

Influence of UV-irradiation on the structure and optical properties of polycarbonate films

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Abstract

Polycarbonate films were prepared by casting technique. The absorption spectral analysis showed that the unirradiated PC has no absorption bands, while the irradiated films have two shoulder bands. This suggests that PC undergoes a photo-degradation process. The absorption coefficient and the optical energy gap (E_{opt}) have been obtained from indirect allowed transitions in K-space. It was found that, E_g decreases with increasing the irradiation time. The width of the tail of localized states in the band gap (ΔE) was evaluated using the Urbach edge method. The refractive index (n) was determined from the analysis of the transmittance data. Analysis of the refractive index (n) yields the values of the long wavelength dielectric constant (ϵ_∞), the average oscillator wavelength (λ_o), average oscillator strength (S_o), average oscillator energy (E_o), the refractive index dispersion parameters (E_o/S_o) and the dispersion energy (E_d). The dependence of refractive index on irradiation time has been discussed. It was found that the photo-induced refractive index changes are very large. These changes suggest the applicability of PC films in optical devices.

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1. Introduction

Organic polymers have received a considerable attention as materials for opto-electronics applications because of their processability and reasonable cost performances. Some organic polymers has already been applied to optical devices, such as optical fibers, micro lenses, liquid crystal display components and polymer light emitting diodes [1–3]. The possibility of organic polymers for opto-electronics applications is not limited, and developments of organic polymers have been more and more promoted.

Photo-chemical reactions in polymer films can induce various changes in physical properties of polymer films such as solubility, transparency, thickness, and refractive index [4]. The photo-chemically induced refractive index change in polymer films is an important method for controlling optical properties of polymers [5]. The photo-chemical reaction can induce larger refractive index modulation in polymer films and the modulation remains after the photo-reaction, leading to the permanent change in refractive index. Therefore, photo-chemically induced refractive index changes in polymer films have been attracted much attention for various applications, such as optical memories, switching devices, holographic image recording and waveguide lithography [6]. Recent publications [7–13] have discussed photo-induced refractive index changes of organic polymers containing photo-chromic dyes.

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In a previous work [14,15] the structural modifications and optical constants of PMMA films doped with different contents of iodine and metal chlorides were studied. The present work was undertaken to investigate the effect of UV-irradiation on the structure and optical properties of polycarbonate films.

2. Experimental procedures

The studied polycarbonate (PC) films were prepared by casting method. The commercial PC dissolved in dichloromethane at room temperature. The solution was left to reach a suitable viscosity and then casted in glass dishes and left to dry in a dry atmosphere at room temperature. The samples were transferred to an electric air oven held at 60 °C for 48 h to ensure the removal of solvent traces. The thickness of the obtained films was in the range 0.05–0.1 mm. The samples were stored in a dark medium to avoid direct exposure to light.

Ultraviolet–visible (UV/VIS) absorption and transmission spectra of the studied samples were carried out in the wavelength range 200–900 nm using a (Perkin–Elmer UV/VIS) spectrophotometer. Irradiation of the samples was carried out using a monochromatic light source of wavelength 254 nm from a low pressure mercury lamp Cole–Parmer (100 W). The distance between the light source and sample was 5.0 cm. The thermal effects of the UV lamp were compensated by regulating the sample temperature to be fixed around 303 K.

3. Results and discussion

3.1. Absorption spectra

The UV/VIS spectrophotometric scans were measured in the wavelength range 200–900 nm before and after UV-irradiation. The electronic absorption spectra of PC films irradiated at various time intervals (IT) are shown in Fig. 1. From this figure, it is clear to observe that the unirradiated PC has no absorption bands in the studied wavelength range. On the other hand, the observed spectra of irradiated films have two shoulder bands at about 315 and 355 nm suggests that PC undergoes a photo-chemical reaction. The two bands may be due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the carbonyl group, respectively. The intensity of these absorbance bands is changing with increasing the irradiation time, while its positions slightly shifted towards higher wavelength side as shown in Fig. 2. It is revealed that the intensity increases linearly with increasing IT. The obtained results can be successfully applied in radiation dosimeter measurements.

The appearance of the bands at 315 and 355 nm upon UV-irradiation can be interpreted on the basis of photo-

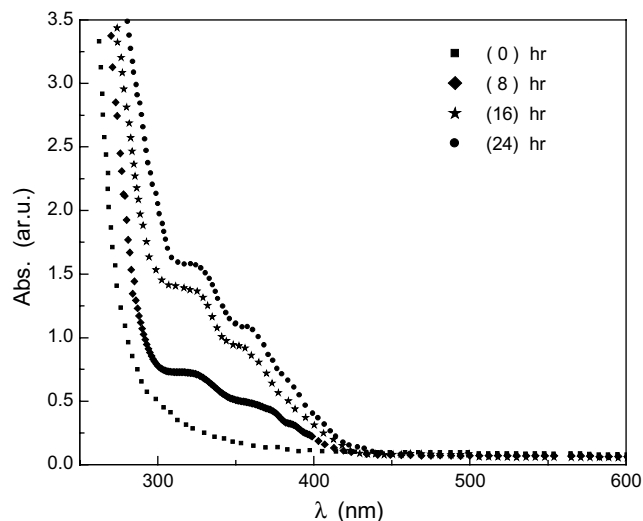


Fig. 1. The electronic absorption spectra for PC films before and after UV-irradiation.

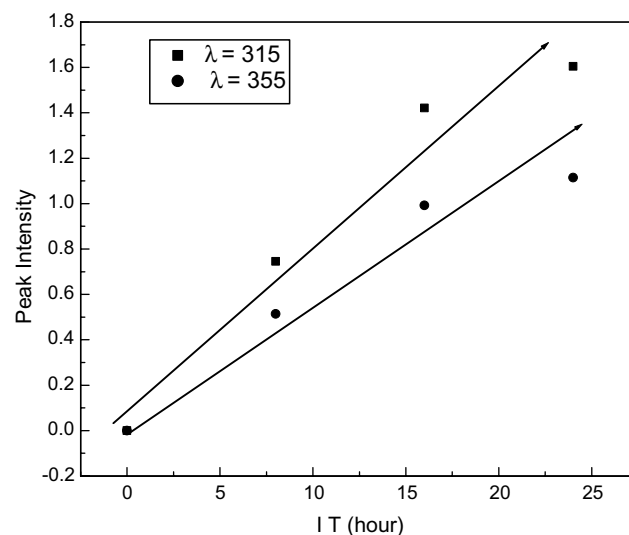
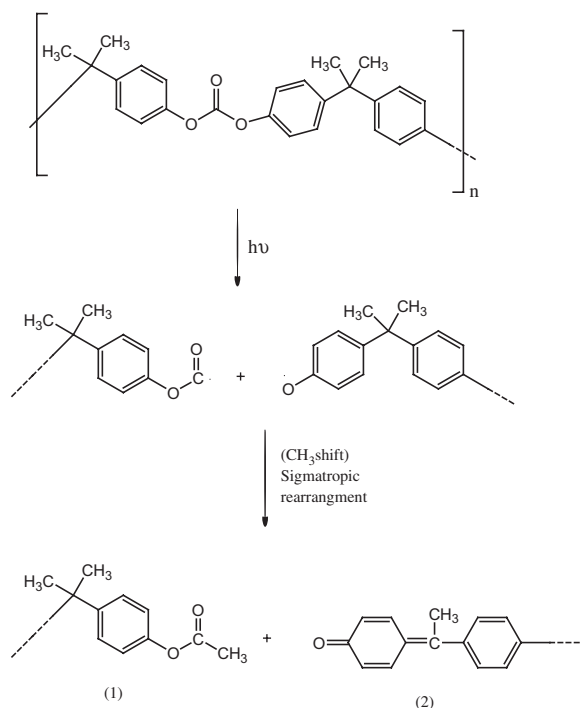


Fig. 2. The dependence of peak intensity on IT for PC films.

degradation of PC. The photo-irradiation of PC causes a bond-cleavage of the carbonate group followed by methyl radical migration (sigmatropic rearrangement) to obtain two new compounds (Scheme 1) containing methyl ester group (1) and quinoied structure (2). The results explain the visual observation of the change in color from transparent to yellow of the original film upon UV-irradiation. The yellow color confirms the formation of quinoied structure due to the resonance. The photo-degradation process proceeds as in Scheme 1.

3.2. Optical energy gap

It is clear that the UV/VIS absorption spectra for the present system (Fig. 1), characterized by a main absorp-



Scheme 1. Photo-degradation of PC.

tion edge for all curves are shifted towards longer wavelength upon UV-irradiation. This indicates that the forbidden band width decreases with increasing the exposure time of UV-irradiation. Also, Fig. 1 shows that there is an exponential rise in the absorption towards the edge, and in all curves 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 [16]:

$$\alpha(h\nu) = 2.303A/X, \quad (1)$$

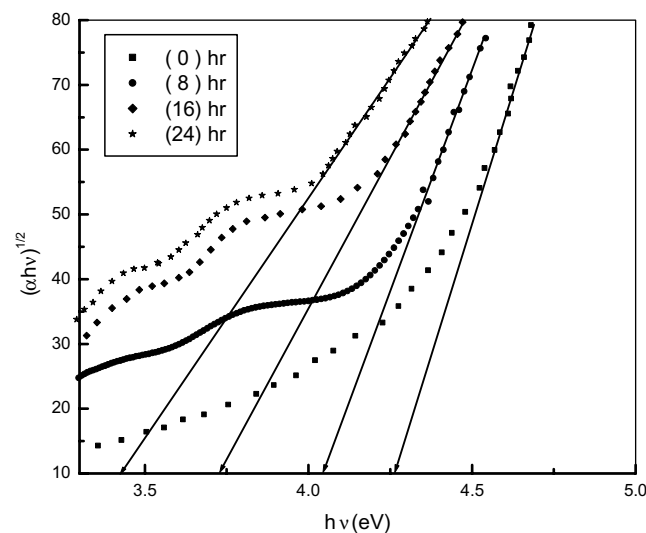
where X is the film thickness in cm and A is defined by $A = \log(I_0/I)$ where I_0 and I are the intensity of the incident and transmitted beams, respectively. The optical band gap was determined from the analysis of the spectral dependence of the absorption near the absorption edge. The absorption coefficient for non-crystalline materials has the following frequency dependence [17]

$$\alpha(h\nu) = A(h\nu - E_g)^r/h\nu, \quad (2)$$

where $h\nu$ is the energy of the incident photons, E_g is the value of the optical energy gap between the valence band and the conduction band, and r is the power, which characterizes the transition process in the K-space. Specially, r is 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The factor A depends on the transition probability and can be assumed to be constant within the optical frequency range. 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 $(h\nu)^{1/r}$ and pho-

ton 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. In other words, the minimum of the conduction band lies in a different part of K-space from the maximum of the valence band. Plots of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ near the absorption edge for PC films with different exposure times produce a linear fit over a wider range of h as shown in Fig. 3. Extrapolating the straight parts of these relations to the $h\nu$ axis yields the corresponding forbidden band width (E_g). The values of E_g for PC films before and after UV-irradiation with different exposure time are calculated from Fig. 3 and listed in Table 1. It was noticed that E_g decreased with increasing IT. This implied that the UV-irradiation leads to the appearance of the energy states induced upon UV-irradiated and depends on IT. Similar behavior recently observed on the spectral analysis of UV-irradiated PVA films filled with $MnCl_2$ and CrF_3 [18].

The absorption spectra (Fig. 1) 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 formed because of the extrinsic origins arising from defects or impurities, to

Fig. 3. The dependence of $(\alpha h\nu)^{1/2}$ on photon energy for PC films before and after UV-irradiation.Table 1
The dependence of E_g and ΔE for PC films on IT

IT (hours)	E_g (eV)	ΔE (eV)
0	4.18	0.297
8	3.96	0.334
16	3.62	0.358
24	3.36	0.383

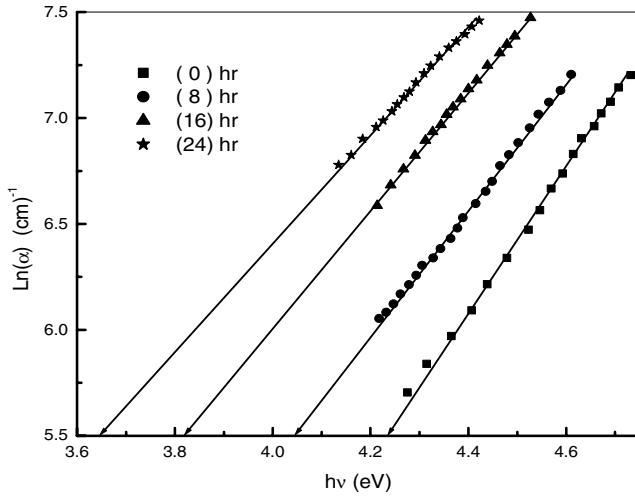


Fig. 4. The dependence of natural logarithm of α on photon energy for PC films before and after UV-irradiation.

extended states in the conduction band. The absorption coefficient $\alpha(\nu)$ is described by the Urbach formula [19],

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

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 [20]. The logarithm of the absorption coefficient $\alpha(\nu)$ was plotted as a function of the photon energy ($h\nu$) for PC films irradiated with different IT's as in Fig. 4. The values of the Urbach energy (ΔE) were calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of these curves. The values of ΔE for the studied system are calculated and listed in Table 1. The values of ΔE for PC films after UV-irradiation were found to be higher than that before irradiation. The increase of ΔE upon UV-irradiation indicates an increase in disorder in PC films.

3.3. Optical constants

The absorption coefficient $\alpha(\nu)$ is related to the optical transmission (T) and reflection (R) as follows:

$$\alpha(\nu) = \frac{1}{x} \log \left[\frac{(1-R)^2}{2T} + \frac{(1-R)^2}{\sqrt{(2T)^2 + R^2}} \right]. \quad (4)$$

A new computer program was developed for calculating the values of R in Eq. (4) at the studied wavelength region and the refractive index can be obtained from the following equation:

$$n = \left\{ \left[\frac{4R}{(R-1)^2} - K^2 \right]^{1/2} - \frac{R+1}{R-1} \right\}, \quad (5)$$

where K is the extinction coefficient which is related to the absorption coefficient (α) and the wavelength (λ) by

$$K = \frac{\alpha\lambda}{4\pi}. \quad (6)$$

Fig. 5 shows the dispersion of the refractive index $n(\lambda)$ for films of PC before and after UV-irradiation with different IT's. The observed spectra show that the refractive index decreases with increasing wavelength and reaches a nearly constant value at long wavelength suggesting a normal dispersion. The change of (n) is a criterion of structure change.

The obtained data of refractive index (n) can be analyzed to yield the long wavelength refractive index (n_∞) together with the average interband oscillator wavelength (λ_0) and the average oscillator strength (S_0) for the present system using the dispersion equation. Using the single term Sellmeir oscillator [21], the refractive index varies as

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_0}{\lambda} \right)^2, \quad (7)$$

where λ_0 and n_∞ can be evaluated from the plots of $(n^2 - 1)^{-1}$ against λ^{-2} illustrated in Fig. 6. Eq. (7) can also be expressed as [22]

$$n^2 - 1 = \left(\frac{(s_0 \lambda_0^2)}{(1 - \lambda_0^2/\lambda^2)} \right), \quad (8)$$

where $S_0 = (n_\infty^2 - 1)/\lambda_0^2$. The values of $n_\infty^2 = \epsilon_\infty$, λ_0 and S_0 can be obtained for PC films before and after UV-irradiation with different IT's and listed in Table 2.

Fig. 7 shows the long wavelength refractive index (n_∞) of PC films as a function of IT. It is observed that the refractive index decreases with increasing IT and the photo-induced refractive index changes are very large.

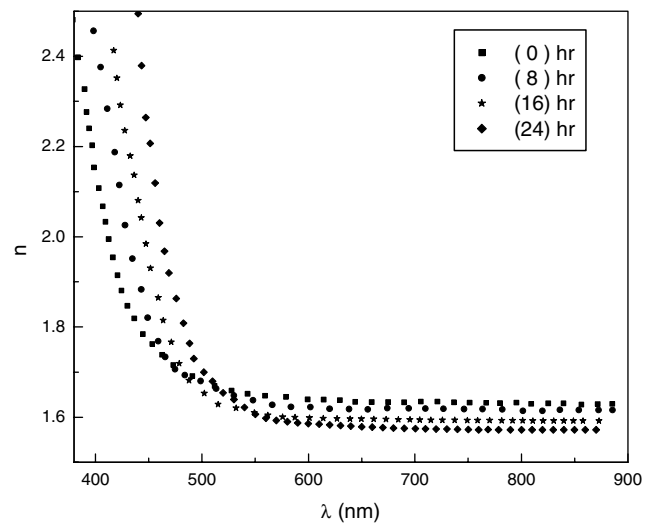


Fig. 5. The dispersion of n for PC films before and after UV-irradiation.

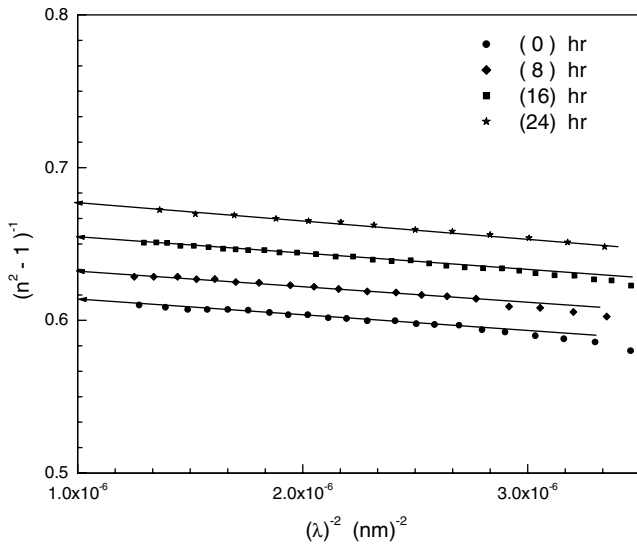


Fig. 6. The plots of $(n^2 - 1)^{-1}$ against λ^{-2} for PC films before and after UV-irradiation.

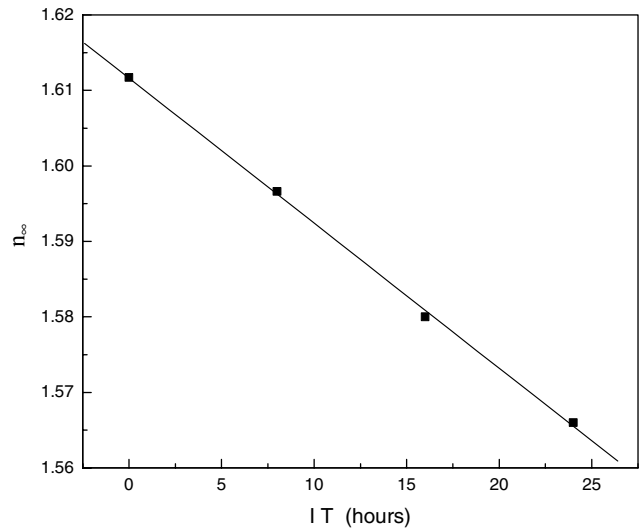


Fig. 7. The dependence of n_∞ on IT for PC films.

These changes show that the PC films are suitable to change refractive index efficiently by photo-irradiation. It has a potential applicability for optical devices, e.g., channel waveguides and photo-optical switching devices. The changes in refractive index during photo-irradiation may be due to the following reasons: (1) the specific refractions of the photo-products, 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.

The energy dependence of the refractive index for the films of PC before and after UV-irradiation can be fitted by the following dispersion relationship [23] as

$$n^2 - 1 = \frac{E_o E_d}{(E_o^2 - E^2)}, \tag{9}$$

where E_o is the single oscillator energy, and E_d is the dispersion energy. These dispersion parameters can be obtained by plotting $(n^2 - 1)^{-1}$ against $(hv)^2$. Fig. 8 shows such plots for the present system. The values of E_d and E_o obtained from the intercept and the slope of the curve and tabulated in Table 2.

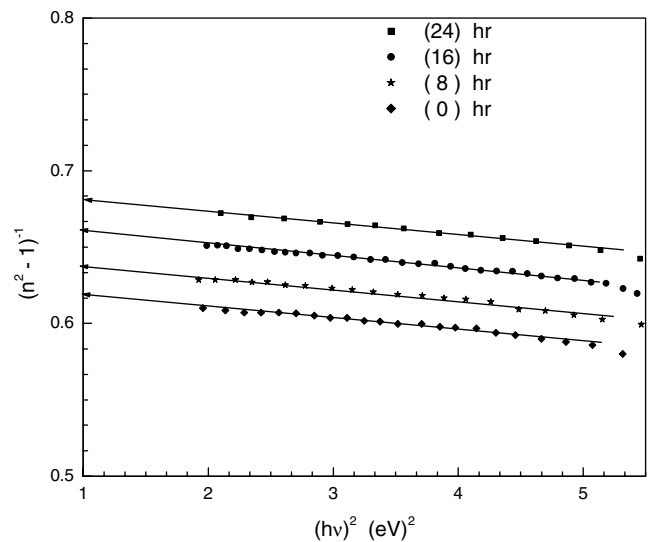


Fig. 8. The plots of $(n^2 - 1)^{-1}$ against $(hv)^2$ for PC films before and after UV-irradiation.

Another parameter deduced from the relation as in [24] using the determined (n) values as

$$n^2 = \epsilon_1 - \left(\frac{e^2}{\pi c^2}\right) \left(\frac{N}{m^*}\right) \lambda^2, \tag{10}$$

Table 2
The dependence of some optical parameters for PC films on IT

IT (hours)	n_∞	ϵ_∞	λ (nm)	S_0 ($10^{13}/m^2$)	E_o (eV)	E_d (eV)	ϵ_1	$(e^2/\pi c^2) * (N/m^*) * 10^{-8} (nm)^{-2}$
0	1.6117	2.598	136	8.68	9.14	14.6	2.694	3.14
8	1.5966	2.549	138	8.13	9.17	14.2	2.63	3.47
16	1.5800	2.496	137	8.00	9.32	13.94	2.563	4.15
24	1.5660	2.452	135	7.97	9.54	13.86	2.509	5.57

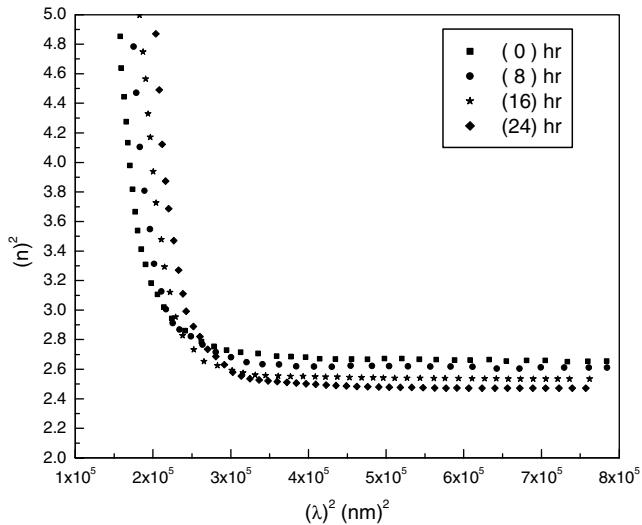


Fig. 9. The dependence of (n^2) on (λ^2) for PC films before and after UV-irradiation.

where ε_1 is the lattice dielectric constant and $(\frac{N}{m^3})$ is the ratio of the carrier concentration to the electron effective mass. The dependence of n^2 on λ^2 is linear at longer wavelength as shown in Fig. 9. The lattice dielectric constant and the values of the carrier concentration are obtained before and after UV-irradiation and are listed in Table 2.

4. Conclusions

Modification of the structure and optical properties of PC was carried out through UV-irradiation. PC irradiation leads to a decrease of optical energy gap and increasing in the Urbach energy. The decrease in optical energy gap could be due to the photo-degradation of PC and the formation of defects and clusters in the material. On the other hand the optical parameters

such as n_∞ , ε_∞ , λ_0 , S_0 , E_0 , E_d and ε_1 have been evaluated. It was found that the photo-induced refractive index changes suggest the applicability of PC films for optical devices.

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