

Synthesis and Calculation of some Linear Optical Properties and the Oscillator Strength Parameters of a New Azo Dye Polymer Compound

Maged A. nattiq 

College of Education for Pure Sciences, University of Basrah/ Basrah

Email: majednatiq@yahoo.com

ABSTRACT

In this paper, azo dye polymer materials was synthesis from P-toludine with Novolac by Fox method. The optical properties of an azo dye polymer film with thickness $10\mu\text{m}$ have been investigated by the transmittance and absorbance spectra in the wavelength range (300-900 nm). The linear optical parameters such as refractive index (n), extinction coefficient (k), absorption coefficient (α), real and imaginary parts of dielectric constant were calculated. The optical energy gap was estimated from the absorption coefficient using Taue's procedure. The oscillator energy (E_0), dispersion energy (E_d) and the static refractive index (n_0) have been determined by the Wemple-DiDomenico method.

Keyword: Azo Dye, Optical Constants, Single Oscillator Model, Novolac.

تحضير وحساب بعض الخصائص الضوئية الخطية ومعاملات قوة التذبذب لصبغة ازو بولمرية جديدة

الخلاصة

في هذا البحث , تم تحضير صبغة ازو بولمرية من تفاعل P-toludine مع بولمر النوفولاك بطريقة Fox حيث نتجت الصبغة 1,3-bis(phenylene)bis(methylene)bis(2-ethyphenol)) بعد ذلك تم استقصاء الخواص البصرية لهذه الصبغة ولسمك ($10\mu\text{m}$) بالاعتماد على طيف الامتصاص والنفاذ المقاس عند الطول الموجي (300 – 900 nm) عند درجة حرارة الغرفة . كما تم حساب المعاملات الضوئية الخطية المتضمنة (معامل الانكسار n , معامل التوهين k , معامل الامتصاص α , وكذلك الجزء الحقيقي والخيالي لدالة العزل الكهربائي ϵ_1, ϵ_2).

تم تحديد فجوة الطاقة الضوئية تم حسابها بالاعتماد على قيم معامل الامتصاص باستخدام طريقة Taue's procedure . واخيراً حسبت طاقة التذبذب (E_0) , وطاقة التشتت (E_d) , معامل الانكسار الثابت (n_0) , ثابت العزل الكهربائي الشبيكي (ϵ^∞) , ثابت العزل الكهربائي عند أعلى تردد (ϵ_∞) وكذلك نسبة التركيز الناقل للإلكترون المؤثر (N/m^*) بطريقة Wemple-DiDomenico .
الكلمات المفتاحية: إصباغ الازو , الثوابت الضوئية , تذبذب أحادي النمط, النوفولاك.

INTRODUCTION

In recent years, the azo dye has become an attractive material due to its optical properties. It has been applied in diverse applications such as the polarized photo induced anisotropy, and the polymers with different optical properties have been attracted much attentions due to their applications in the sensors [1,2], light-emitting diodes [3-5], and others [6,7]. The optical properties of these materials can be easily tuned by controlling contents of the different concentrations. Though a great deal of excellent work has been reported on such materials [8-10], it is still meaningful to extend the research of these polymers.

The optical behavior of a material is utilized to determine its optical constants. Films are ideal specimens for reflectance and transmittance, therefore, an accurate determination of the optical constants is extremely important [11]. The study of optical absorption, particularly absorption edge has proved to be very useful for elucidation of the electronic structure of the materials. It is possible to determine indirect and direct transition occurring in band gap by optical absorption spectra [12]. The data transmittance can be analyzed to determine optical constants such as refractive index, absorption index and dielectric constant. The refractive index is one of the fundamental properties of a material, because it is closely related to the electronic polarizability of ions and the local field inside the material. The evaluation of refractive indices of optical materials is considerable importance for applications in integrated optics devices such as switches fillers and modulators, etc., where the refractive index of a material is the key parameter for device design [13].

The goal of the present work is to the synthesis of the new azo dye and study fundamental optical properties of poly (6, 6'-(2-hydroxy-5-(p-tolyldiazenyl)-1, 3-phenylene) bis (methylene) bis(2-ethylphenol) film in the wave-length range (300-900) nm. (Furthermore, calculated the energy gap optical, single oscillator model and dielectric constants).

EXPERIMENTAL DETAILS

Synthesis of the azo dye- polymer compound

The azo dyes-polymer compound prepared by Fox method *P* [14, 15]. In the present method The azo dyes-polymer compound was prepared as following :

(0.535 gm, 0.005 mole) of *P*-toluidine was dissolved in 2 ml of Cone. HCl and then add (10 ml) of dionized water. The solution was then cooled to (0 – 5)°C in an ice-bath and maintained at this temperature. Sodium nitrite (0.36gm) solution in water (5 ml) was then added dropwise. Stirring was continued to produce diazonium salt at the same temperature. The diazonium solution was added portion wise to the coupling component solution prepared by mixing of novolac (Fluke Co.) (0.538 gm, 0.005 mole) in ethanol (Fluke Co.) /water ratio (1:3) with sodium hydroxide (2 gm) dissolve in (100 ml) of water. During the procedure the pH value was maintained with 9 – 10, and the temperature at (0 – 5)°C. The mixture was stirred for 30 min, and then the pH value was decreased to ~ 6. The mixture was left overnight at temperature (0 – 5)°C. The precipitated crude dyes were collected by filtration and washed with water, ethanol and acetone. Figure (1) Shows the chemical structure of anew azo dye- polymer compound (poly (6,6'-(2-hydroxy-5-(p-tolyldiazenyl)-1,3-phenylene) bis (methylene) bis(2-ethylphenol) PHTP.

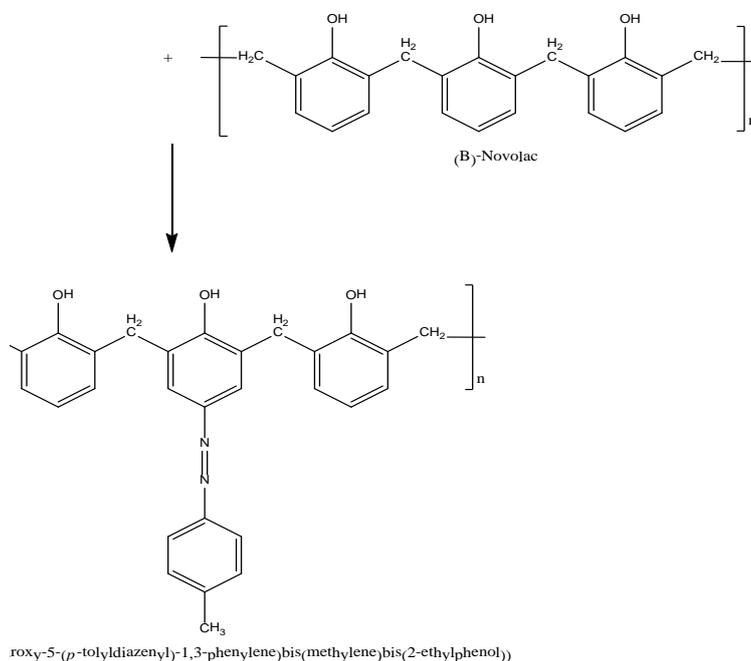


Figure (1) Chemical Structure of the new azo dye (poly (6,6'-(2-hydroxy-5-(p-tolyldiazenyl)-1,3-phenylene) bis (methylene) bis(2-ethylphenol)).

Table (1) the structure of azo dye compounds.

Compound	No.mol.	Molecular formula	M. wt	Wt.
Novolac	0.005 mol	/	106 g/mol	0.538g
P-toludine	0.005 mol	C ₇ H ₉ N	107.17g/mol	0.535g

Table (2) the some physical properties of azo dye compounds.

Compound	M. P (°C)	Compound State	Colour	Yield %
P-toludine	Over 250C	Powder	Red	80%

Preparation of the Film

A thin film of azo dye-polymer compound PHTP was prepared on glass substrate that has dimension (1.4 × 2 cm) using spin coating method with 2500 r/min, the film was heated at 80 °C for 1hr to evaporation the solvent used. The thickness of PHTP film kept around 10 μm. The thickness of the film was measured by digital micrometer. Finally, the transmittance (T) and the absorbance (A) of the sample measurements using spectrophotometer CE7200 ENGLAND. The measurements were performed at room temperature.

RESULTS AND DISCUSSION

Linear optical properties

The analysis of optical transmission spectra is on of the most productive for understanding and developing the band structure and energy band gap of materials. The transmittance (T) and reflectance spectra(R) of the film are shown in Figure (2).

The spectra curve of absorbance (A) of the film is show in Figure (3).

The absorption coefficient (α) can be calculated using the following relation [16]:

$$\alpha = 2.303 \frac{A}{d} \quad \dots(1)$$

Where A represents the optical absorbance and d is the thickness of the film, and the extinction coefficient (k) relates with absorption coefficient by the following relation [17]:

$$k = \frac{\alpha \lambda}{4\pi} \quad \dots(2)$$

The reflectance was calculated by the following relation [18]:

$$R = 1 - \sqrt{\frac{T}{\exp(-A)}} \quad \dots(3)$$

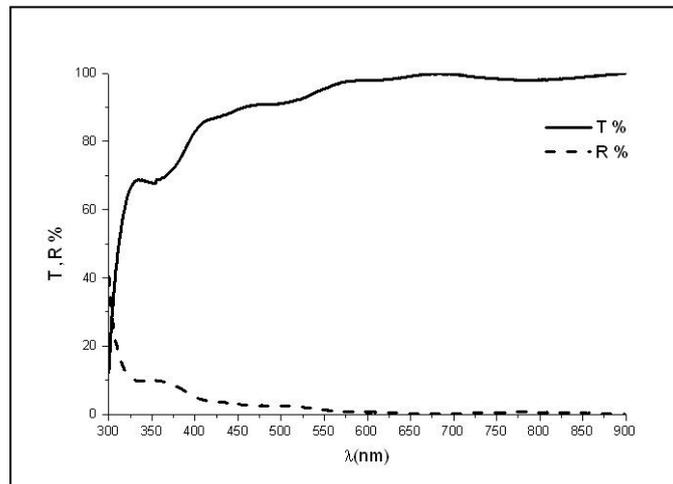


Figure (2) The transmittance (T), the Reflectance(R), as a function of wavelength (λ).

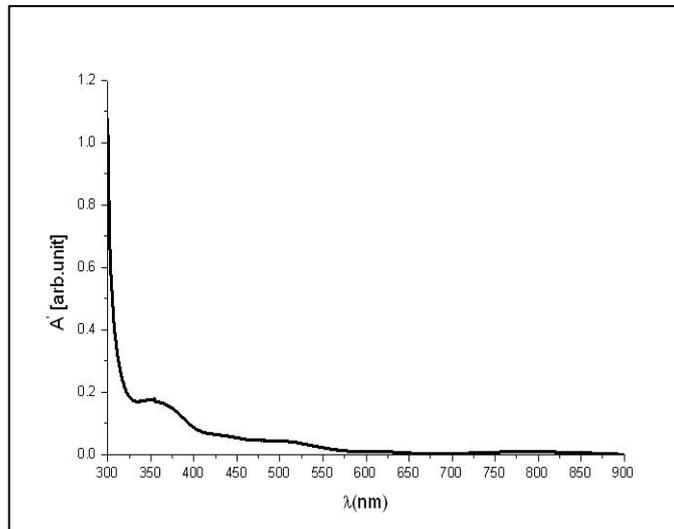


Figure (3) Absorbance (A) as a function of wavelength (λ)

The refractive index (n) and the Reflectance (R) spectra are related by this equation : [19]

$$n = \frac{(1-R^{1/2})}{(1+R^{1/2})} \dots (4)$$

The variation of the refractive index (n) as a function of wavelength is shown in Figure (4). From this figure, the dispersion curve of the refractive index is fairly flat in the long wavelength region (300- 900 nm) range and rises rapidly towards shorter wavelength. The variation of extinction coefficient (k) of the PHTP film can be seen in Figure (5) .

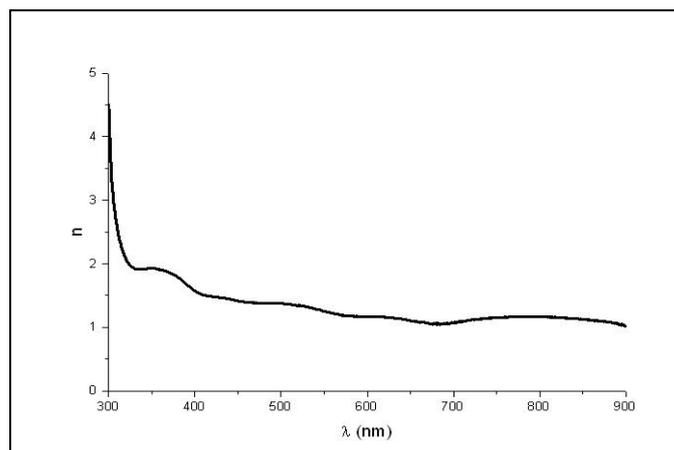


Figure (4) Refractive index (n) as a function of wavelength (λ) PHTP film.

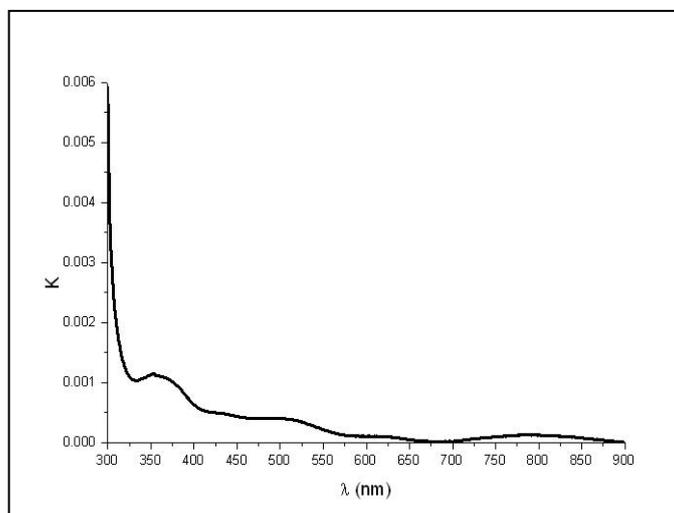


Figure (5) Extinction coefficient (k) as a function of wavelength (λ) of PHTP film.

It can be shown that the refractive index has anomalous dispersion in the region of the high frequency ($\lambda < 700nm$). As the refractive index increases, there is also an increase of the absorption of electromagnetic radiation associated with an increase of the frequency. Furthermore, the refractive index becomes high when the frequency of the radiation crosses with the characteristic frequency of the electron.

Hence, there is no propagation of electromagnetic radiation through PHTP films.

Determination of energy gap

The applicability of using band theory to describe the electronic in the organic systems was suggested by various authors [20-22]. The optical absorption near the absorption band edge is a standard method for investigating the optically induced transitions and it is also gives information about the internal structure as well as the optical energy gap in the films [23].

The optical energy gap (E_g) and the type of the optical transition for crystalline and non crystalline materials can be determined from the analysis of the absorption coefficient as a function of the photon energy near the fundamental absorption (α) edge, neglecting exciton effects, using the following expression[24,25]:

$$\alpha h\nu = B(h\nu - E_g)^m \quad \dots (5)$$

Where B is the characteristic parameter (independent of photon energy) for respective transitions, $h\nu$ denotes photon energy, E_g is optical energy gap and m is the number which characterizes the transition process. Different authors [26-28] have suggested different values of m for different materials, $m=2$ for indirect allowed transition and $m=1/2$ for direct allowed transition. For higher values $\alpha \geq 10^4 cm^{-1}$ the absorption coefficient, α (where the absorption is associated with interband transitions), the energy band gap can be determined. Figure (7) The values of E_g is give in Table (3) is a typical best fit of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for PHTP

film. The version of the absorption coefficient α as a function of photon energy is shown in the Figure (6).

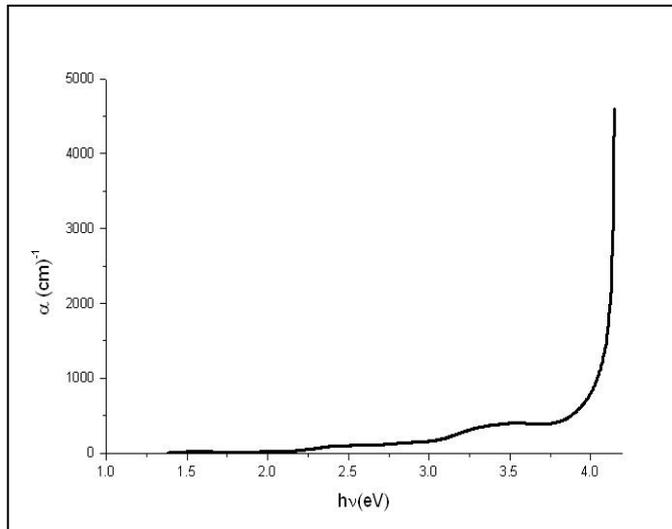


Figure (6) The version of absorption coefficient (α) as a function of photon energy ($h\nu$).

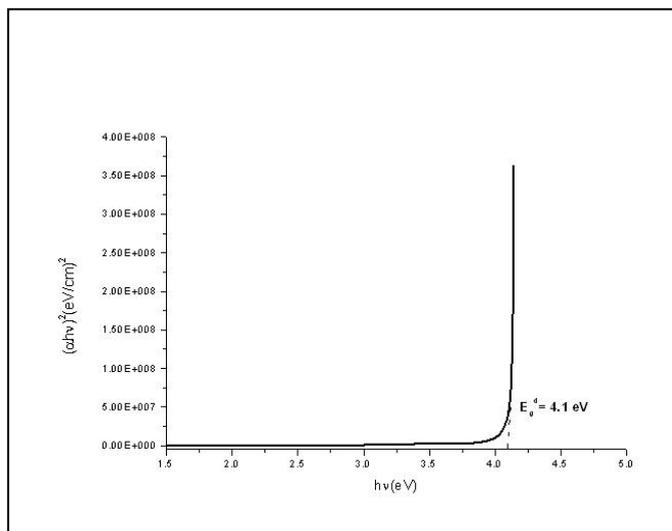


Figure (7) The plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$).

Single oscillator parameters

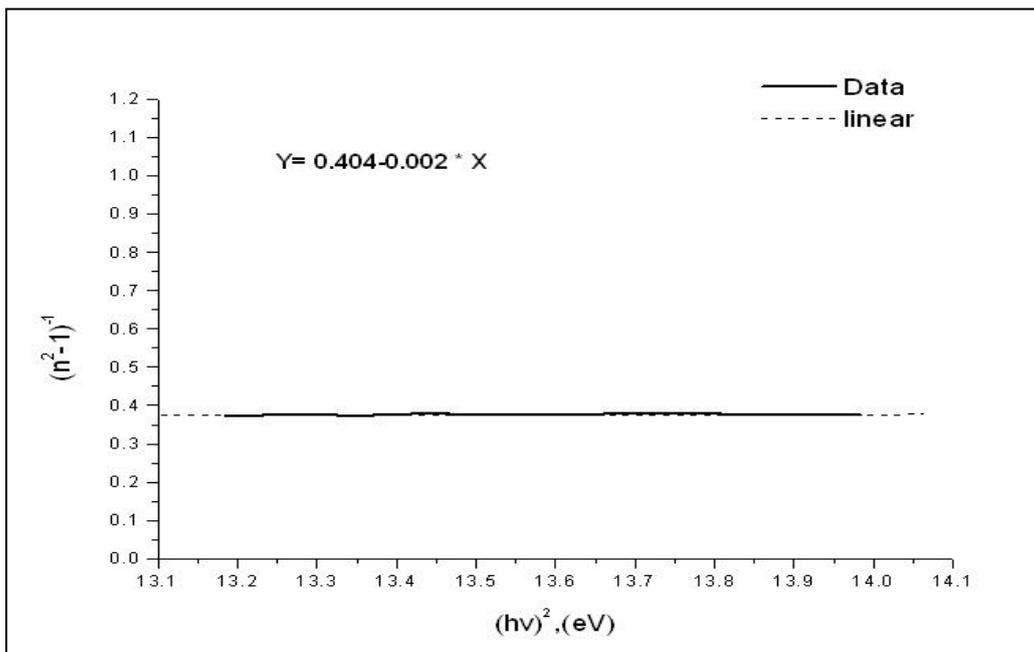
The observed dispersion behavior of PHTP film can be explained if it is assumed to be the response of a set of Lorentzian oscillators of adjustable strength and position [29]. Using this postulation, the refractive index as a function of photon energy can be analyzed on the basis of the single oscillator model, for photon

energies below the interband absorption edge. On the basis of this theory, Wemple and DiDomenico [30, 31] introduced two parameters; one is named the dispersion of the refractive index (E_d) and the second is named single oscillator energy (E_o). Using these parameters, the refractive index can be expressed as follow [32].

...(6)

$$n^2 - 1 = \frac{E_d E_o}{E_o^2 - (h\nu)^2}$$

Where $(h\nu)^2$ is the photon energy ,the parameter E_d , which is a measure of the intensity of the inter-band optical transition ,does not depend significantly on the band gap . A plot of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ for PHTP film is illustrated in Figure (8). The values of E_d and E_o were obtained from the slope $(E_o E_d)^{-1}$ and the intercept (E_o/E_d) with the vertical axis. Extrapolating the linear part towards long wavelengths, the point of interception with the ordinate at $(h\nu)^2=0$ yields the value of the dielectric constant at higher wavelength ($\epsilon_\infty = n_\infty^2$) . The static refractive index (n_0) can be calculated using the relation $(n^2 ((h\nu)=0)= E_d / E_o)+1$ [1].



Figure(8) Variation of (n^2-1) versus $(h\nu)^2$ for PHTP film.

A simple connection between the single oscillator parameters E_o and E_d and the imaginary part of the dielectric constant ϵ_2 spectrum can be expressed in terms of the r th moments of the ϵ_2 [30] as follows:

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \quad \dots(7)$$

and

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad \dots(8)$$

The oscillator energy E_0 is independent of the scale of ϵ_1 . The values of M_{-1} and M_{-3} are 2.471 and 0.01225 eV⁻², respectively, for PHTP film.

In transparent region the relation between the real part of the dielectric function, and the square of the wavelength λ , and the refractive index can be expressed by the following relation [33]:

$$\epsilon_1 = \epsilon_L - \left(\frac{e^2}{4\pi c^2 \epsilon_0}\right)\left(\frac{N}{m^*}\right)\lambda^2 \quad (9)$$

where ϵ_L is the lattice dielectric constant, ϵ_0 is the permittivity of free space, N is the free carrier concentration and m^* is the effective mass of the charge carriers. The nature of the dispersion of ϵ_1 as a function of wavelength squared λ^2 is shown in Figure (9).

$$\epsilon_1 \approx n^2$$

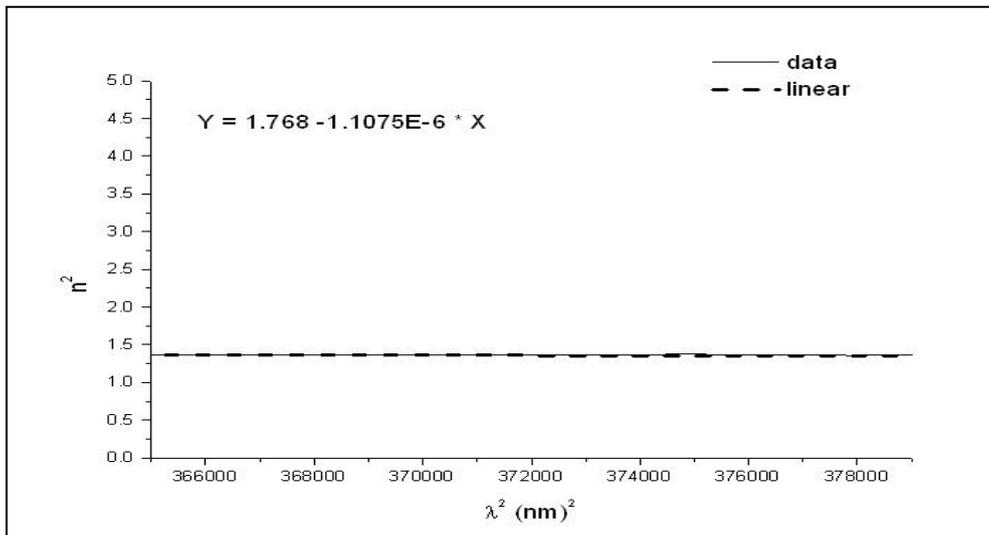


Figure.(9) the plot of n^2 as a function λ^2 for PHTP film

As shown in Figure (9), the dependence of n^2 is linear at the longer wavelengths. The value of the lattice dielectric constant (ϵ_∞, n_0) is determined from the intersection of the straight line with $\lambda^2=0$. the values of $\epsilon_L, E_0, E_d,$ the ratio $\epsilon_L N/m^*$ are listed in Table (3).

Table (3) Estimated valued of the optical parameters of the PHTP film.

E_g^d (eV)	ϵ_L	E_0 (eV)	E_d (eV)	ϵ_∞	n_0	$N/m^*(cm^{-3} \cdot g^{-1})$
4.1	1.768	14.2	35.1	3.91	1.97	$4.32 * 10^{17}$

Dielectric constant

The real and imaginary parts of the dielectric constant can be determined using the following formules [34-35]:

$$\epsilon_1 = n^2 - k^2 \quad \dots(10)$$

$$\epsilon_2 = 2nk \quad \dots(11)$$

The dependence of ϵ_1 and ϵ_2 on the photon energy (hv) is shown in the Figure(10) and Figure(11), respectively. the real and imaginary parts follow the same pattern and it can be seen that values of real part are higher than those of the imaginary part.

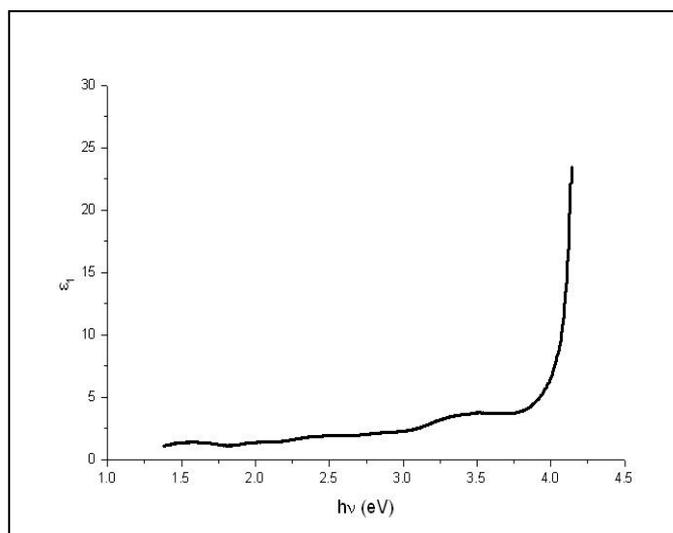


Figure (10) Real part ϵ_1 of the dielectric constant as a function of photon energy(hv) of PHTP film.

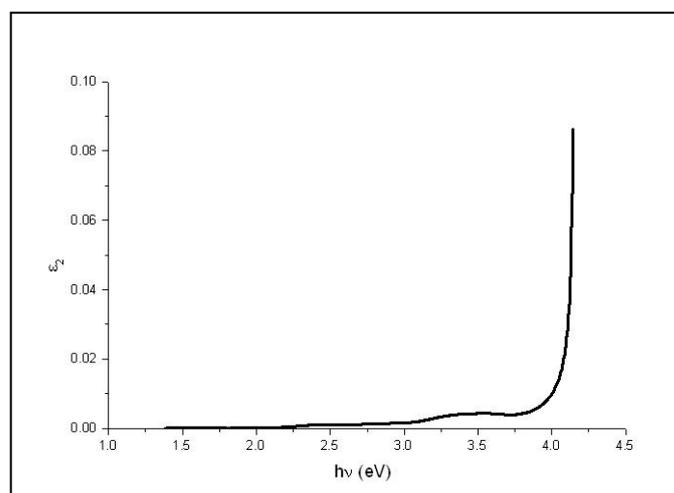


Figure (11) the imaginary part ϵ_2 of the dielectric constant as a function of photon energy ($h\nu$) of PHTP film.

CONCLUSIONS

The azo dye polymer material has been synthesized from P-toluidine and novolac by the Fax method. The optical constants such as the refractive index (n), the extinction coefficient (k), the optical energy gap, and the real and imaginary parts of dielectric constants of the azo dye polymer film were calculated. From the reflectance and transmittance curves, it can be concluded that the refractive index (n) decreases with increasing wavelength. Optical data are frequently used to get some information about the optical energy gap, the transition between valence band and conductor band PHTP film is direct allowed transition. The oscillator energy in the azo dye polymer E_0 and dispersion energy E_d have been determined by the Wemple - DiDomenico method.

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