film becomes transparent as undoped one). (c) The long wavelength refractive index (n_{∞}) increases with increasing doping level of azo dye while it decreases as IT increases. The increase in the values of n in PMMA films due to the effect of azo dye doping can be reduced by UV-irradiation. (d) The photo-induced refractive index changes suggest the applicability of PMMA films doped with azo dye for optical devices. (e) The optical parameters such as n_{∞} , ϵ_{∞} , λ_o , S_o , E_o , and E_d have been evaluated.

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