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### Optical Spectroscopic Studies of Perylene Dye Doped in Copolymer of ST/MMA as Solar Collector

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## Optical Spectroscopic Studies of Perylene Dye Doped in Copolymer of ST/MMA as Solar Collector

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*Spectral characteristic of perylene dye doped in copolymer of ST/MMA was studied. The changes in the optical absorption spectrum and optical parameters including the band tail width and band gap energies for the samples were investigated before and after irradiation by  $\gamma$ -ray and also after a continuous exposure to filtered and UV radiation for 10 h. The study was extended to calculate the rate constants of photodegradation and the fluorescence quantum yield of the samples.*

**Keywords:** absorption spectra, fluorescence, gamma radiation, perylene, photostability

### INTRODUCTION

The fluorescent solar collector, FSC, appears to be promising for low cost solar energy conversion into electrical energy [1]. The operation of FSC is based on the absorption of solar radiation in a collector containing fluorescent species in which the emission bands have little or no overlap with the absorption bands. The emission light is trapped by total internal reflection and concentrated at the edges of the collector, which is usually a transparent material. There are some factors that

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are desirable in the development of FSC, such as the high extinction coefficient of the molecules of the used dye, strong fluorescence properties, and a high photostability [2].

In the present article, a trial was carried out to make a detailed characterization of the chosen dye. The measurements made include optical absorption spectrum, fluorescence quantum yield together with the photostability of perylene dye embedded in copolymer of ST/MMA. The changes in the optical absorption spectrum and the optical parameters including the band tail width and band gap energies for the samples have been demonstrated.

## EXPERIMENTAL

### Materials

From Aldrich, perylene dye (molecular weight of  $996 \text{ g}\cdot\text{mol}^{-1}$ ), styrene, ST, and methylmethacrylate, 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

Different concentrations of perylene dye were doped in copolymer of 50/50 ST/MMA by a thermal polymerization process [2]. The polymerization of perylene/copolymer was performed with BP as an initiator (1 wt%) and the mixture was poured into a glass mold. The mold was then immersed in a water bath at  $80^\circ\text{C}$  for 4 h and then at  $60^\circ\text{C}$  for 72 h, followed by a final drying at  $80^\circ\text{C}$  for 4 h.

### UV Radiation

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

### Fluorescence Spectra

Spectrofluorimeter, Shimadzu RF-5031, PC Japan, was used for recording the fluorescence spectra of the samples at room temperature.

### Absorption Spectra

The absorption spectra was recorded using a Perkin-Elmer Lambda 4B spectrophotometer from 200 nm up to 900 nm.

## Gamma Irradiation

A  $^{60}\text{Co}$  gamma source model, GB150 type B, manufactured by the AEA of Canada and located at the NCRRT, Egypt, was used for irradiating the samples at a dose rate of 9.23 kGy/h and the temperature during the irradiation was about 40°C.

## RESULTS AND DISCUSSION

### 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 Eq. 1 [3]:

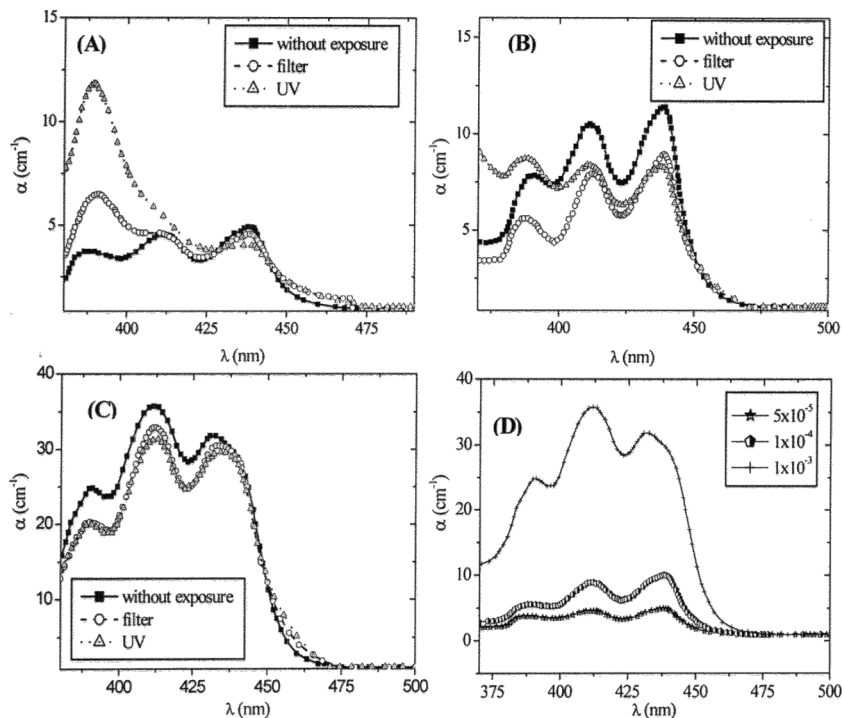
$$\alpha(\nu) = 2.3 \log(I_0/I)/d = 2.3 A/d \quad (1)$$

where  $I_0$  and  $I$  are the intensity of the incident and transmitted light;  $A$  is the absorbance; and  $d$  is the film thickness.

Copolymer of 50/50 ST/MMA has been selected from the previous study [4] of different concentrations of copolymer ST/MMA to be a good host matrix for perylene dye because of its enhancement properties with respect to its homo-polymers.

The optical absorption spectra for copolymer of 50/50 ST/MMA doped with different concentrations of perylene dye before and after exposure to filtered and UV radiation was recorded from 300 nm up to 500 nm and plotted in Figure 1. From Figure 1d, the presence of major bands at 390, 412, and 432 nm are apparently detected, corresponding to the electronic transition to the first excited singlet ( $S_0 \rightarrow S_1$ ) of the dye molecules [5–6]. In addition, an increase in the absorption coefficient values was observed by increasing the concentration of doped dye, which is credited to the increased number of the absorbing species according to Beer's law, in agreement with Reference [7].

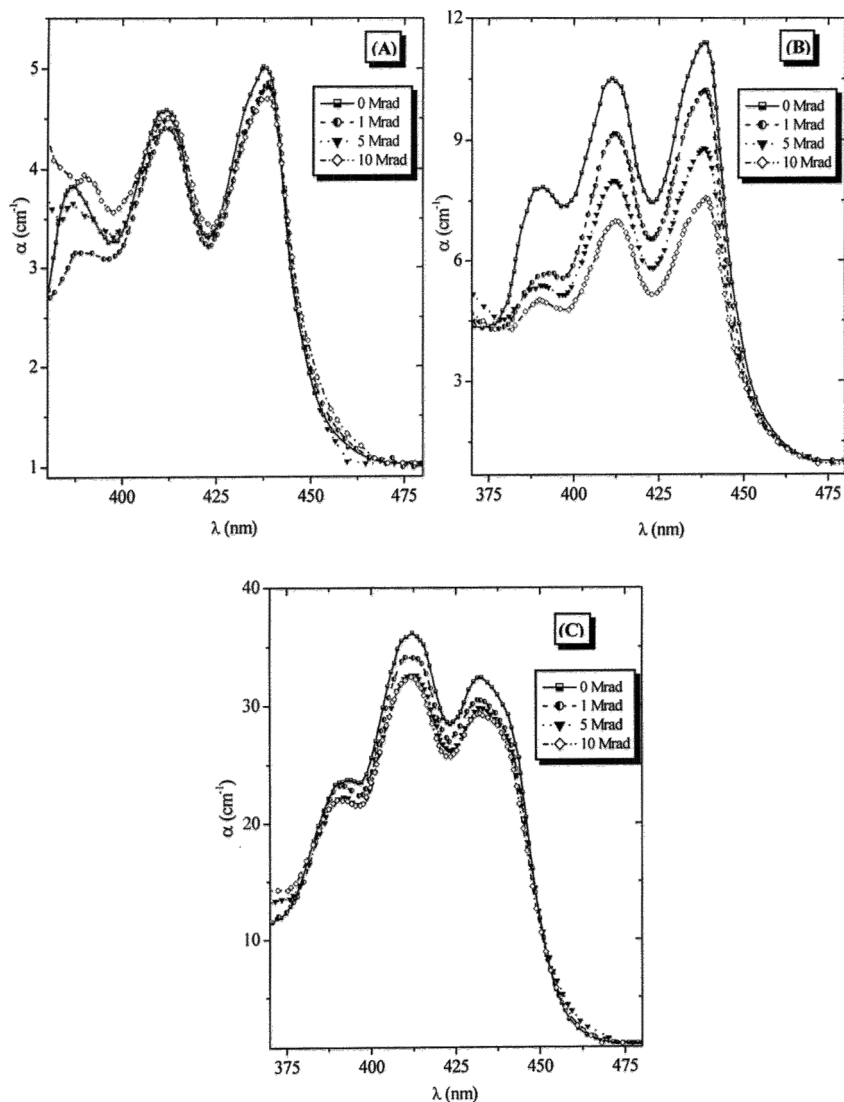
The percentages of decrease of the absorption coefficient  $\alpha$  ( $\text{cm}^{-1}$ ) at the wavelength  $\approx 438$  nm for concentrations of perylene dye  $5 \times 10^{-5}$  and  $1 \times 10^{-4}$  and at the wavelength  $\approx 432$  nm for concentration of perylene  $1 \times 10^{-3}$  doped in the copolymer are 6.9%, 21.3%, and 4.12%, respectively after a continuous exposure to filtered light for 10 h but they are 18.36%, 27.02%, and 6.77%, respectively, for the same samples after a continuous exposure to UV light for 10 h. This reduction can be attributed to photochemical decomposition of the dye caused by the absorption of UV part of the xenon arc lamp spectrum, because the absorbed



**FIGURE 1** Absorption spectrum of perylene dye doped in copolymer of 50/50 ST/MMA before and after exposure to filtered and UV radiation for different concentrations (A)  $5 \times 10^{-5}$ , (B)  $1 \times 10^{-4}$ , and  $1 \times 10^{-3}$  mol.% for 10 h. Also, the absorption spectrum of perylene dye doped in copolymer of 50/50 ST/MMA with different concentrations before exposure to radiation (D).

quantum is higher than the energy of any molecular bond in agreement with Reference [5]. In addition, there is an important fact that most synthetic, that is, PS and PMMA, and natural polymers degrade when exposed to UV radiation due to the presence of photosensitive impurities and/or abnormal structural moieties that are introduced during polymerization such as peroxides, which are implicated in polymer degradation [8]. Therefore the photo-stability of the samples can be increased by covering them by thin glass cover to protect them from the effect of UV radiation, in agreement with Reference [6].

Moreover, Figure 2 illustrates the optical absorption spectra for perylene dye doped in copolymer of 50/50 ST/MMA at different concentrations after irradiation by  $\gamma$ -ray with different doses 1, 5, 10 Mrad. From Figure 2, a depreciation of the intensity of the absorption spectrum is



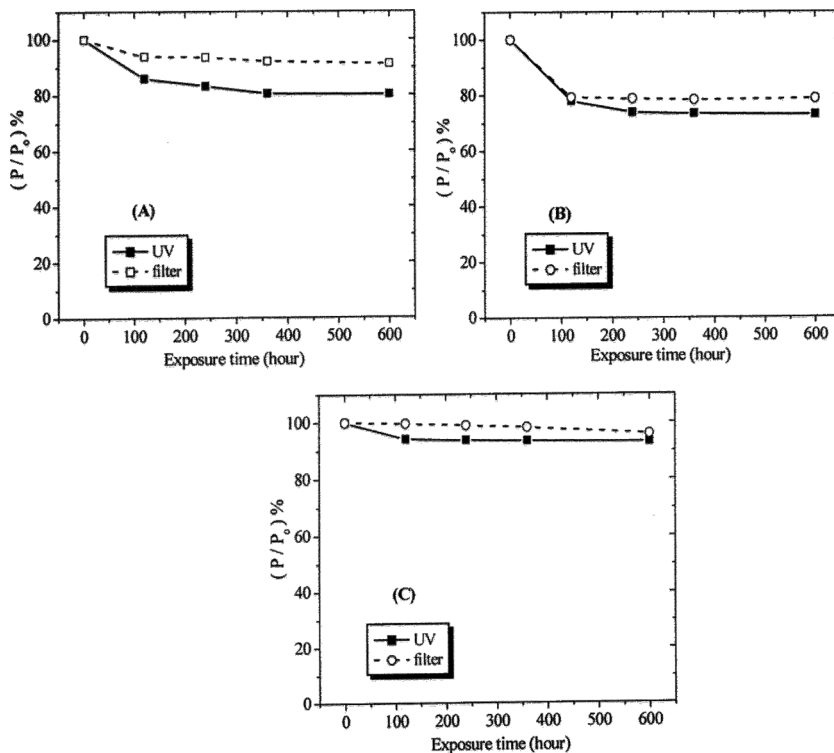
**FIGURE 2** Absorption spectrum of perylene dye doped in copolymer of 50/50 ST/MMA with different concentration (A)  $5 \times 10^{-5}$ , (B)  $1 \times 10^{-4}$ , and (C)  $1 \times 10^{-3}$  mol. % after irradiation by  $\gamma$ -ray with different doses 0, 1, 5, and 10 Mrad.

apparent for each sample that can be attributed to the idea that when the radiation from  $\gamma$ -ray interacts with a polymer material, its energy is absorbed by the polymer molecules and active species such as radicals

are produced, thereby initiating various chemical reactions. One of these reactions is degradation, which the copolymer suffers from due to the presence of a methyl group corresponding to PMMA in spite of the presence of aromatic polymer of PS that is usually radiation resistant [9].

### Photostability and Degradation

The perylene dye doped in 50/50 ST/MMA copolymer was exposed indoors to UV-Vis radiation and the percentage of change in the absorption spectra (Photodegradation,  $P/P_0\%$ , where  $P = P_0$  at  $t = 0$  min) was achieved at different times during irradiation period 600 min of filtered and UV light and plotted as seen in Figure 3.



**FIGURE 3** The photodegradation curves of perylene dye doped with different concentrations in copolymer of 50/50 ST/MMA (A)  $5 \times 10^{-5}$ , (B)  $1 \times 10^{-4}$ , and (C)  $1 \times 10^{-3}$  after exposure to filtered and UV radiation for 600 min.

**TABLE 1** Rate Constant,  $k$  and Half Life Time,  $t_{1/2}$ , of the Photodegradation of Perylene Dye Doped with Different Concentrations in Copolymer of 50/50 ST/MMA

Concentrations of Perylene doped in 50/50 ST/MMA mol. %	After exposure to filtered radiation for 600 minutes		After exposure to UV radiation for 600 minutes	
	Rate constant $\text{min}^{-1}$	Half life time, $t_{1/2}$ min	Rate constant $\text{min}^{-1}$	Half life time, $t_{1/2}$ min
$5 \times 10^{-5}$	$1.3 \times 10^{-4}$	5326	$3.2 \times 10^{-4}$	2164
$1 \times 10^{-4}$	$3.0 \times 10^{-4}$	2286	$4.3 \times 10^{-4}$	1597
$1 \times 10^{-3}$	$0.7 \times 10^{-4}$	9711	$0.9 \times 10^{-4}$	7693

Rate constants of photodegradation of dye can be estimated according to Eq. 2 [10]:

$$k = \frac{2.3}{t} \log \frac{A}{A_0} \quad (2)$$

where  $A_0$  and  $A$  are the absorption before and after irradiation,  $t$  is the time of exposure in minutes, and  $k$  is the rate constant. The kinetics of Photodegradation, including  $k$  and half life time  $t_{1/2}$  are listed in Table 1. It is observed that the effect of UV radiation is more than that of filtered radiation on the photodegradation of perylene dye, as mentioned previously. From the earlier results it can be concluded that the filtration of light from UV causes more photo-stability for doped dye and therefore the sample has a long life.

### Interband Transitions

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. In high absorption region, the absorption coefficient  $\alpha$  for a direct transition in the crystalline and non-crystalline materials is given by Eq. 3 [11]:

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

where  $B$  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.



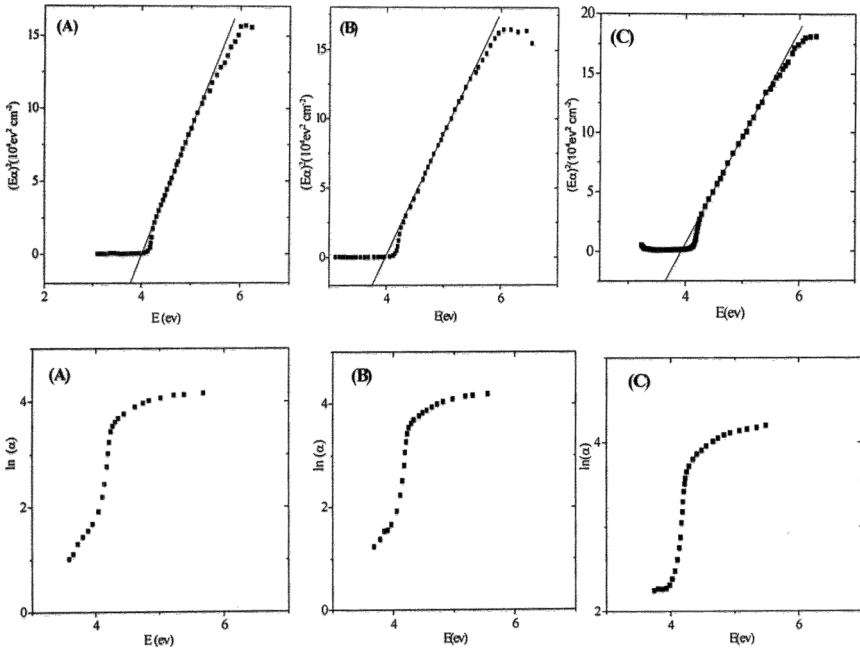
The absorption spectra indicate an extending tail for lower photon energies below the band edge, which can be described by Eq. 4 [12–13]:

$$\alpha = \alpha_0 \exp(E/E_u) \quad (4)$$

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.

To estimate a fundamental role involved in the degradation of the samples, the band gap energies  $E_g$  and the band tail width  $E_u$  are estimated from Eqs. 3 and 4, respectively, before and after a continuous exposure to UV and filtered light for 10 h.

Figure 4 illustrates the values of  $E_u$  and also the plots of  $(\alpha E)^2$  versus  $E$  (eV) before exposure to light, which have a linear fit over a wide range of photon energy. This linearity indicates the existence of direct allowed transitions and the extrapolation of this linear dependence to the abscissa yields the corresponding values of  $E_g$ . The values of  $E_g$



**FIGURE 4** The dependence of  $(\alpha E)^2$  and  $\ln \alpha$  on photon energy  $E$  (eV) for perylene dye doped in copolymer of 50/50 ST/MMA with different concentrations (A)  $5 \times 10^{-5}$ , (B)  $1 \times 10^{-4}$ , and (C)  $1 \times 10^{-3}$  mol.% without exposure to light.

**TABLE 2** The Values of (I) energy GAP,  $E_g$ , and (II) the Band Tail Width,  $E_u$ , for Different Concentrations of Perylene Dye Doped in Copolymer of 50/50 ST/MMA after a Continuous Exposure to UV and Filtered Radiation for 10 h

Concentrations of Perylene doped in 50/50 ST/MMA mol. %	Exposure light	(I) Exposure time (hour)							Percentage of decrease of $E_g$ (%)
		0	1	2	4	6	8	10	
$5 \times 10^{-5}$	filter	3.77	3.76	3.74	3.68	3.67	3.65	3.65	3.18
	UV		<b>3.61</b>	<b>3.45</b>	<b>3.37</b>	<b>3.37</b>	<b>3.25</b>	<b>3.22</b>	<b>14.59</b>
$1 \times 10^{-4}$	filter	3.75	3.67	3.64	3.60	3.60	3.60	3.60	4.00
	UV		<b>3.36</b>	<b>3.15</b>	<b>3.11</b>	<b>3.11</b>	<b>3.10</b>	<b>3.09</b>	<b>17.60</b>
$1 \times 10^{-3}$	filter	3.64	3.59	3.56	3.48	3.46	3.45	3.42	6.04
	UV		<b>3.38</b>	<b>3.21</b>	<b>3.16</b>	<b>3.13</b>	<b>2.98</b>	<b>2.93</b>	<b>19.51</b>
		(II) Exposure time (hour)							
		0	1	2	4	6	8	10	
$5 \times 10^{-5}$	filter	0.230	0.241	0.250	0.270	0.296	0.300	0.306	
	UV		<b>0.330</b>	<b>0.380</b>	<b>0.450</b>	<b>0.520</b>	<b>0.590</b>	<b>0.600</b>	
$1 \times 10^{-4}$	filter	0.290	0.310	0.340	0.390	0.390	0.410	0.470	
	UV		<b>0.430</b>	<b>0.460</b>	<b>0.500</b>	<b>0.530</b>	<b>0.610</b>	<b>0.610</b>	
$1 \times 10^{-3}$	filter	0.300	0.350	0.357	0.380	0.398	0.400	0.409	
	UV		<b>0.430</b>	<b>0.530</b>	<b>0.690</b>	<b>0.710</b>	<b>0.710</b>	<b>0.720</b>	

and  $E_u$  before and after exposure to UV and filtered light for 1 h at different exposure times are tabulated in Table 2.

From Table 2, it can be deduced that with increased concentration of perylene dye, the value of  $E_g$  decreased and  $E_u$  increased. It is noted that the dependence of  $E_g$  on the sample preparation does not match with  $E_u$  values because the sample having a narrower band gap is expected to have a wider band tail. The change in  $E_u$  is probably affected by potential fluctuations associated with the polymer structure, but not the change in  $E_g$  because the initial and final states are practically of the same potential [14]. In addition, the percentage of decrease of  $E_g$  for the dye doped samples after exposure to filtered light is less than that after exposure to UV light due to the effect of UV radiation, which has an energy higher than that of any molecular bond [5–6].

Furthermore, the values of band gap energies  $E_g$  and the band tail width  $E_u$  have been calculated for all the previous samples after irradiation by different doses of  $\gamma$ -ray, and tabulated Table 3. The values of the optical band gap decreased by increasing the doses of  $\gamma$ -ray and that may be attributed to the increase in the disorder caused by the presence of structural defects, which is known to increase the

**TABLE 3** The Values of Energy GAP,  $E_g$ , and the Band Tail Width,  $E_u$ , for Different Concentrations of Perylene Dye Doped in Copolymer of 50/50 ST/MMA after Irradiation by  $\gamma$ -ray with Different Doses 0, 1, 5, and 10 Mrad

Concentrations of perylene doped in 50/50 ST/MMA mol. %	Doses of $\gamma$ -ray Mrad	$E_u$	$E_g$	Percentage of decrease of $E_g$ %
$5 \times 10^{-5}$	0	0.230	3.77	—
	1	0.372	3.50	7.16
	5	0.378	3.45	8.49
	10	0.400	3.21	14.85
$1 \times 10^{-4}$	0	0.290	3.75	—
	1	0.356	3.38	9.87
	5	0.445	3.14	16.30
	10	0.447	3.12	16.80
$1 \times 10^{-3}$	0	0.300	3.64	—
	1	0.426	3.54	2.75
	5	0.476	3.20	12.10
	10	0.625	2.96	18.70

width of the localized states, and consequently reduce the value of the optical gap [15]. Also, the percentage of decrease of  $E_g$  after irradiation by 10 Mrad of  $\gamma$ -ray is more than that after irradiation by UV light. Moreover, the values of  $E_u$  increase by increasing the dose of irradiation.

### Fluorescence Spectroscopy

The fluorescence quantum yield has been calculated for the previous samples before and after irradiation by  $\gamma$ -ray, relative to BASF-241

**TABLE 4** Spectroscopic Properties of Perylene Dye Doped in Copolymer of 50/50 ST/MMA Before and After Irradiated by  $\gamma$ -ray

Concentrations of perylene doped in 50/50 ST/MMA mol. %	Doses of $\gamma$ -ray Mrad	$\Phi_{flu.}$ %	$E_f$
$5 \times 10^{-5}$	0	76.6	0.617
	10	24.0	0.222
$1 \times 10^{-4}$	0	37.8	0.305
	10	19.1	0.178
$1 \times 10^{-3}$	0	23.4	0.189
	1	15.4	0.143
	5	10.4	0.097
	10	2.16	0.020

dye doped in PMMA as a reference ( $\phi_f \approx 99\%$ ) [16] from the following Eq. (5) [17], and listed in Table 4:

$$\phi_f = \phi_{f,\text{ref}}(A_{\text{ref}}/A)(n/n_{\text{ref}})(a/a_{\text{ref}}) \quad (5)$$

where  $\phi_{\text{ref}}$  is the fluorescence quantum yield of a reference,  $A$  is the absorbance at the excitation wavelength,  $n$  is the index of refraction and  $a$  is the area under fluorescence curve.

Moreover, the energy yield of fluorescence  $E_f$  was estimated for the samples, before and after irradiation by  $\gamma$ -ray, from Eq. 6 [18], and tabulated in Table 4:

$$E_f = \frac{\phi_f \lambda_a}{\lambda_f} \quad (6)$$

where  $\lambda_a$  and  $\lambda_f$  are the maximum absorption and fluorescence wavelength, respectively.

The values of fluorescence quantum yield  $\Phi_{\text{flu0}}$  are decreased by increasing the concentration of the doped dye due to an important fact that when the dye concentration is high, each molecule becomes perturbed by the fields from neighboring dye molecule, resulting in the expected decrease in quantum efficiency, or quenching of the fluorescence [19]. Also, the values of fluorescence quantum yield  $\Phi_{\text{flu0}}$  is decreased by increasing the doses of  $\gamma$ -ray irradiating the sample, due to the chemical decomposition of dye caused by irradiation by a high energy  $\gamma$ -ray.

Moreover, the energy yield of fluorescence  $E_f$  decreased by increasing the concentration of the dye, in agreement with Reference [20]. On the other hand,  $E_f$  decreased by increasing the doses of  $\gamma$ -ray irradiating the samples.

## CONCLUSION

In the present work, perylene dye, doped at different concentrations in copolymer of 50/50 ST/MMA, was examined. The spectral characteristics, absorption, fluorescence quantum yield together with photostability and degradation, have been studied. The optical absorption spectra has been measured for the samples before and after exposure to  $\gamma$ -radiation and also after exposure to filtered and UV light from xenon arc lamp. The results have illustrated that a reduction in the optical spectra of the samples was observed after irradiation by  $\gamma$ -ray and also after exposure to direct light, which

were higher than that observed after exposure to filtered light. The calculated values of fluorescence quantum yield have shown that irradiation the samples by  $\gamma$ -ray for FSC applications is not desired because of its low values compared with those before irradiation for the same samples. Moreover, the lowest concentration of perylene dye doped in copolymer 50/50 ST/MMA by thermal polymerization process is the best from all studied samples, and suggested to be used for FSC applications.

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