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Linear Optical Properties of Bromocresol Green Dye Doped Poly Methyl Methacrylate Thin Films

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Abstract

In this study, we investigated the effect of Bromocresol green dye (BCG) of the PMMA thin films optical properties. Films of Poly Methyl Methacrylate doped by 10% BCG doping ratio to prepared two concentrations $2x10^{-4}$ and $6x10^{-4}$ M of PMMA-BCG dye were deposited on glass substrate using free casting method at room temperature. The optical properties of the films were determined using UV-Visible absorbance and transmittance spectra at the 300 - 900 nm wavelength range. The linear absorption coefficient and the extinction coefficient were calculated. The results showed that the optical properties were increasing by increasing the dye concentration, while the optical energy gap was decreasing with the doping. Also from the linear optical properties result the PMMA-BGC thin films are a promised materials for nonlinear optics applications.

Keywords: Thin films, Optical properties, Dye doped polymer.

الخواص البصرية الخطية لاغشية بولي مثيل ميثاكرلايت المطعمة بصبغة بروموكريسول الخضراء

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الخلاصة

درسنا تاثير التطعيم بصبغة بروموكريسول الخضراء على الخواص البصرية الخطية لاغشية البوليمر (بولي مثيل ميثا اكريلايت). تم تحضير هذه الاغشية المكونة من بولي مثيل ميثا اكريلايت المطعم بنسبة 10% صبغة بروموكريسول الخضراء لتحضير تركيزين (2×10^{-4}، 6×10^{-4} مولاري) من غشاء بولي مثيل ميثاكرلايت – بروموكريسول الخضراء بواسطة طريقة الصب الحر على الواح زجاجية بدرجة حرارة الغرفة). تم قياس الخواص البصرية الخطية من خلال قياس اطياف الامتصاص والنفاذية ضمن المدى الطيفي 300– 900 نانو متر، اذ تم حساب المعاملات البصرية مثل معامل الامتصاص، معامل الانكسار، معامل الخمود، وفجوة الطاقة. اظهرت النتائج بأن المعاملات البصرية الخطية تزداد بأزدياد نسبة التطعيم للصبغة فيما لاحظنا نقصان في فجوة الطاقة البصرية مع ازدياد نسبة التطعيم. كما اظهرت النتائج ايضا ان هذا المادة ممكن ان تكون مادة واعدة لتطبيقات البصريات اللاخطية.

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Introduction

Organic dye doped polymers have a great deal of concern in recent years due to their great potential in many important applications such as optical storage, optical switching, optical limiting, signal processing, optical modulators, holography and nonlinear optical devices as well as various kinds of photonic devices [1-3]. The unique properties of polymers such as low density, ability to form intricate shapes, good mechanical strength versatile, electrical properties and low manufacturing cost made them promising materials that have been successfully used as host matrices for dyes. The wide range of polymer applications can be even more extensive by incorporation of filler into polymer matrix, because dispersed filler may increase the concentration of absorptive or fluorescence centers as well as the opto-chemical and opto-physical stability of host polymer [4-7].

In this study, we present the effect of Bromocresol green dye (BCG) on the optical properties of poly methyl methacrylate (PMMA) polymeric matrix (guest - host system). Poly methyl methacrylate (PMMA) is a transparent plastic material with high solidity, durability and flexibility [6].

The optical properties such as absorption coefficient, refractive index and optical energy band gap of dye doped polymers were investigated using spectroscopic absorbance combined with transmittance measurements.

Materials and Samples Preparation

The Bromocresol green dye was obtained from (Sigma -Aldrich) with a molecular formula of $C_{21}H_{14}Br_4O_5S$ and its chemical structure is depicted in Figure-1. The bromo group can improve the transparency and the thermal stability of compounds. Bromocresol Green (BCG) is a pH sensitive triphenylmethane dye useful in a variety of colorimetric detection technologies. BCG is used as a tracking dye for DNA agarose gel electrophoresis, in protein determinations and in charge-transfer complexation processes, BGC melting point is 225 ^oC and the peak absorption in 423 nm [8, 9].

Poly methyl methacrylate (PMMA) polymer was purchased from (Sigma -Aldrich) and used as host material for laser dye due to its excellent optical properties. The molecular formula of PMMA is $(C_5O_2H_8)_n$. It is highly amorphous with average M_w of about 120,000, and glass transition temperature 105 °C [5]. It is an aromatic polymer made from the aromatic monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum by the chemical industry. PMMA is a thermoplastic substance and one of the most widely used kinds of plastic [3].

Dye doped polymer films were prepared by casting method. The PMMA solution was prepared by adding 0.6 g of PMMA powder in 10 ml of chloroform under vigorous stirring for 30 min at 60 ^oC. Each of dye and polymer was dissolved separately in $1x10^{-3}$ M chloroform. Then, the solution of polymer was mixed with 10% dye solution. Two $2x10^{-4}$ and $6x10^{-4}$ M dye-polymer mixtures were casted on a clean glass plate (washed in acetone, ethanol, and distilled water respectively). Finally, the films were dried in an oven at 60 ^oC for 3 hours to remove the residual solvent. The uniform surface films with thickness around 50-60 μm were obtained. The absorption and transmission of the prepared samples were investigated by UV-Vis T70/T80 spectrophotometer in the spectral range (300-900) nm.

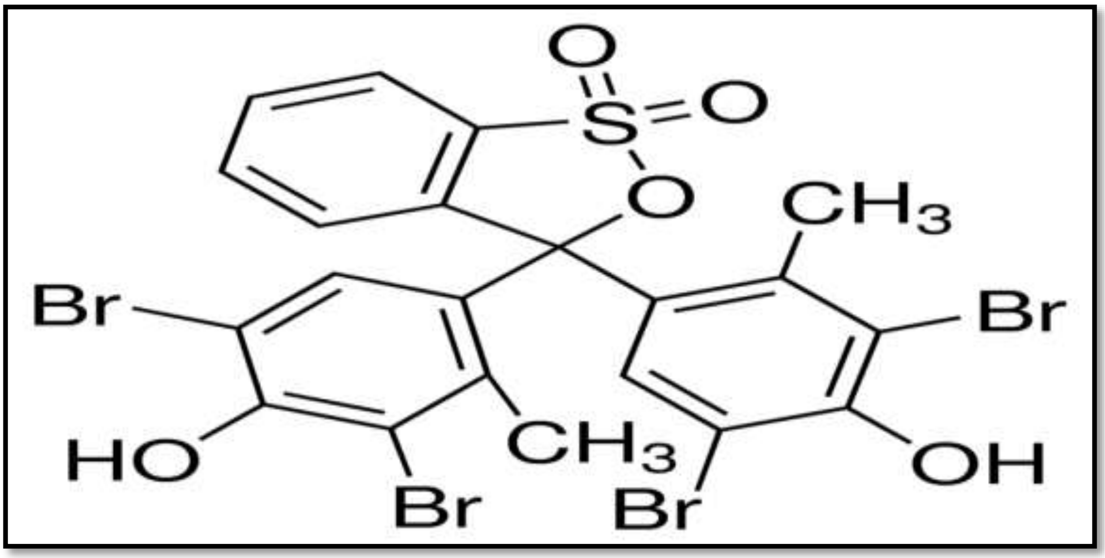

Figure 1-Chemical structure and molecular formula of Bromocresol green dye.

Results and Discussion

Figures-(2, 3) show the Absorption (A) and Transmittance (T) spectra of PMMA films measured by UV-vis spectrophotometer before and after doping by BCG dye of 2 $x10^{-4}$ and 6 $x10^{-4}$ M concentrations. The results from Figure-2 shows the absorbance spectra as a function of the wavelength of the incident light for PMMA film with different concentrations of BCG dye. As it is clear, increasing the concentration of BCG dye in the polymer matrix leads to a corresponding increase in the peak intensity. Figure-3 shows the transmission spectra of PMMA polymer reaches to the maximum value 87% at 480 nm for pure polymer after that it's begin to decrease because of increases in absorbance value for this wave length region due to the logarithmic relation between the transmission and absorption. The effect of increasing BCG doping ratio lead to decrease the transmission to 79% at $2x10^{-4}$ M concentration and by increasing the concentration to 6 $x10^{-4}$ M it also reduced the transmission to 56% at 480 nm due to the increase in absorbance values.

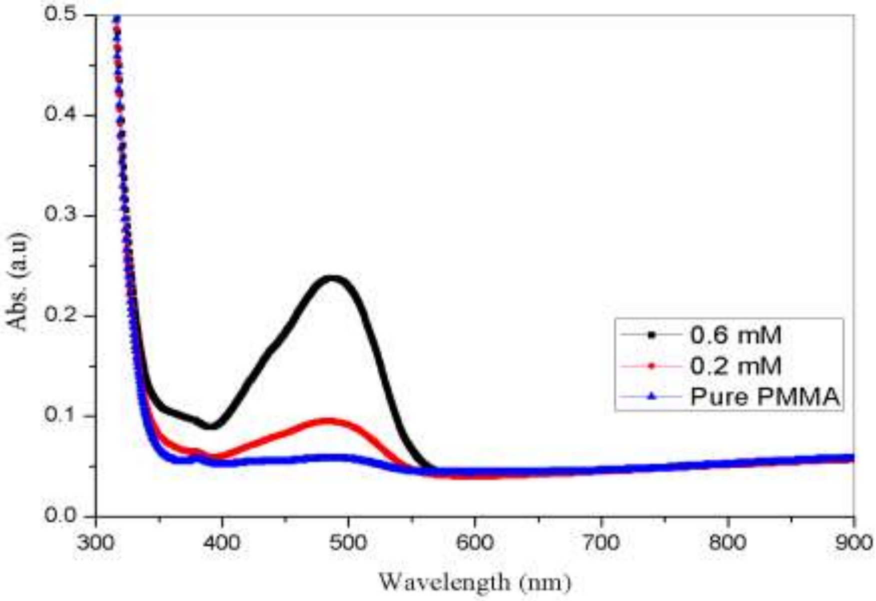

Figure 2-Absorption spectrum of pure and doped PMMA by BCG dye.

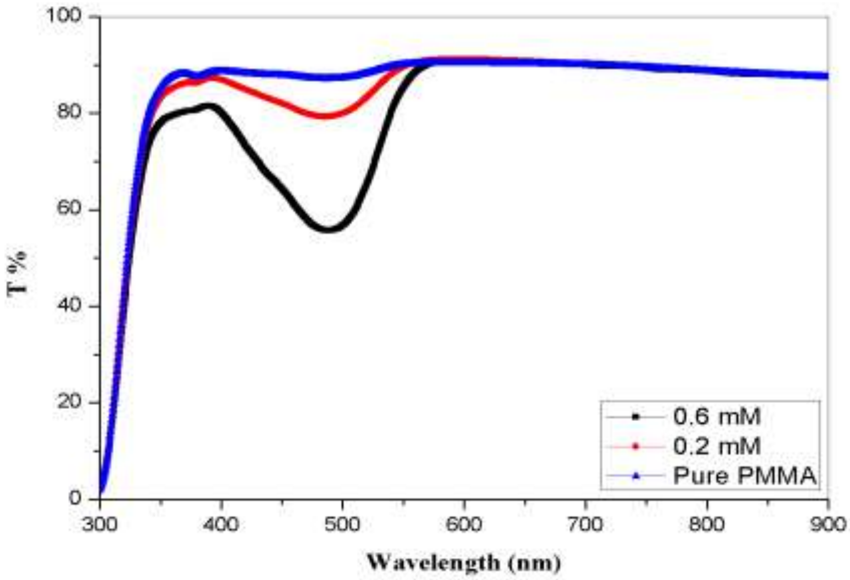

Figure 3-Transmittance spectrum of pure and doped PMMA by BCG dye**.**

The Reflection spectra (R) for PMMA films before and after doping by BCG dye are presented in Figure-4 where the reflectance R can be obtained from the relation 1 [10]:

$$A + T + R = 1 \quad (1)$$

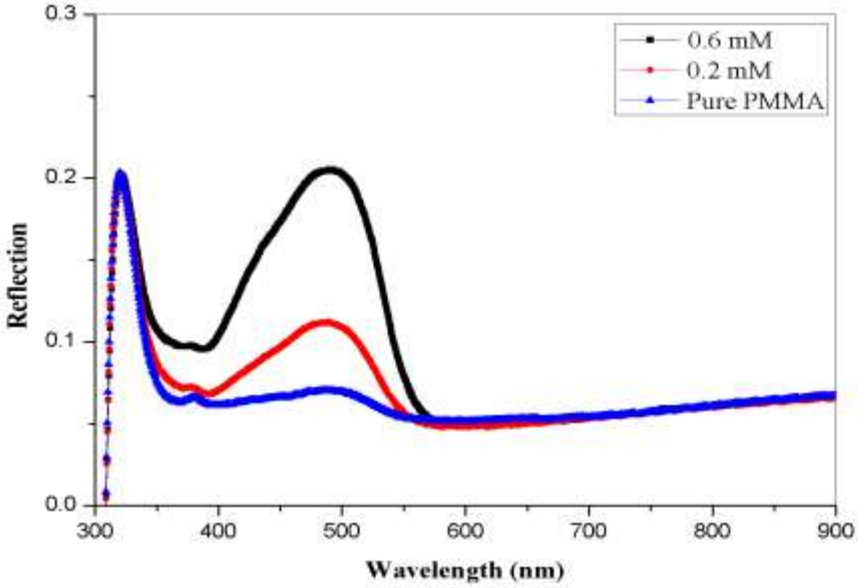

Figure 4-Reflection spectrum of pure and doped PMMA by BCG dye**.**

The optical constant such as refractive index (n) and extinction coefficient (k) can be determined by the equations [11].

$$n = \frac{(1+R^{\frac{1}{2}})}{(1-R^{\frac{1}{2}})} \quad (2)$$

$$K = \frac{\alpha\lambda}{4\pi} \quad (3)$$

Where λ is the wavelength of incident light (nm) and α is absorption coefficient, and this can be calculated by [12] as follows:

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

Where t is the thin film thickness.

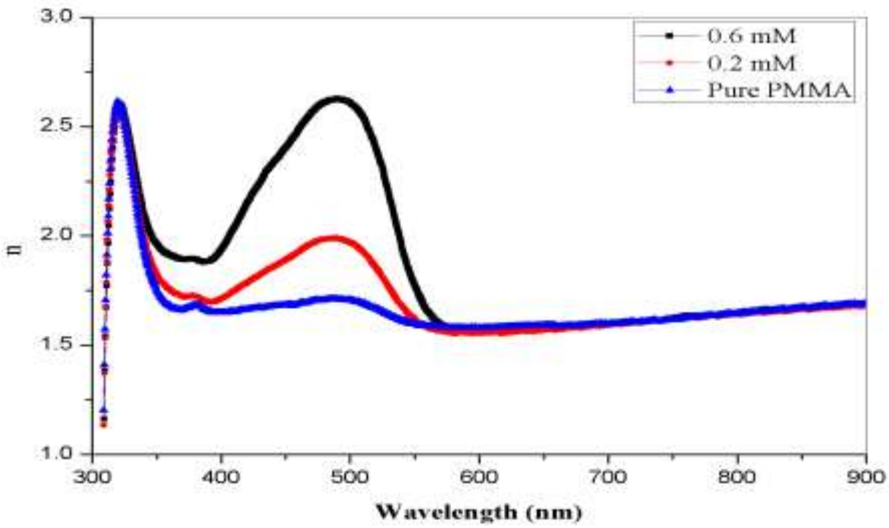

Figure 5-Refractive index of pure and doped PMMA by BCG dye.

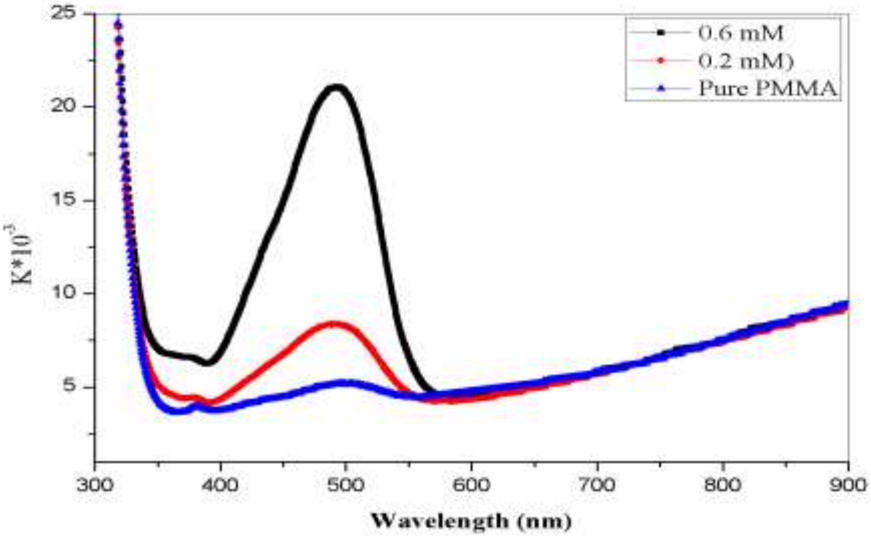

Figure 6-Extinction coefficient of pure and doped PMMA by BCG dye**.**

Figures-(5, 6) depict the refractive index (n) and extinction coefficient (k) of pure and doped PMMA polymer, respectively. The increase of n values with increasing doping ratio led to increase absorbance and make the films denser which in turn decreased propagation velocity of light through them resulting to increase (n) values. While (n) represents the ratio of light velocity through vacuum to velocity through any material. Then, the material become more opaque to the incident lights thus the velocity of light decreases and consequently n and k increases [11, 12]. This result indicates that the dopant atoms of BCG will modify the structure of the host polymer [13]. BCG dopant has increased the absorbance in the visible region

In addition, the optical conductivity ($\sigma_{opt)}$ can be obtained from the equation as [14].

$$\sigma_{opt} = \frac{n\,c\,\alpha}{4\,\pi} \qquad (5)$$

The optical conductivity of pure and doped PMMA film is shown in Figure-7, in which an increase in optical conductivity with increasing the doping percentages was observed.

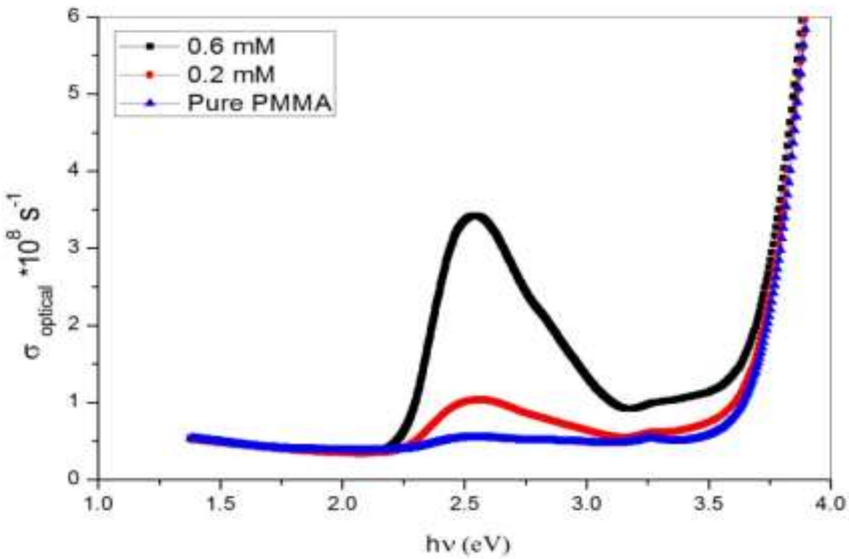

Figure 7-The optical conductivity of pure and doped PMMA by BCG dye**.**

From the equation (4) and observing the absorption coefficient (α) as a function of the wavelength shown in Figure-8, it can be concluded that absorption is relatively small at long wavelengths. The absorption coefficient helps to conclude the nature of electronic transitions. When the high absorption coefficient values (α>104 cm-1) at higher energies, we expected direct electronic transitions, and the energy and momentum preserve of the electron and photon .Whereas the values of absorption coefficient is low (α<104 cm-1) at low energies, we expected indirect electronic transitions, and the energy and momentum preserve of the electron and photon by phonon helps.[15, 16] In our results, the value of α for all samples less than 104 cm-1,so that the indirect electronic transitions will deduced.

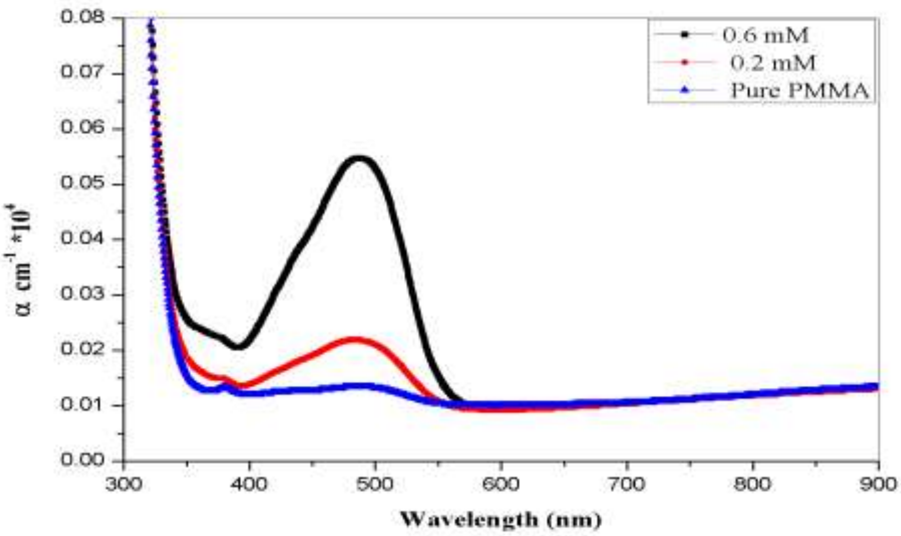

Figure 8-Absorption coefficient of pure and doped PMMA by BCG dye.

Finally, the determination of the optical energy band gap (E_g) is often necessary to develop the electronic band structure of film material. Absorption coefficient (α) is related to the energy (*hυ*) of the incident photons by the relation **[**17].

$$\alpha h\upsilon = B\,(h\upsilon - E_g^{\ opt})^r \qquad (6)$$

Where B is a constant and depended on type of material, *υ* is the frequency of incident photon, and r is the exponential constant, its value depends on the type of transition, where r =1/2 for allowed direct transition, r =3/2 for the forbidden direct transition, r =2 for allowed indirect transition, and r =3 for the forbidden indirect transition.

Figure-9 shows The optical indirect energy gap ($E_{g\ indirect}$) values which was calculated by the evaluation of the straight line of $(\alpha h\upsilon)^{½}$ plot against photon energy in the high absorption range followed by extrapolating the linear region of the plots to $(\alpha h\upsilon)^{1/2}=0$.

The indirect energy gap of the PMMA was found to be equal 3.79 eV, as shown in Figure-9 (A), and this value begins to decrease to 3.59 eV when the polymer is doped by 0.2 m mol/L dye as shown in Figure-9 (B), with increasing the concentration of BCG dye to 0.6 m mol/L, the indirect energy gap will decrease to 2.17 eV, as shown in Figure-9 (C). Figure-9 shows that the values of energy gap decrease with increasing of the dye concentration**.** This decrease can be attributed to the creation of the site levels in forbidden indirect energy gap leading to facilitate the crossing of electron from the valence band to the local levels to conduction band [14].

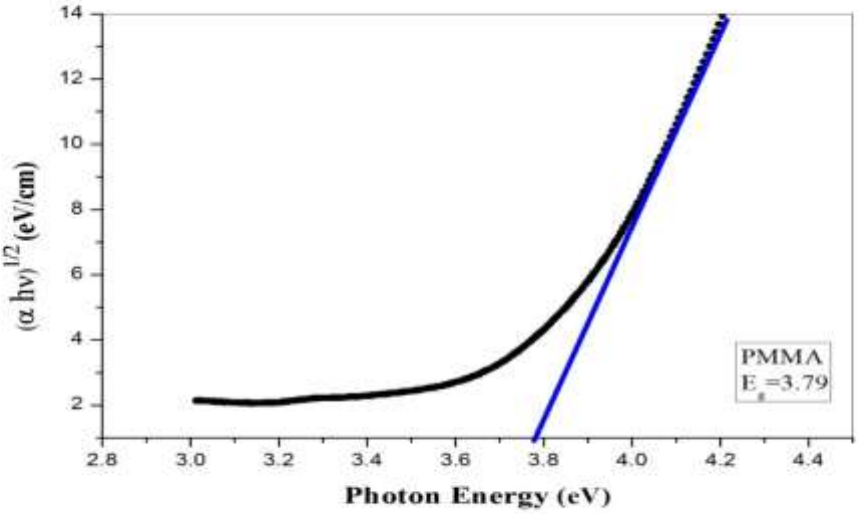

Figure 9 (A)-Indirect energy gap of pure PMMA polymer.

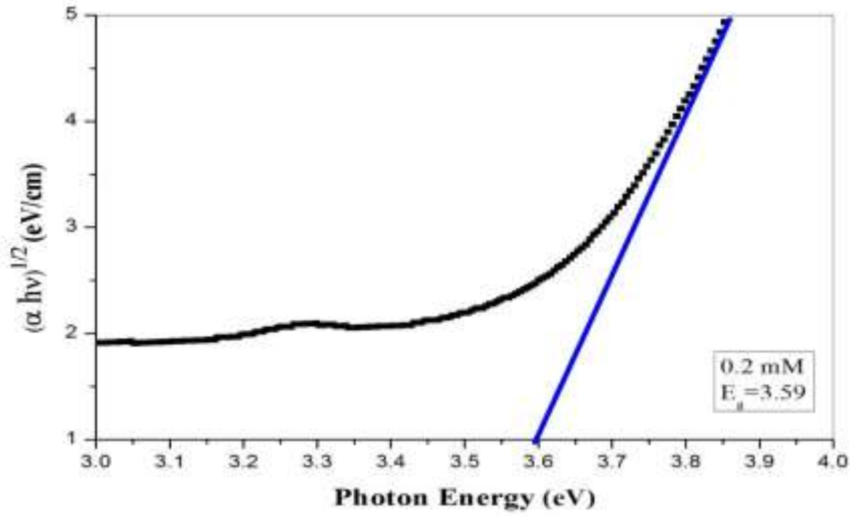

Figure 9(B)-Indirect energy gap of doped PMMA polymer at 0.2 m mol/L.

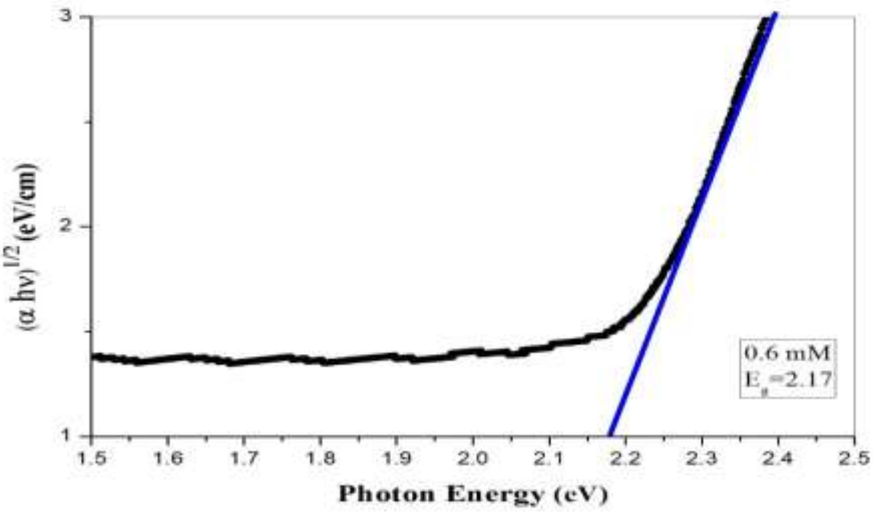

Figure 9(C)-Indirect energy gap of doped PMMA polymer at 0.6 m mol/L.

Conclusion

In this experimental work we have investigated the effects of dye concentration on the optical properties of BCG-doped PMMA thin films. Using transmittance and absorption spectrum for pure PMMA and doped PMMA/BCG thin films, absorption coefficient, refractive index, extinction coefficient, and optical conductivity, have been studied. BCG increment effect in the structure of film led to enhance the optical properties of PMMA, represented by increasing the optical constant while the adding BCG in the structure of PMMA has been leaded to decreasing the band gap energy of films according to smaller band gap energy of BCG dye. So, it can be concluded that the BCG/PMMA thin films consider a promised materials for nonlinear application.

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