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Optical Properties Characterization of Celestin Blue B Dye Doped Polymer Films

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ABSTRACT

In the present work, film samples of pure and doped poly(methylmethacrylate) (PMMA) polymer with different concentrations of Celestin Blue B dye were prepared using casting method. The optical properties of these films were investigated. The optical absorbance and transmittance spectra of the film samples were measured in the UV–Visible wavelength range 300 - 900 nm. From these spectra, the main optical coefficients of these samples, such as, absorption coefficient (α), extinction coefficient (k), refractive index (n), reflectance (R), dielectric constants (the real (ε_r) and imaginary (ε_i) parts), were determined. The values of band gap energy (E_g) of the samples were also determined. Results indicate that the Celestin Blue B dye is a promising candidate for the photonic device applications.

1. Introduction

Optical materials with large nonlinear coefficients and fast optical responses have received a great deal of attention due to their interesting optical and electrical properties [1-7]. These materials can play a major role in the various optical devices such as, optical communications, signal processing, optoelectronic, all-optical switches, optical solar cells, optical sensors, light emitting diodes (LED's), and optical power limiters [8-19]. Organic materials are of considerable interest due to their large optical nonlinearities and broadband spectral range. Among the various organic materials, polymers and dyes can display a remarkable role in the optical devices [20-26]. The most important and widely used polymeric material is poly(methylmethacrylate) (PMMA) polymer due to its interesting advantages such as, excellent optical transparency, structural flexibility, easy synthesis, stability in environmental, high damage resistance to intense laser beams, and relatively low cost [27, 28]. Improvement of optical and electrical properties of the polymeric materials has been the subject of intense research efforts. In the case of organic dyes, investigation of these properties is essential for developing the potential applications of optical devices. To improve the properties of the polymeric materials, some modifications of these materials are required. It is found that an addition of suitable organic dye to a pure polymer matrix leads to significant changes in its optical parameters.

In this paper, we present results of investigation of the optical properties of PMMA polymer films doped with Celestin Blue B dye. The main optical parameters were determined and the effect of dye concentrations on the values of these parameters was studied.

2. Experimental Methods

Dye Celestin Blue B, obtained from Sigma-Aldrich, was chosen for the present study. The molecular formula of Celestin Blue B dye is $C_{17}H_{18}ClN_3O_4$ with a molecular weight M_W = 363.80 g/mole. The chemical structure of this dye is shown in Fig. 1. Poly(methylmethacrylate) (PMMA) polymer in the form of small grains (crystalline polymer) was used in this study. It has high purity and good optical transparency, with a molecular weight M_w = 84000 g/mole. Samples of dye - doped polymer films were prepared using the casting method. A certain weight of Celestin Blue B dye powder was dissolved in a mixed solution of Tetrahydrofuran (THF) with a small quantity of methanol, which is suitable solvent for both dye and PMMA polymer. Then required weight of pure PMMA polymer was added. The mixture was stirred using a magnetic stirrer till a clear solution was formed. This solution was diluted by the solvent and samples of solutions with different dye concentrations were obtained. Proper quantities of the prepared solutions were poured on thin glass slides and kept for drying for 48 hours at room temperature. Dye - doped polymer film samples of different concentrations (0.05, 0.06, 0.07, 0.08, and 0.09 mM) and an average thickness of 0.9 mm, were obtained. The polymer films were examined carefully and found that are uniform with good optical quality.

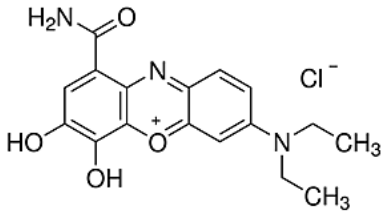

Fig. 1 Chemical structure of Celestin Blue B dye

3. Theoretical Relations

The laser beam attenuates exponentially as it is passed through an optical medium and the reduction of transmitting laser beam can be quantified by the absorption coefficient (α) of the optical medium. According to the Beer - Lambert law, if a laser beam with incident intensity I_0 enters an optical medium of thickness t, then the transmitted intensity (I) of the laser beam is given by the following relation [29],

$$I = I_0 e^{-\alpha t} \quad (1)$$

or $$\alpha = \frac{2.303}{t}\log\left(\frac{I_0}{I}\right) \quad (2)$$

Since the absorbance (A) of the optical medium is related to its transmittance (T) according to the following relation [30, 31]:

$$A = \log\left(\frac{1}{T}\right) \quad (3)$$

Therefore, we can rewrite Eq. (2) as follows:

$$\alpha = \frac{2.303\ A}{t} \quad (4)$$

where, $T = I/I_0$.

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The extinction coefficient (k) of the optical medium in terms of absorption coefficient (α) can be determined from the following relation [32]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (5)$$

where λ is the wavelength of the incident laser beam.

The absorption coefficient (α) is related to the reflectivity (or reflectance) (R) of the optical medium through the following relation [32-34]:

$$R = 1-(Te^{\alpha t})^{1/2} \quad (6)$$

We have assumed here, that the front and back surfaces of the optical medium have equal reflectivities (i. e., $R_1 = R_2 = R$), as for the samples in our present work.

The linear refractive index (n) of the optical medium is related to both reflectance (R) and extinction coefficient (k) according to the following relation [33]:

$$n = \left(\frac{1+R}{1-R}\right) + \left(\frac{4R}{(1-R)^2} - k^2\right)^{1/2} \quad (7)$$

The complex dielectric constant (ε) of the optical medium is described by the following relation [32]:

$$\varepsilon = \varepsilon_r + i\,\varepsilon_i \quad (8)$$

where ε_r and ε_i are the real and imaginary parts of the dielectric constant (ε), respectively. Both ε_r and ε_i are related to the refractive index (n) and the extinction coefficient (k) of the optical medium according to the following relations:

$$\varepsilon_r = n^2 + \kappa^2 \quad (9)$$

and $$\varepsilon_i = 2n\kappa \quad (10)$$

The relation between the linear absorption coefficient (α) and the band gap energy (E_g) of the semiconductor is described by the following relation [30, 33, 35],

$$(\alpha h\nu)^m = B(h\nu - E_g) \quad (11)$$

where h is the Planck's constant, ν is the frequency of incident photons, and m is an index, its value depends on the kind of optical transition between the valence band and the conduction band of the semiconductor. m takes the values: 1/2, 3/2, 2, and 3 for indirect allowed, indirect forbidden, direct allowed, and direct forbidden transitions, respectively. B is constant; its value depends on the properties of the bands. In the present work, it is found that the mechanism of the measured absorption spectra of the samples is the indirect allowed transition, Therefore, we have taken m = 1/2 for E_g calculations; using Eq.(11).

4. Results and Discussion

The absorbance (A) and the transmittance (T) spectra of Celestin Blue B dye -doped polymer films at different concentrations were recorded over the wavelength range 300 - 900 nm by using the double - beam UV-Vis spectrophotometer. These spectra are shown in Figs. 2 and 3. It is noticed that the peak of the absorbance curve is located at the wavelength 605 nm and the highest value of the absorbance is 16.8 % for the dye - doped polymer sample with the dye concentration 0.09 mM. It is also noticed that the film samples exhibit high transmittance at low dye concentrations, and it is decreased as the dye concentration increases.

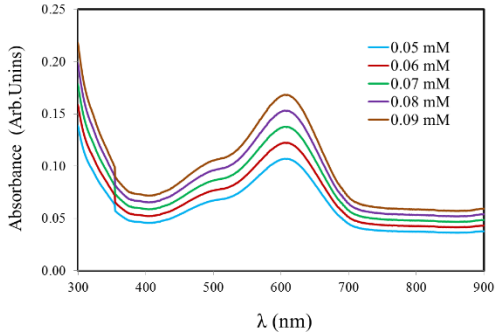

Fig. 2 UV - Vis absorbance spectra of the Celestin Blue B dye – doped polymer films at different dye concentrations

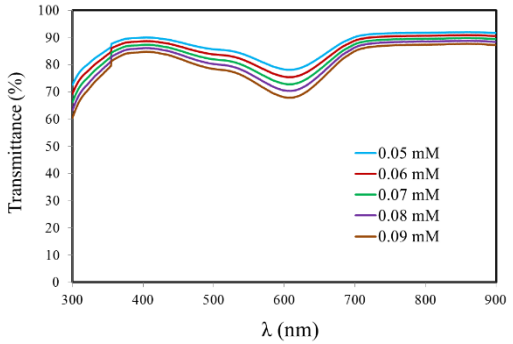

Fig. 3 UV-Vis transmittance spectra of the Celestin Blue B dye – doped polymer films at different dye concentrations

The reflectance (R) values of the Celestin Blue B dye - doped polymer films, at different dye concentrations, were calculated using Eq.(6). The obtained values of R were plotted as a function of the wavelength (λ), as illustrated in Fig. 4. It is clearly noticed, from these spectra, that the increase of the dye concentration leads to an appreciable increase in the reflectance (R) of the film sample. It is also noticed that all the peaks of transmittance curves are located at the same wavelength 600 nm and the highest value of R is approximately 10.5 for the films with dye concentration 0.09 mM.

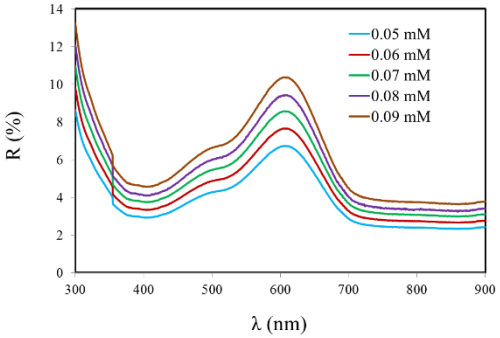

Fig. 4 UV - Vis reflectance (R) spectra of the Celestin Blue B dye – doped polymer films at different dye concentrations

The absorption coefficient (α) values of the Celestin Blue B dye - doped polymer films were calculated using Eq.(4). Fig. 5 displays the relation between the linear absorption coefficient (α) and the incident photon energy (hν), for the dye - doped polymer samples at different dye concentrations. It is clearly evident that the value of α increases with increasing the incident photon energy (hν). All the peaks of absorption coefficient curves are located at the same value of the incident photon energy (hν) (≈ 2.05 eV) and the highest value of α is 3.9 cm^{-1} at the dye concentration of 0.09 mM.

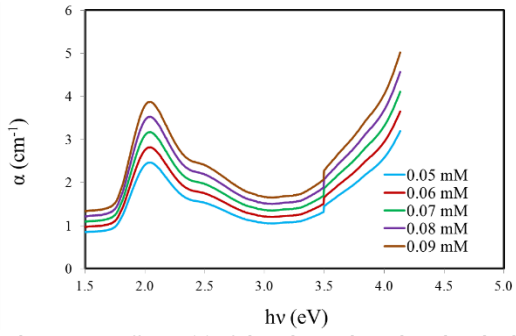

Fig. 5 The absorption coefficient (α) of the Celestin Blue B dye - doped polymer film versus the incident photon energy (hν), for different dye concentrations

The extinction coefficient (k) of the Celestin Blue B dye-doped polymer films was calculated using Eq.(5). Fig. 6 illustrates the relation between the extinction coefficient (k) and the incident photon energy (h ν), for the dye-doped polymer samples at different dye concentrations. It can be seen that the value of k increases with increasing the dye concentration. The position of the peaks of the extinction coefficient curves is at the photon energy (h ν) ≈ 2.05 eV and the highest value of k at this position is 1.9×10^{-5} for the film sample with dye concentration the of 0.09 mM. Also, it can be seen that the behavior of the extinction coefficient (k) versus the incident photon energy (h ν) is similar to that for the absorption coefficient (α), and this is due to the corporate relation between the two coefficients.

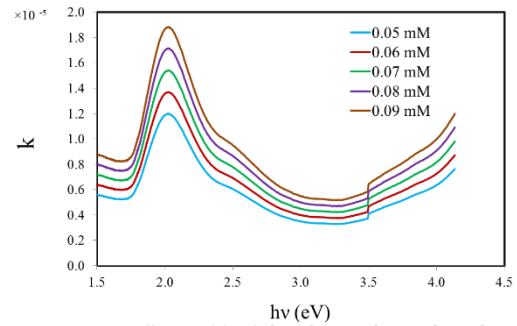

Fig. 6 The extinction coefficient (κ) of the Clestin Blue B dye – doped polymer film versus the incident photon energy (hν), for different dye concentrations

The values of the linear refractive index (n) of the Celestin Blue B dye - doped polymer films were calculated using Eq.(7). The relation between the refractive index (n) and photon energy (hν) for the dye - doped polymer samples at different dye concentrations is shown in Fig. 7. The highest value of n is 1.9 at the point hν = 2 eV, for the dye - doped polymer sample with the dye concentration of 0.09 mM.

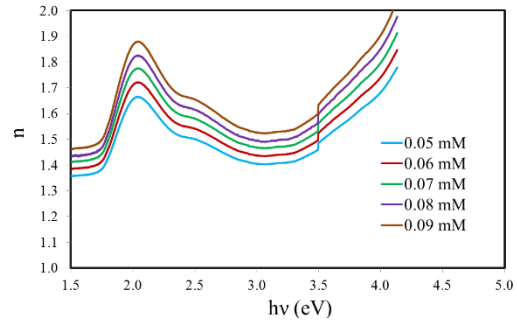

Fig. 7 The refractive index (n) of the Celestin Blue B dye - doped polymer film versus the incident photon energy (hν), for different dye concentrations

The values of the real (ε_r) and the imaginary (ε_i) parts of the dielectric constant (ε) of the Celestin Blue B dye - doped polymer films were calculated using Eqs. (9) and (10), respectively. Figs. 8 and 9 illustrate the relation between ε_r, ε_i and the photon energy (h ν) for the dye - doped polymer samples at different dye concentrations. It is clearly seen that the variation of the dye concentration plays an important role on both values of ε_r and ε_i. These values are appreciably increased with increasing the dye concentration The highest value of ε_r is 3.5, at the point hν ≈ 2.05 eV for the dye concentration of 0.09 mM, which is much bigger than that for ε_i, ($\varepsilon_i = 0.071\times10^{-5}$).

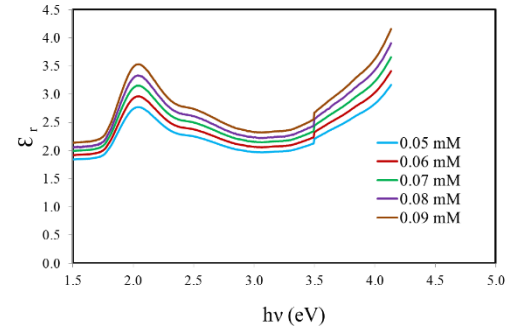

Fig. 8 The real part of the dielectric constant (ε_r) versus the incident photon energy (h ν) for the Celestin Blue B dye - doped polymer films at different dye concentrations

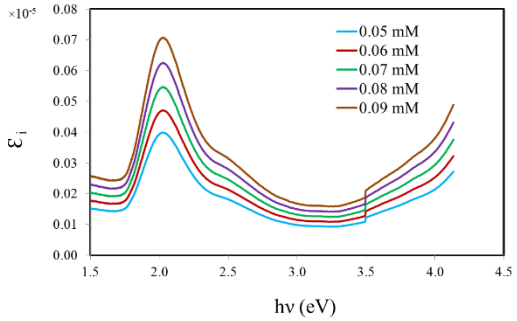

Fig. 9 The imaginary part of the dielectric constant (ε_i) versus the incident photon energy (h ν) for the Celestin Blue B dye-doped polymer films at different dye concentrations

The values of the band gap energy (Eg) of the pure PMMA polymer film and Celestin Blue B dye - doped polymer films were obtained from the intercept of the extrapolated linear part of the plot of $(\alpha h\nu)^{1/2}$ versus the incident photon energy (hν) with hν –axis (where αhν = 0) [35], as shown in Fig. 10 for the pure PMMA polymer film and the Celestin Blue B dye - doped polymer films, at different dye concentrations. The calculated values of Eg are summarized in Table 1. As can be seen in this table, the value of Eg for the pure PMMA polymer is 4.73 eV and it is appreciably decreased when the polymer doped with Celestin Blue B dye. It is found that the value of Eg is considerably affected by the change of Celestin Blue B dye concentration; where the value of Eg of samples decreased by increasing the concentration of dye in PMMA films.

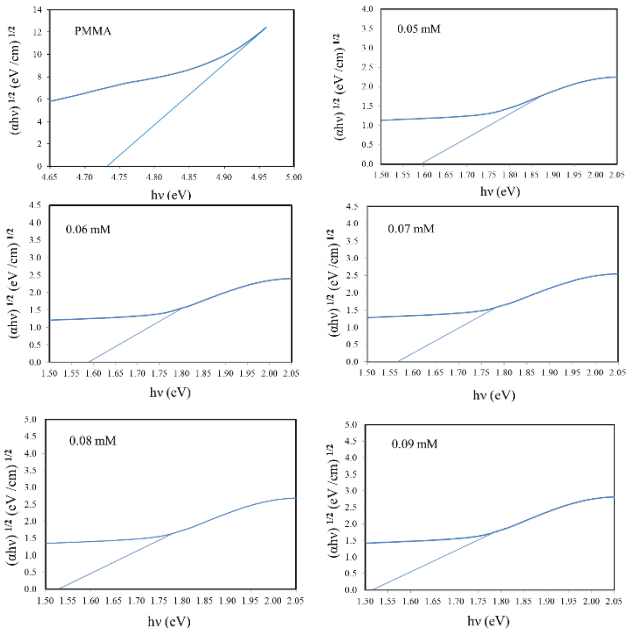

Fig. 10 The plots of $(\alpha h\nu)^{1/2}$ versus hν for pure PMMA polymer film and Celestin Blue B dye - doped polymer films at different dye concentrations

Table 1 The obtained values of optical energy band gap (E_g) for the pure PMMA polymer film and the Celestin Blue B dye - doped polymer films at different dye concentrations

Sample	Optical energy band gap (E_g) (eV)
PMMA	4.73
CBB 0.05 mM	1.60
CBB 0.06 mM	1.59
CBB 0.07 mM	1.57
CBB 0.08 mM	1.53
CBB 0.09 mM	1.51

5. Conclusion

The samples of pure PMMA polymer film and Celestin Blue B dye - doped polymer films were prepared using the casting method. The optical properties of these film samples were investigated. The optical absorbance and transmittance spectra of the film samples were measured in the UV - Visible wavelength range 300 - 900 nm. These spectra were used to determine the main optical parameters of the samples as a function of incident photon energy (hν). The values of the band gap energy (E_g) of the pure PMMA polymer film and Celestin Blue B dye - doped polymer films were also determined. It is found that the band gap energy (E_g) is dye concentration dependence and its value decreases with increasing dye concentration. Results show that Celestin Blue B dye is suitable material for photonic applications.

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