

# OPTICAL PROPERTIES of PMMA / DYE COMPOSITE IRRADIATED with LASER

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**Abstract**—The effect of high energy irradiation on polymeric materials has been intensively studied over the past 70 years. The effect of exposure polymers to high energy irradiation will lead to some changes in its properties. In this paper, we report the laser- beam irradiation effect of different energies during the polymerization process of undoped and doped poly methyl methacrylate (PMMA) with different dye concentrations. The optical properties of PMMA (undoped and doped) polymerized by laser beam irradiation have been compared with those polymerized without laser beam irradiation in order to establish the superiority of the laser beam irradiation process over the conventional polymerization methods. The variation of the optical bulk absorption coefficient,  $\alpha$ , with wavelength is a unique parameter of the medium. It provides the most valuable optical information available for material identification. Two bands lie in the UV region (at  $\sim 330\text{nm}$  characterizing  $\pi-\pi^*$  absorption band of PMMA and  $550\text{nm}$  corresponding to the electronic transition to the first excited singlet state ( $S_0-S_1$ ) of the dye molecules) were detected from the absorption coefficient measurements in the range (200-1000nm). A percentage decrease of the absorption coefficient  $\alpha(\text{cm}^{-1})$  at the wavelength  $\sim 550\text{nm}$  for the different concentrations of dye doped in the PMMA (0.003, 0.005, and 0.01%wt) with laser energies was detected. The optical band gap (for direct allowed transition) was decreased with increasing dye concentrations meanwhile the band tail width increases with dye concentrations. Finally, one found that the value of both  $E_g$  and  $E_u$  increases for all tested samples by increasing laser beam energies during polymerization.

**Keywords**—poly methyl methacrylate dyes, laser irradiation, optical properties

## Introduction

In the recognition of the energy demand increase and fossil fuel depletion, as well as the environmental pollution from fuel combustion, the search and utilization of clean renewable energies is becoming one of the greatest challenges for our society. Solar

energy is the largest renewable energy source, which can potentially provide about 124 PW (PW=  $10^{15}$  Watts) energy globally, more than 8000 times of the total worldwide energy consumption in 2004 (15 TW,  $1\text{TW} = 10^{12}$  Watts).

The variation of the optical bulk absorption coefficient,  $\alpha$ , with wavelength is a unique parameter of the medium. It provides the most valuable optical information available for material identification.

Due to the relatively high material and production costs of solar cells and solar thermal absorbers, it is desirable to find alternative ways of reducing the cost of photovoltaic electricity and solar heat. One approach is to use concentrators that increase the irradiance on the modules or absorbers and thus the electricity or heat production per unit receiver area, which in turn reduces the needed for a given output.

The use of polymer alloys and blends and composites has grown constantly at 9% in the last 10 years and it is four times the growth rate of total plastic industry.

The effect of high energy irradiation on polymeric materials has been intensively studied over the past 70 years. These studies parallel the growth of polymeric materials and the availability of electrically generated radiation sources [1]. The effect of radiation on materials has importance in the areas of wire and cable insulation, heat shrinkable articles, curing of elastomers, plastics, paints, and inks electron beam lithography, medical sterilization, polymer property control and over space applications [2,3]. In general, the effects of exposure of polymers to high energy irradiation will lead to some change in the properties of the polymer.

Irradiation process is known to imitate several processes which include, e.g. displacement, mixing, radiation enhanced diffusion, and radiation enhanced segregation [4]. Further the investigation on radiation-enhanced short range ordering and clustering precipitation and self-diffusion has also been reported [5]. Laser-beam irradiation could be used during the polymerization process of polymeric materials to enhance their properties.

## Experimental

From Aldrich methylmethacrylate and rhodamine dye were purchased to be used in this study .Pure grad. benzoyl peroxide (BP) supplied by BDH (England) was used as an initiator. Thick films of pure PMMA with different dyes concentrations were prepared by thermal polymerization method [6].

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 4h then at 60°C for 72h, followed by a final drying at 80°C for 4h. After curing , the samples were removed and then cut as desired .The MMA monomer was doped with different concentrations of Rhodamine dye (0,0.003,0.005, and 0.01 wt%).

### Laser beam irradiation

A Laser beam source model Big Sky Nd-Yag Laser located at the National Institute of Laser Science, Cairo University was used for irradiating the samples during polymerization process at different energies (0-200J at 50J step).

The samples of PMMA doped with 0.003,0.005 and0.01 wt% dye were chosen to test the effect of Laser-beam irradiation energy after polymerization process on their optical properties.

All samples were cut into disc form of 0.1 cm thick and 1cm in diameter for characterization by measuring optical properties using Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer a-normal set up.

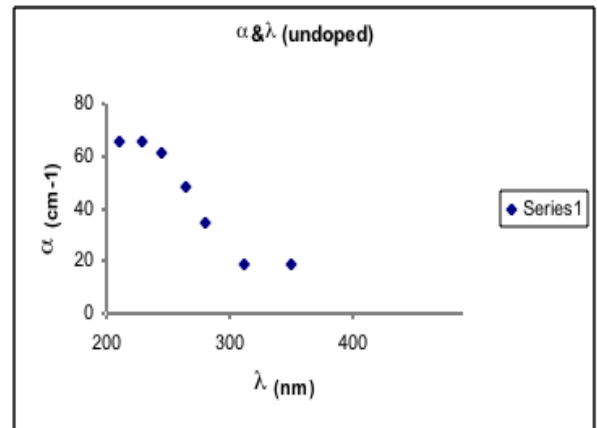
## Results and Discussion

### Optical properties of doped and undoped PMMA

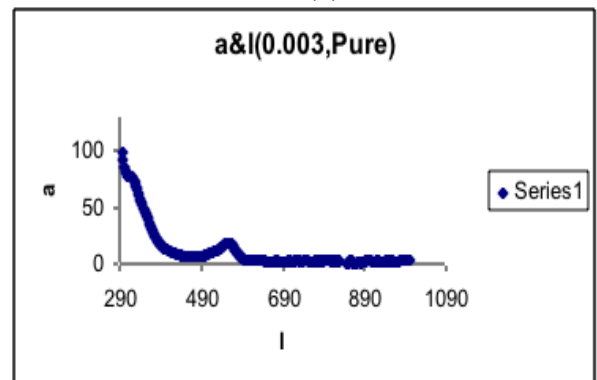
#### Optical Absorption spectroscopy

The variation of the optical bulk absorption coefficient,  $\alpha$ , with wavelength is a unique parameter of the medium .It provides the most valuable optical information available for material identification .The absorption coefficient  $\alpha$  can be expressed by equation (1) [7]:

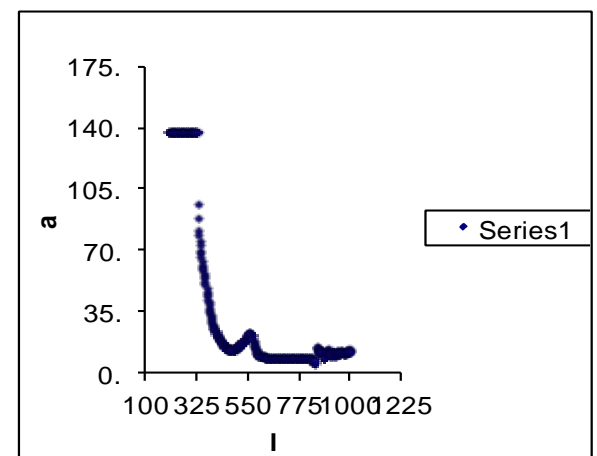
$$\alpha(\gamma) = 2.3 \log\left(\frac{I_i}{I_t}\right) / d = 2.3 \frac{P}{d} \quad (1)$$



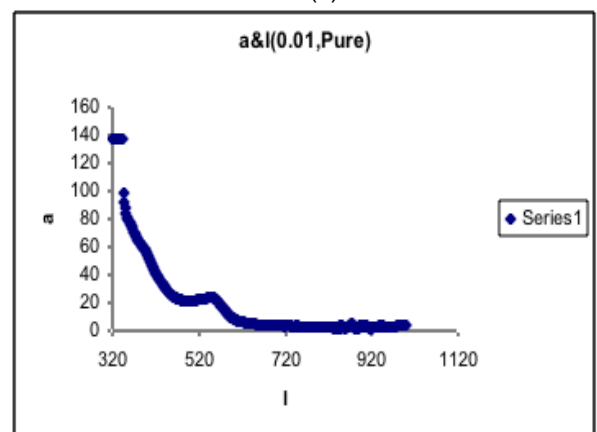
(a)



(b)



(c)



(d)

**Figure (1 a-d): The absorption spectrum at room temperature for un-doped and doped PMMA (with 0.003, 0.005 and 0.01% dye particles) un-irradiated samples**

Figure (1a-d) show the absorption spectrum at room temperature for un-doped and doped PMMA (with 0.003, 0.005 and 0.01% dye particles) un-irradiated samples. Where  $I_i$  and  $I_t$  are the intensities of the incident and transmitted light ;and  $d$  is the film thickness.

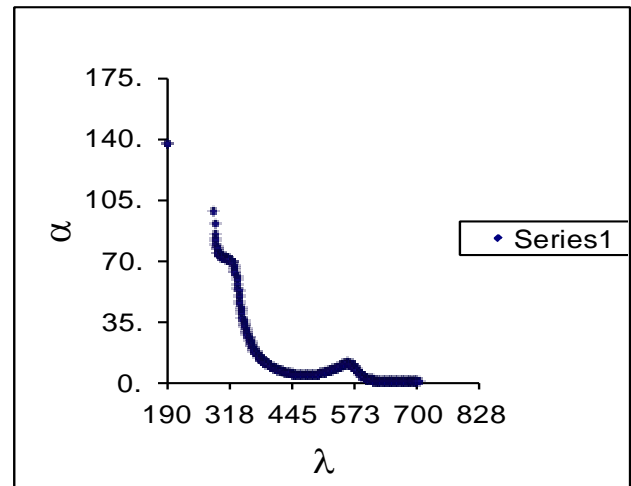
A major band lies in the UV region  $\sim 330\text{nm}$  characterizing  $\pi-\pi^*$  absorption band of PMMA. Moreover, from Figure (1a-d), it is apparently detected the presence of major band (550 nm) corresponding to the electronic transition to the first excited singlet state ( $S_0-S_1$ ) of the dye molecules [8].

In addition a slight increase in the absorption coefficient values by increasing the concentration of doped dye is observed, which reflects the increase of the number of absorbing species according to Beer's law [9].

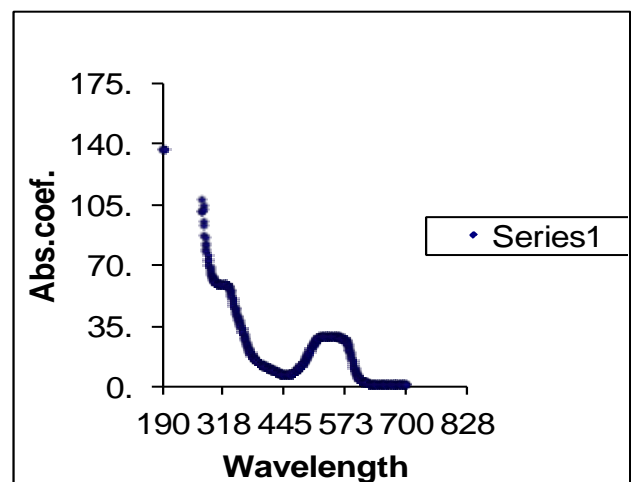
As seen in Figure (2a-c), after exposure of these doped PMMA samples to laser beam energies during polymerization, the peaks (at 330nm and 550nm) are red shifted (longer wavelength) and the peak height decreases with laser energies (Table 1).

**Table (1): Exposure of doped PMMA samples to laser beam energies during polymerization**

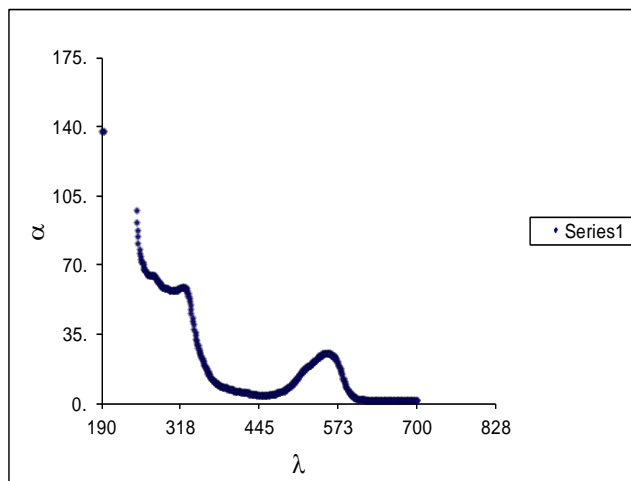
| Concentration of Rhodamine dye in PMMA | Laser energy (J) | First peak              |                             | Second peak             |                             |
|--|------------------|-------------------------|-----------------------------|-------------------------|-----------------------------|
|  |                  | $\lambda_{(\text{nm})}$ | $\alpha_{(\text{cm}^{-1})}$ | $\lambda_{(\text{nm})}$ | $\alpha_{(\text{cm}^{-1})}$ |
| 0.003                                  | 100              | 323                     | 55.97                       | 559                     | 11.75                       |
|  | 150              | 327                     | 57.91                       | 559                     | 11.75                       |
|  | 200              | 328                     | 58.5                        | 560                     | 25.43                       |
|  | 50               | 319                     | 75.8                        | 557                     | 18                          |
| 0.005                                  | 100              | 319                     | 75.8                        | 557                     | 19.43                       |
|  | 150              | 320                     | 44.11                       | 558                     | 25.71                       |
|  | 200              | 320                     | 68.26                       | 561                     | 26                          |
|  | 50               | 320                     | 71.13                       | 558                     | 17.38                       |
| 0.01                                   | 100              | 322                     | 75.82                       | 559                     | 19.36                       |
|  | 150              | 326                     | 75.79                       | 560                     | 31.418                      |
|  | 200              | 326                     | 76.82                       | 560                     | 30.6                        |



(a<sub>1</sub>)

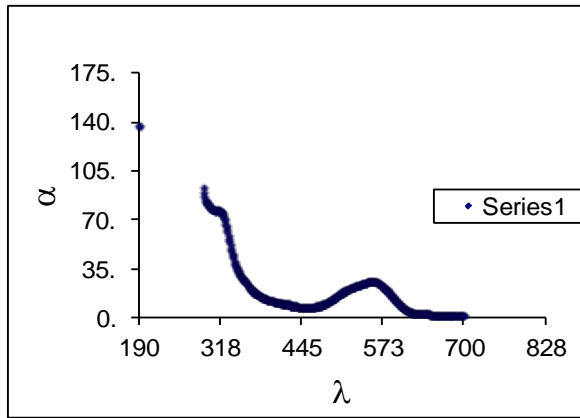


(a<sub>2</sub>)

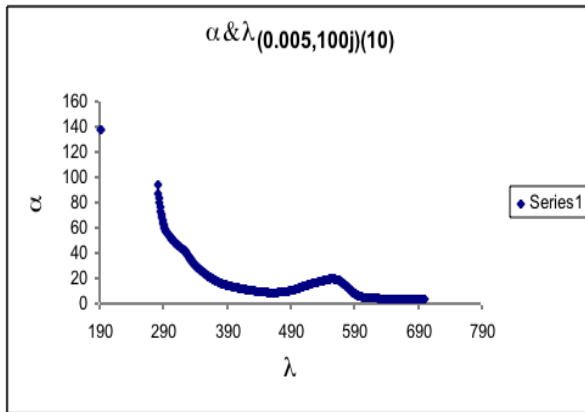


(a<sub>3</sub>)

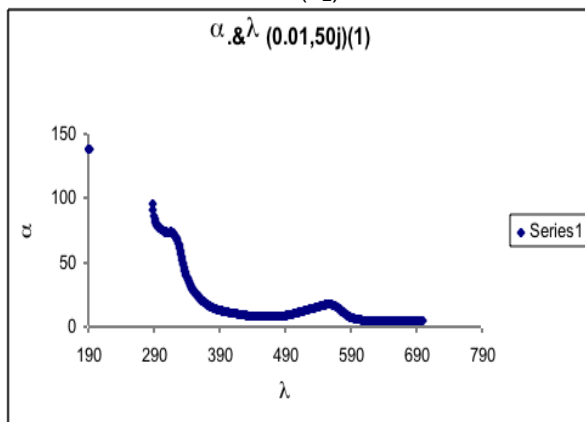
Figure (2 a(1-3))



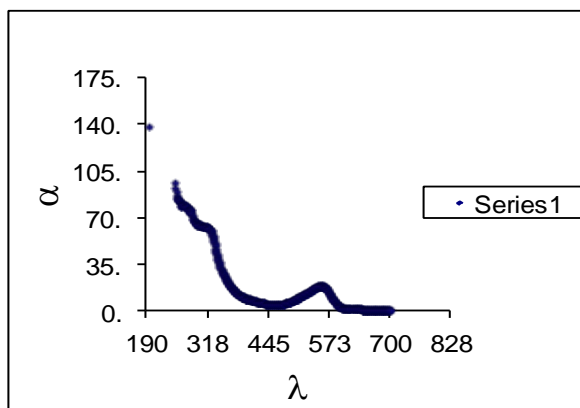
(b<sub>1</sub>)



(b<sub>2</sub>)

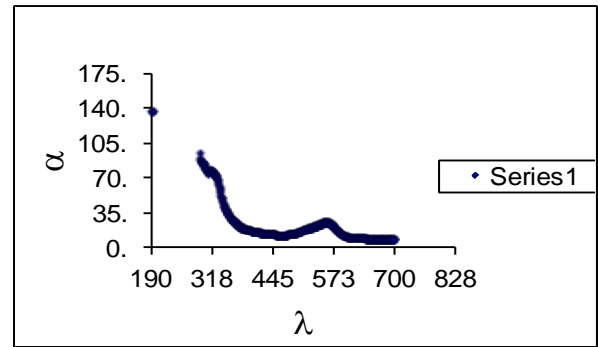


(b<sub>3</sub>)

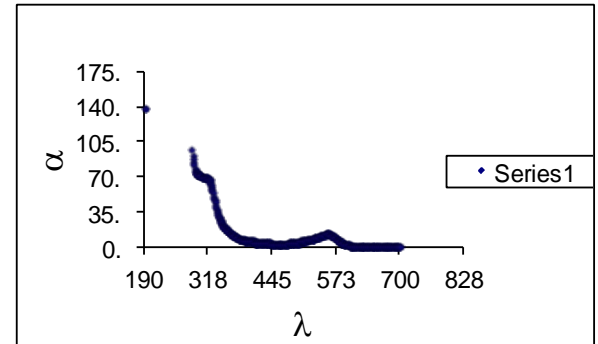


(b<sub>4</sub>)

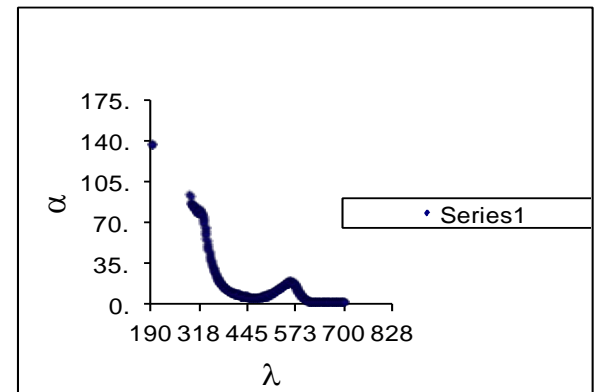
Figure (2 b(1-4))



(c<sub>1</sub>)



(c<sub>2</sub>)



(c<sub>3</sub>)

Figure (2 c(1-3))

**Figure (2a-c): The absorption spectrum at room temperature for doped PMMA (with 0.003, 0.005 and 0.01% dye particles) irradiated samples**

The percentage of decrease of the absorption coefficient  $\alpha(\text{cm}^{-1})$  at the wavelength  $\sim 550\text{nm}$  for the different concentrations of dye doped in the PMMA (0.003, 0.005, and 0.01%wt) CF Figure (2a-c) with laser energies tabulated in Table (2). This reduction can be attributed to photochemical decomposition of the dye caused by the absorption laser beam, since the absorbed quantum is higher than the energy of any bond molecule. Therefore a thin glass cover is recommended to protect the sample from the effect of UV radiation.

Mean while PMMA samples loaded with 0.003 and 0.01 showed an increasing behavior of its absorption coefficient with laser beam energies reflecting the rearrangement process of the dye molecules inside the PMMA matrix.

**Table (2): The percentage of change of the absorption coefficient  $\alpha(\text{cm}^{-1})$  at the wavelength  $\sim 550\text{nm}$  for different concentrations of dye doped in the PMMA (0.003, 0.005, and 0.01%wt) different laser energies.**

| Concentration of Rhodamine dye in PMMA | Laser energy (J) | Percentage of decrease (%) |                          |
|--|------------------|----------------------------|--------------------------|
|  |                  | First peak                 | Second peak              |
|  |                  | $\alpha(\text{cm}^{-1})$   | $\alpha(\text{cm}^{-1})$ |
| 0.003                                  | 100              | 0                          | 0                        |
|  | 150              | 16                         | 0                        |
|  | 200              | 15                         | 53                       |
|  | 50               | 0                          | 0                        |
| 0.005                                  | 100              | 0                          | 25                       |
|  | 150              | 41                         | 14                       |
|  | 200              | 9.9                        | 40.83                    |
|  | 50               | 0                          | 0                        |
| 0.01                                   | 100              | 13                         | -11.1                    |
|  | 150              | -6                         | -80                      |
|  | 200              | -7                         | 10                       |

**Interband Transitions**

One of the most productive methods in developing and understanding the structure and energy gap of amorphous non-metallic materials is the measurement of the optical absorption spectra.

When a quantum of radiation is absorbed by a material the absorption coefficient  $\alpha$  (which its calculated values are found to lie in the range  $1 \leq \alpha \leq 10^4 \text{ cm}^{-1}$ ) as a function of photon energy for simple parabolic band can be expressed by equation (2):

$$\alpha(\gamma) = 2.3 \log\left(\frac{I_i}{I_t}\right) / d = 2.3 \frac{P}{d} \quad (2)$$

Where Z is a constant,  $E_g$  is the optical band gap of the specimen and r is an index having the values of 2, 3, 1/2 and 3/2, depending on the nature of electronic transition responsible for the absorption [10].

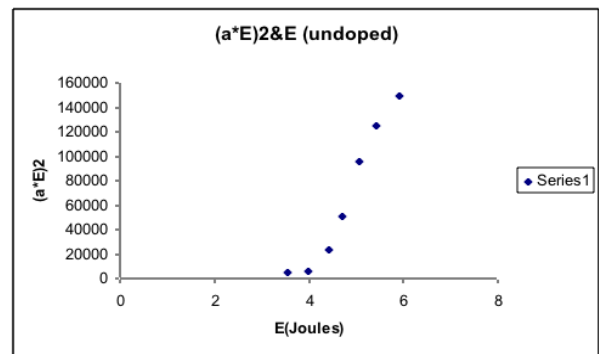
The absorption spectra clarifies an extending tail for the lower photon energies the band edge, which can be described by an equation (3) [11,12].

$$\alpha E = Z(E - E_g)^r \quad (3)$$

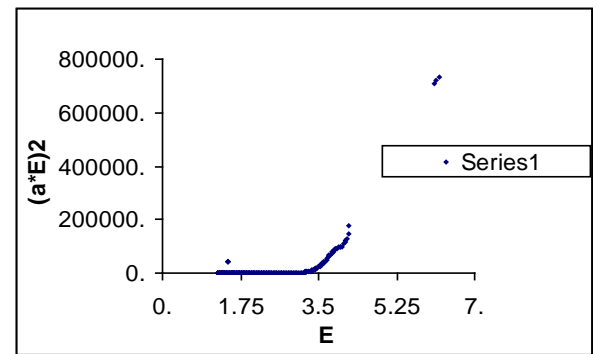
Where  $E_u$  is the energy of Urbach corresponding to the width of the band gap, the values of  $E_u$  were calculated as the reciprocal gradient of the linear portion of the plot.

Figure (3a-d) illustrates the dependence of  $(\alpha E)^2$  on the photon energy E(ev), for doped and un doped PMMA, which brought in to view a linear behavior that can be considered as an evidence of the direct

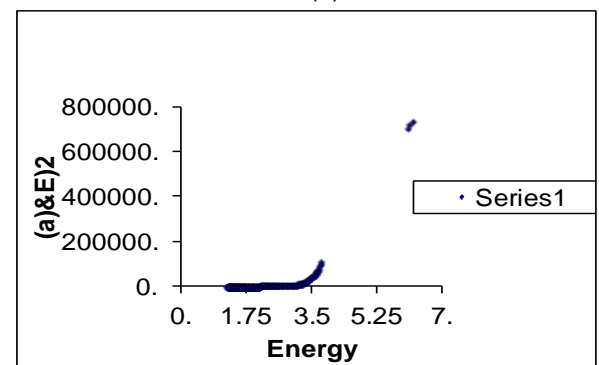
transition(i.e. for  $r = 1/2$ ) [13,14]. The optical gap was estimated from the intercept on the energy axis of the linear fit of the large data of the plot [15].



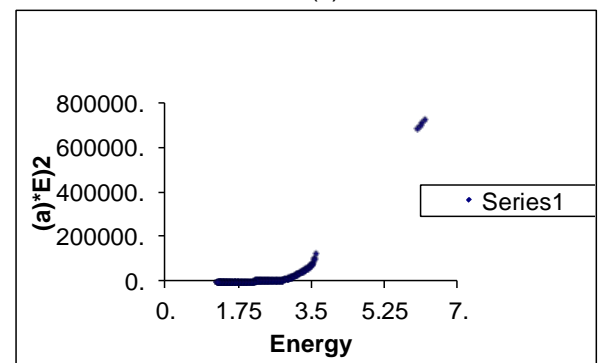
(a)



(b)

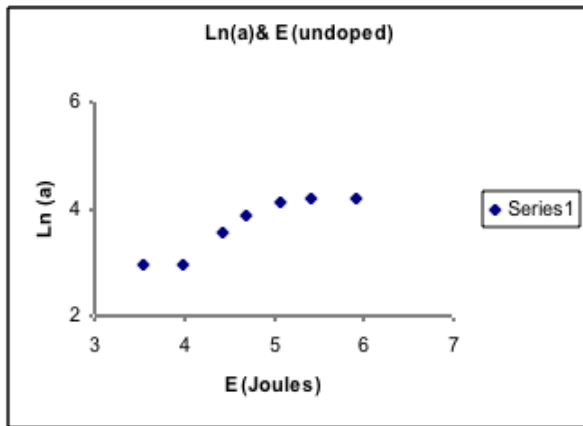


(c)

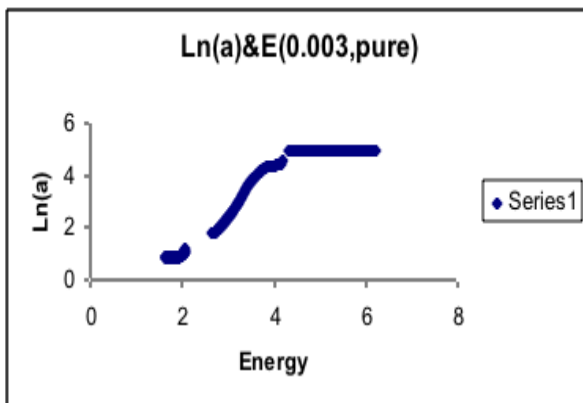


(d)

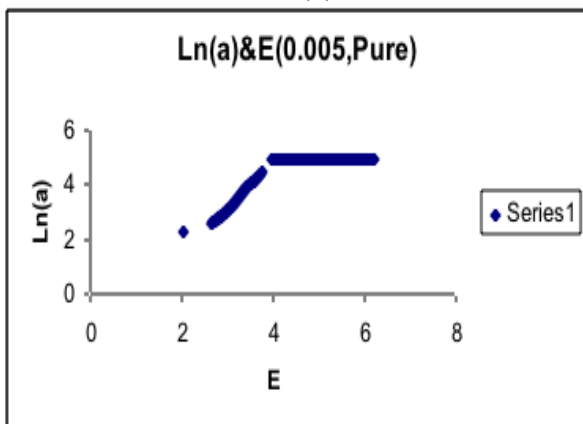
**Figure (3a-d): The plot of  $(\alpha E)^2$  versus photon energy E (ev), for doped and un-doped PMMA**



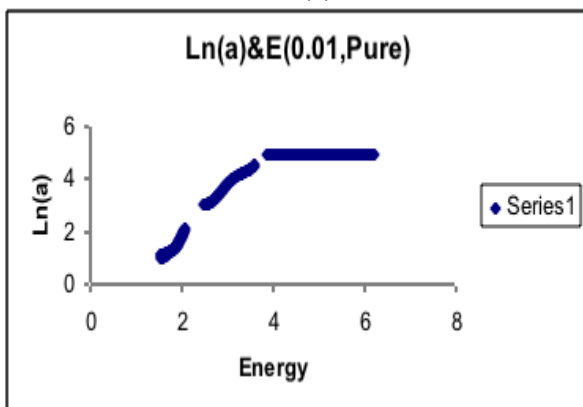
(a).



(b)



(c)



(d)

Figure (4 a-d): The plot of  $(\ln\alpha)$  versus photon energy  $E$  (ev), for un-doped and doped PMMA

Moreover, figure (4a-d) shows the plot of  $(\ln\alpha)$  versus photon energy  $E$ (ev), for doped and un doped PMMA.

Tables (3) and (4), summarized the optical parameters ( $E_g, E_u$ ) of undoped and doped PMMA respectively.

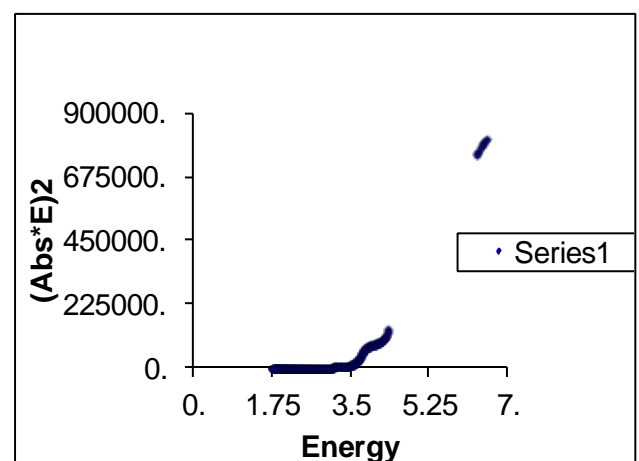
Tables (3): The optical parameters ( $E_g, E_u$ ) of undoped PMMA

| Concentration of Rhoda mine dye in PMMA | Before exposure to laser |            |
|---|--------------------------|------------|
|   | $E_g$ (ev)               | $E_u$ (ev) |
| 0.0                                     | 4                        | 0.14       |
| 0.003                                   | 3.6                      | 0.46       |
| 0.005                                   | 3.3                      | 0.61       |
| 0.01                                    | 3.1                      | 0.63       |

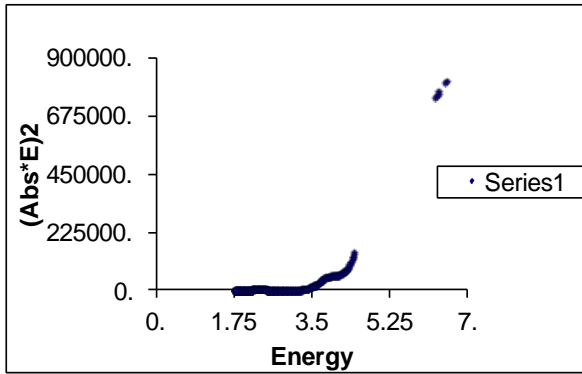
It is observed from Table (4) that with increasing concentration of the doped dye, the value of  $E_g$  decreased and  $E_u$  increased. This could be interpreted on the bases of Tich et al assumption[16], that the dependence of  $E_g$  on the sample preparation doesn't match with  $E_u$  values because the sample having a narrower band gap expected to have a wider band tail.

Moreover, the change in  $E_u$  is properly affected by potential fluctuations associated with the polymer structure but not the change in  $E_g$  because the initial and final states are practically has the same potential.

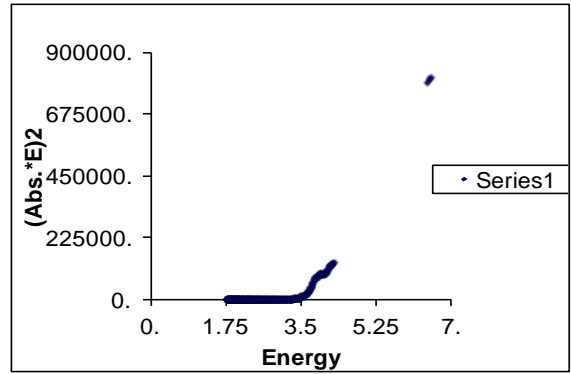
PMMA samples doped with 0.003, 0.005 and 0.01 dye concentrations were irradiated by different energies of laser beam (50, 100, 150 and 200J) and their  $(\alpha E)^2$  versus  $E$ (ev) are shown in Figure (5a-c), and their  $\ln(\alpha)$  versus  $E$ (ev) are shown in Figure (6a-c).



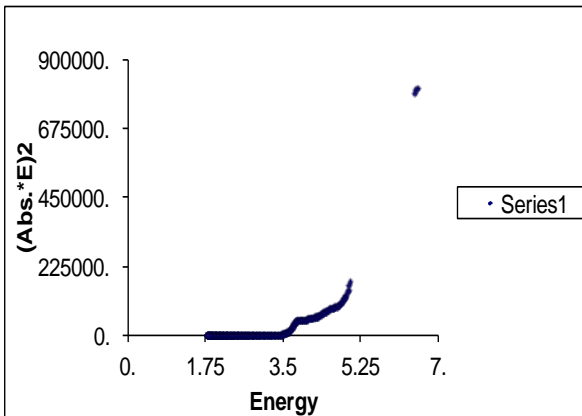
(a<sub>1</sub>)



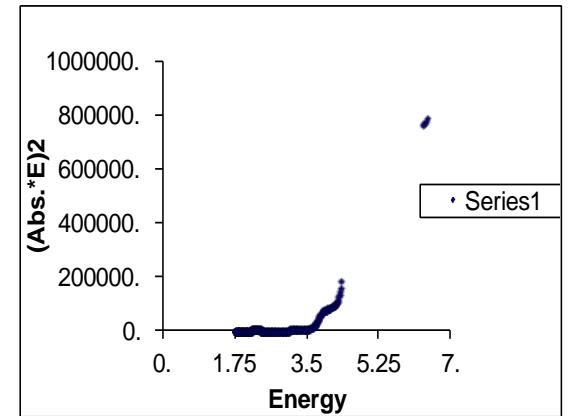
(a2)



(b3)



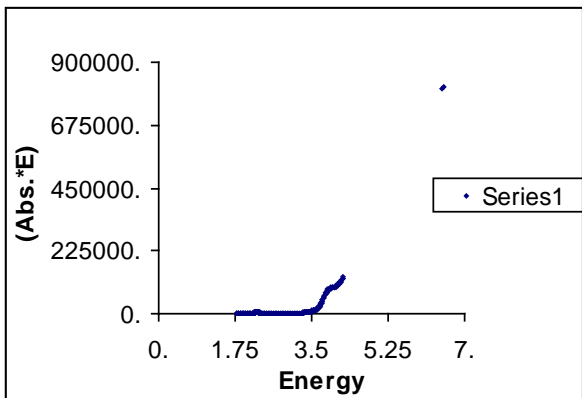
(a3)



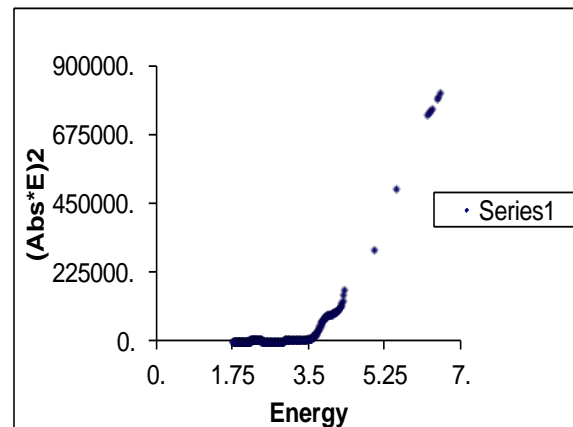
(b4)

Figure (5a<sub>1-3</sub>)

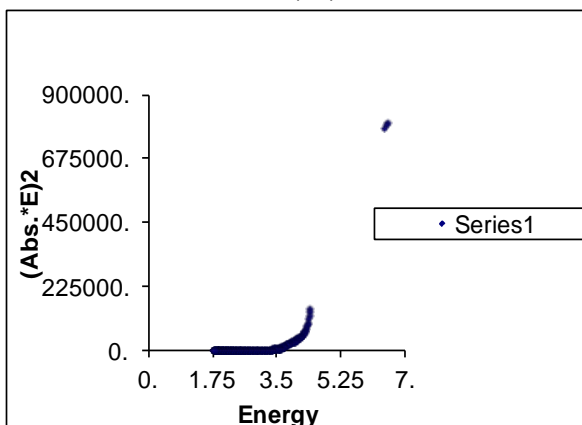
Figure (5b<sub>1-4</sub>)



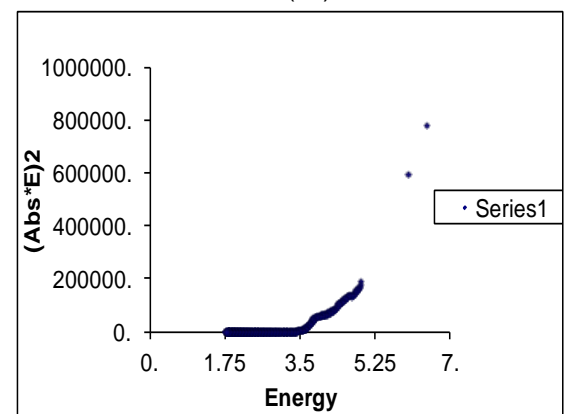
(b1)



(c1)

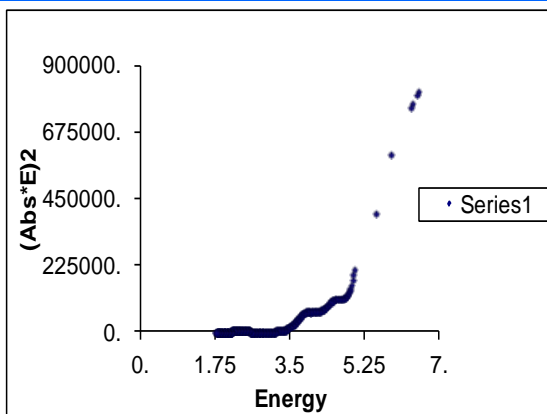


(b2)

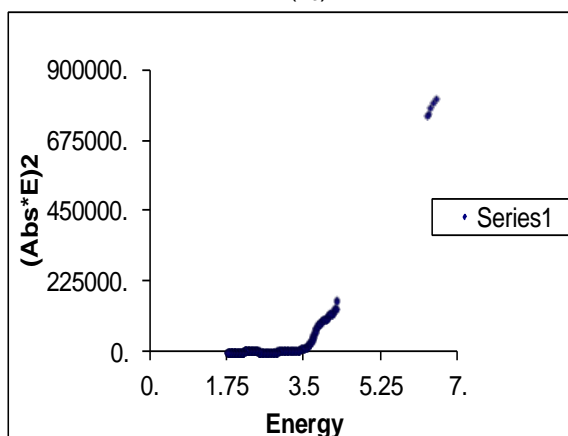


(c2)





(c<sub>3</sub>)



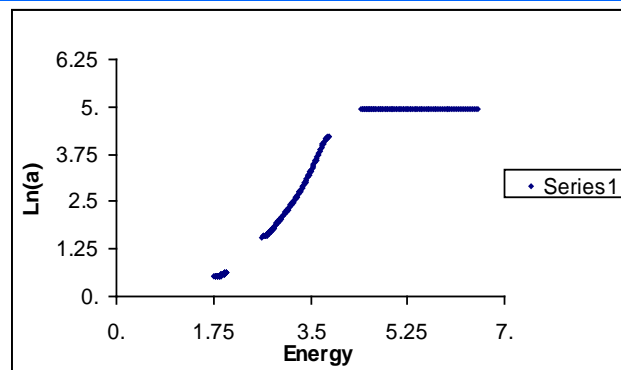
(c<sub>4</sub>)

Figure (5c<sub>1-4</sub>)

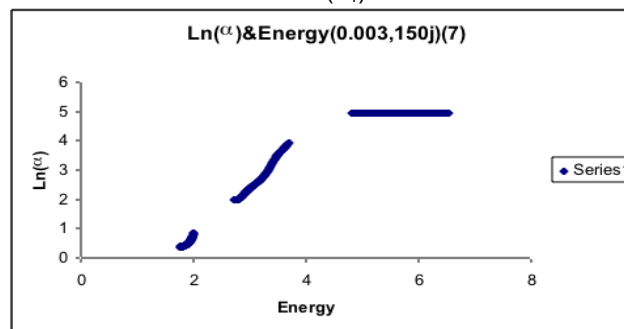
Figure (5a-c): PMMA samples doped with 0.003, 0.005 and 0.01 dye concentrations were irradiated by different energies of laser beam (50, 100, 150 and 200J) and their  $(\alpha E)^2$  versus E(ev)

Table (4): The optical parameters ( $E_g, E_u$ ) of doped and irradiated PMMA

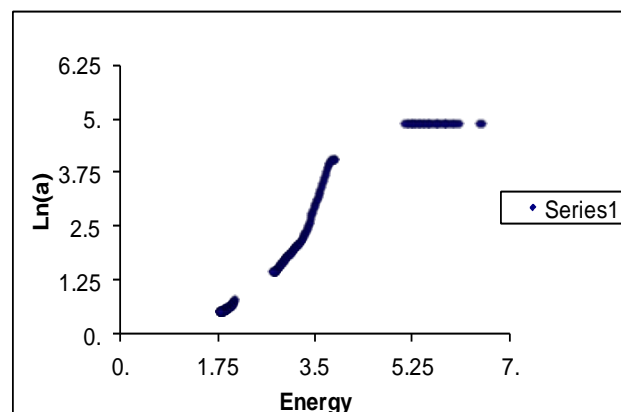
| Concentration of Rhoda mine dye in PMMA | Laser energy | After exposure to laser |            |
|---|--------------|-------------------------|------------|
|   | (J)          | $E_g$ (ev)              | $E_u$ (ev) |
| 0.003                                   | 100          | 3.8                     | 0.44       |
|   | 150          | 3.9                     | 0.497      |
|   | 200          | 4.5                     | 0.59       |
|   | 50           | 4                       | 0.51       |
| 0.005                                   | 100          | 4.1                     | 0.56       |
|   | 150          | 4.2                     | 0.647      |
|   | 200          | 4.2                     | 0.61       |
|   | 50           | 3.85                    | 0.527      |
| 0.01                                    | 100          | 4.47                    | 0.53       |
|   | 150          | 4.5                     | 0.533      |
|   | 200          | 3.73                    | 0.61       |



(a<sub>1</sub>)

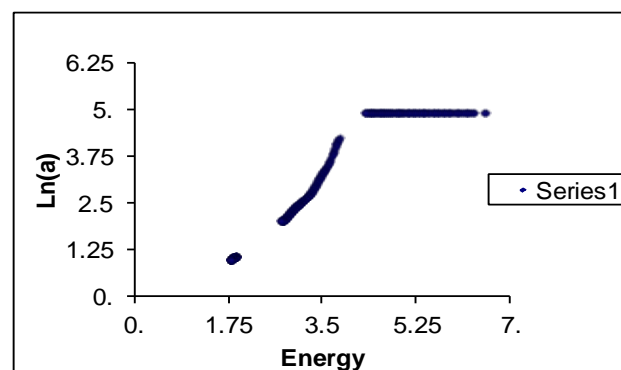


(a<sub>2</sub>)



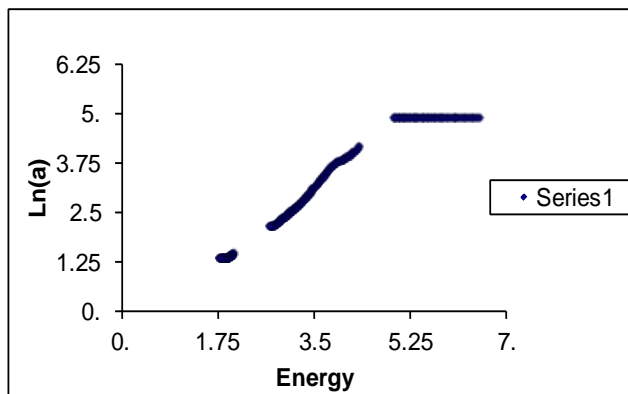
(a<sub>3</sub>)

Figure (6a<sub>1-3</sub>)

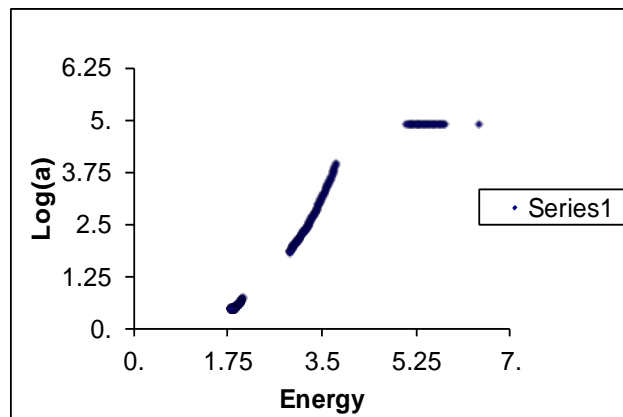


(b<sub>1</sub>)

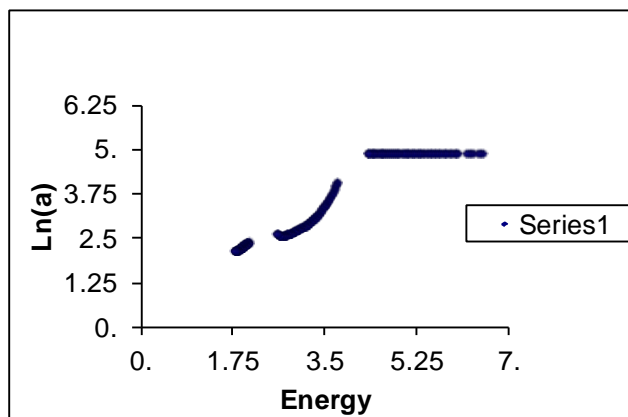




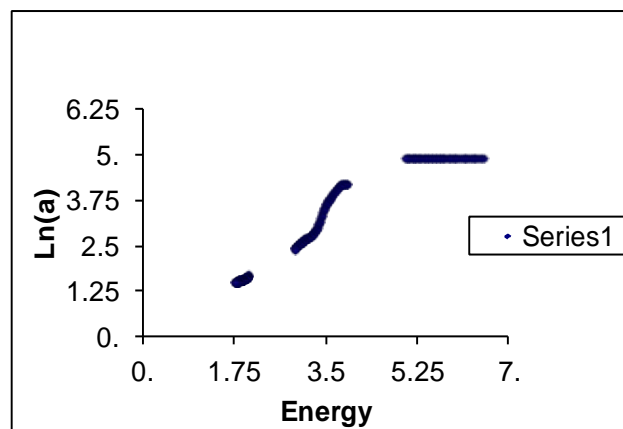
(b<sub>2</sub>)



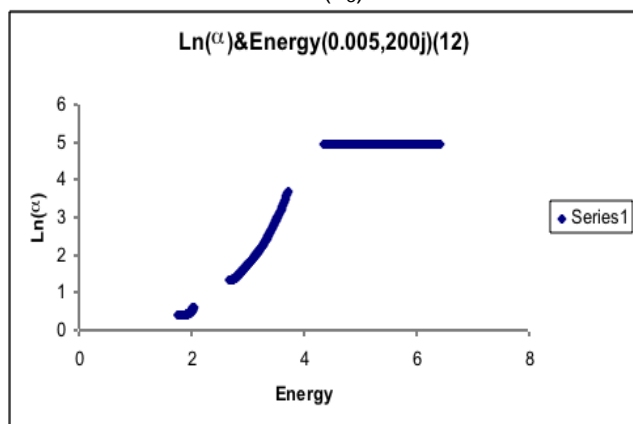
(c<sub>2</sub>)



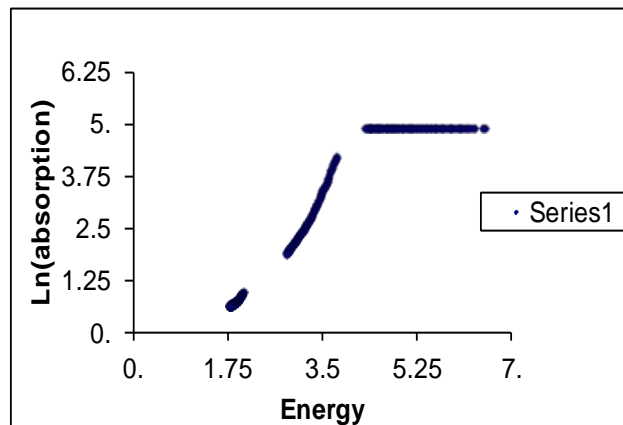
(b<sub>3</sub>)



(c<sub>3</sub>)



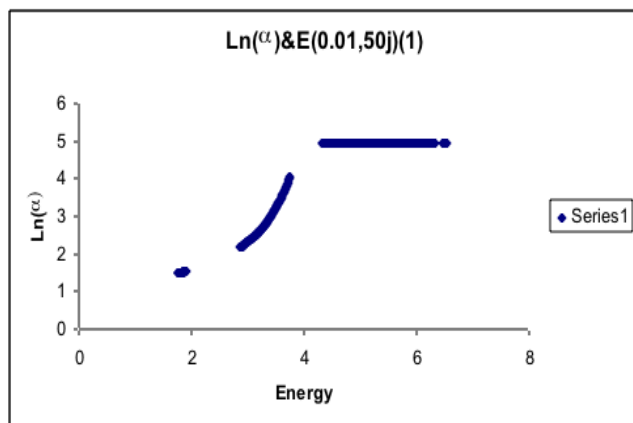
(b<sub>4</sub>)



(c<sub>4</sub>)

Figure (6b<sub>1-4</sub>)

Figure (6c<sub>1-4</sub>)



(c<sub>1</sub>)

**Figure (6a-c): PMMA samples doped with 0.003, 0.005 and 0.01 dye concentrations were irradiated by different energies of laser beam (50, 100, 150 and 200J) and their Ln( $\alpha$ ) versus E(ev)**

The behavior is obviously linear fit over a wide range of photon energy, and also the values of  $E_u$  which is calculated as the reciprocal slope of the obtained straight line from the relation between  $\ln \alpha$  versus E (ev).

Table (3.6) illustrates that the values of  $E_g$  increased by increasing the laser energy and that can be attributed to the increase in the disorder caused by

the presence of structural defects, which is known to increase the width of localized states thus reduce the value of the optical gap[17], on the other hand, the values of  $E_g$  increased by increasing the laser beam energy exposed to the sample.

**Table (5): The values of  $E_g$  by different laser energies**

| Concentration of Rhodamine dye in PMMA | Laser energy (J) | $E_g$ (ev) |
|--|------------------|------------|
| 0.003                                  | 100              | 3.7        |
|  | 150              | 3.9        |
|  | 200              | 4.5        |
|  | 50               | 3.5        |
| 0.005                                  | 100              | 4          |
|  | 150              | 3.6        |
|  | 200              | 3.7        |
|  | 50               | 3.5        |
| 0.01                                   | 100              | 4          |
|  | 150              | 4.5        |
|  | 200              | 3.4        |

So, dye particles increase the value of  $E_g$  as well as the energies of laser beam. And the 550 nm peak shifts to higher wave length with both laser energy and dye concentration.

**Conclusion**

From the forgoing results and discussion one may conclude that:

Optical absorption edge and optical energy gab (direct) showed a shift toward lower energies with increase dye concentration. The laser irradiation energies during polymerization leads to a significant shift in both optical absorption edge and optical energy gab towards higher energies.

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