Synthesizing and determining the optical properties and the surface, volume energy loss function of novel azo dye polymer (PHPP)

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Abstract

In this paper, azo dye polymer materials were synthesized from aniline with Novolac by Fox method. The fundamental optical constants of PHPP film measured at thickness 5µm film have been calculated by depending on the curve of absorption and transition spectra over the spectral of 300-900 *nm* in the room temperature. The energy gap was valued 4.176 eV. Finally, the interband transition strength, surface and volume energy loss function have been obtained depending on dielectric constant of the film.

Keywords: Azo dye polymer, dielectric constant, interband transition strength, SELF and VELF.

1- Introduction

Recently, the search for optical properties increases because of their applications in integrated optics such as optical modulation, optical information, and optical data storage [1]. The optical behavior of a material is utilized to determine its optical constants. Films are ideal specimens for the reflectance and the transmittance, therefore, an accurate determination of the optical constants is extremely important [2].The study of optical absorption, particularly absorption edge has proved to be very useful for the 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 [3]. Quantitative optical properties are playing an increasingly important role in electronic structure studies of materials [4]. All optical properties can be derived from the complex dielectric function $\varepsilon(\omega)$. This function is therefore of prime importance, and can be determined in many ways, using either incident photons or electrons.

The Novolac can be classified to two types of phenol resins: resold and Novolac. The first one is synthesized under basic pH conditions with excess formaldehyde, and the second is carried out at acidic pH (with

an excess of phenol). They are widely used in industry because of their chemical resistance, electrical insulation, and dimensional stability [5].

The interaction of the photons with the material results in the excitation of electrons into unoccupied energy levels in the conduction band as well as collective excitation of valence electrons. Interband transitions originate from the excitation of electrons in the valence band to an empty state in the conduction band, so these can be identified as transition in a band structure model [6]. The excitation of the electrons valence band can be distinguished between collective plasma oscillations and single electron interband transition. The latter depends on critical point in the band structure [7].

There are two regions for electronic energy loss function. The first region is the high loss energy region (>1eV), analysis of the first (10 eV) of spectra after the ionization edge can give information about the oxidation state. The second region is the low energy loss (<1 eV) which can provide information about composition and electronic structure [6]. The energy loss function results from the dielectric constant of the materials within the range of validity of the dielectric theory [8-10].

This paper reports the results of some optical properties of (poly (6,6'-2-hydroxy-5-(phenyldiazenyl)-1,3-phenylene) bis (methylene) bis(2-ethylphenol)) PHPP film with 5µm thickness in the wavelength (300 -900 *nm*). The study covers the measurement of optical spectra, reflectivity, extinction coefficient, refractive index, interband transition strength, surface and volume energy loss functions.

2- Experimental:
2-1 Synthesis of azo dye polymer compound

The azo dyes compound of (poly (6,6'-(2-hydroxy-5-(phenyldiazenyl)-1,3-phenylene) bis (methylene) bis(2-ethylphenol)) PHPP prepares using the Fox method *P* [11] (0.465g ,0.005 mole) of aniline was dissolved in 2 ml of Cone. HCl and then (10 ml) of dionized water were add . The solution was then cooled to 5°C in an ice - bath and maintained at this temperature . Sodium nitrite (0.36g) 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 (0.538 g , 0.005 mole) in ethanol /water ratio (1:3) with sodium hydroxide (2 gm) dissolves in (100 ml) of water . During the procedure. The pH value was maintained with 9 – 10 , and the temperature at 5°C . The mixture was stirred for 30 min , and then the pH value was decreased to ~ 6. The mixture was left overnight . The precipitated crude dyes were collected by filtration , and washed with water , ethanol and acetone .

The structure and some physical properties of azo dyes compounds of (poly (6,6'-(2-hydroxy-5-(phenyldiazenyl)-1,3-phenylene) bis (methylene) bis(2-ethylphenol)) PHPP were given in Fig.(1) and Table (1).

Fig.(1) The chemical structure of the azo dye compounds (poly (6,6'-(2-hydroxy-5-(phenyldiazenyl)-1,3-phenylene) bis (methylene) bis(2-ethylphenol)) PHPP.

Table (1) Physical properties of azo dyes compounds

Compound	No.mol.	Molecular formula	M. wt	Wt.	M.P (^{0}C)	Compound State	Colour	Yield %
Novolac	0.005 mol	/	106 g/mol	0.53g	/	/	/	/
Aniline	0.005 mol	C_6H_7N	93.13g/mol	0.465g	Over 250C	Powder	red	77%

2-2 Preparation of the thin Film

A thin film of azo dye-polymer compound PHPP was prepared on glass substrate that has dimension (1.4 × 2 cm) using spin-coating method with 2500 r/min . The thickness of PHTP film kept around (5µm). The thickness of the film was measured by digital micrometers. Finally, the film was heated at 80 ^{0}C for   1hr to evaporate the of solvent used.

3- Results and discussion
3-1 Linear optical properties

The spectra curve of absorbance (A$'$) of the film is shown in Fig.(2), and the peak in the curve is appeared at (350 *nm*) which represents the transition $\pi \longrightarrow \pi^*$. The value of the absorption coefficient was determined from the relation ($\alpha = \frac{1}{d} ln(\frac{1}{A'})$

) [12], where A$'$ is the absorption corrected of the film d is the thickness of film.
The extinction coefficient(k)is related with the absorption coefficient (α) by the following relation $k = \frac{\alpha\lambda}{4\pi}$ [13].
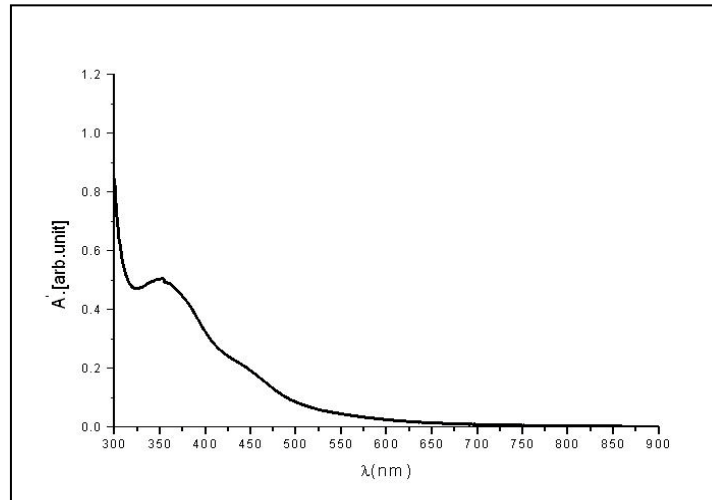
Fig.(2): The spectrum absorbance (A$'$) as a function the wavelength (λ) of PHPP film.

The reflectance was calculated using the following equation [14].

$$R = 1 - \sqrt{\frac{T}{\exp{(-A')}}} \qquad (1)$$

Fig.(3) shows the transmittance spectrum in the UV – Visible region of PHPP The curve showed high transparency in wavelength range $> 500nm$. The reflectance of the film as a function of wavelength has been shown in the Fig.(4). It is clear from the figure that the most reflectance occurs at wavelength range (300-900 *nm*), Then decreasing to zero at the range (750-900 *nm*).
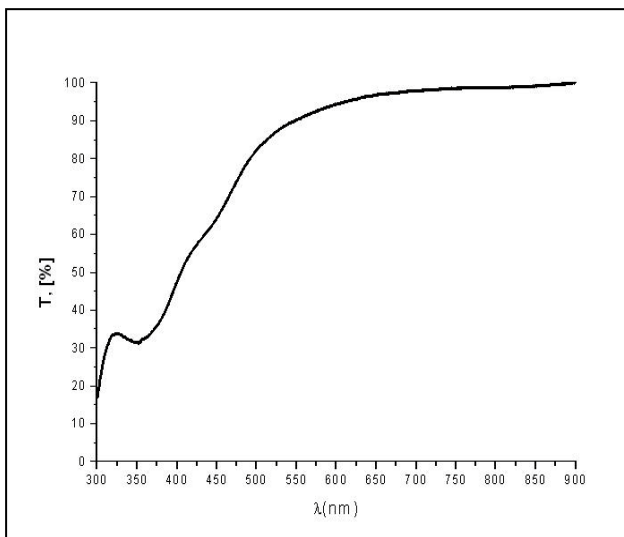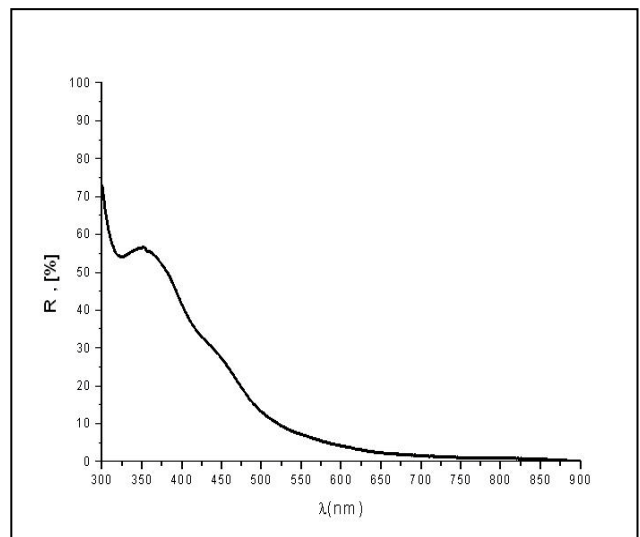

Fig.(3): The spectrum transmittance as a function the wavelength of PHPP film.

Fig(4): The Reflectance as a function the wavelength of PHPP film.

The refractive index of the PHPP film was calculated by the following relation [15]:

$$n = \frac{(1+R)}{(1-R)} - \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad (2)$$

The refractive index and extinction coefficient (k) of PHPP films were determined from the measured transmittance and reflectance at normal light incidence. The spectral dependences of both n(λ) and k(λ). are shown in Fig.(5) and Fig.(6), respectively.

It can be seen from the figure (5) that the extinction coefficient (k) is small at longer wavelengths, showing that the prepared film is highly transparent. The Evaluation of the refractive indices of

optical materials is considerably important for the applications in integrated optical devices, such as switches, fillers and modulation, etc., in which the refractive index (n) is a key parameter for the device design [16].

The refractive index (n) of PHPP film shows anomalous dispersion in the spectra range (340-500 *nm*) and normal dispersion in the spectra range (500-900 *nm*). This anomalous behavior is due to the resonance effect between the incident electromagnetic radiation and the electrons polarization, which leads to the coupling of electrons in PHPP film to the oscillating electron field [16].
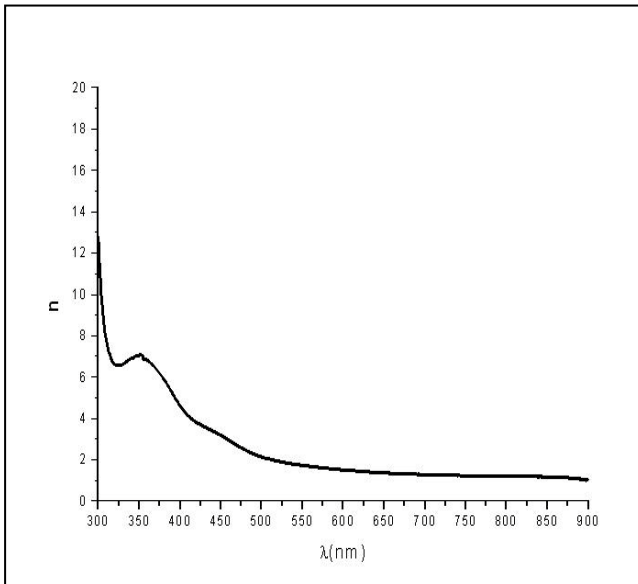

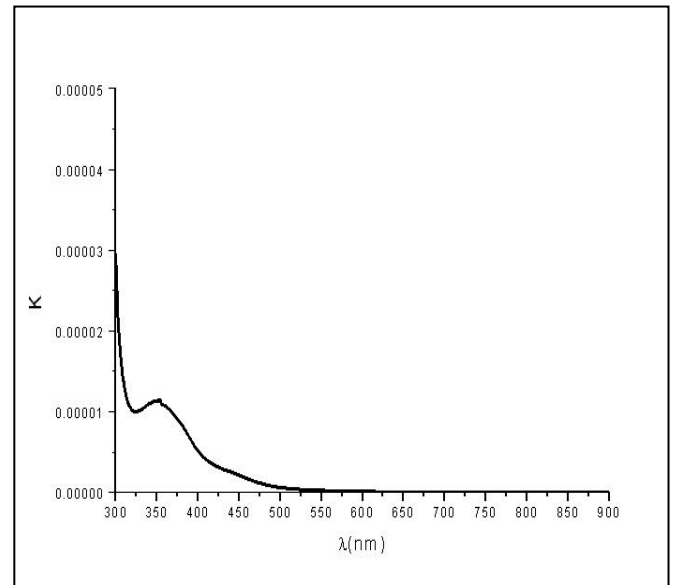**Fig.(5): The refractive index as a function the wavelength of PHPP film.**

Fig. (6): The extinction coefficient as a function the wavelength of PHPP film.

3-2 Determination of Energy Gap

The optical energy gap and the type of optical transition for crystalline and non crystalline materials can be determined from the analysis of the absorption coefficient (α) as a function of the photon energy near the fundamental absorption edge. Fig (7), neglecting the excitation effects, using the following expression [17,18]:

$$\alpha h\nu = B(h\nu - E_g^{opt})^r \qquad (3)$$

where B is the characteristic parameter (independent of photon energy) for respective transitions and inversely proportional to amorphousity , $h\nu$ denotes photon energy , E_g^{opt} is optical energy gap and r is the number which characterizes the transition process, and is theoretically equal to 1/2, 2, 3/2 or 3 for direct allowed (α $\geq 10^4$cm $^{-1}$) indirect allowed, direct

forbidden and indirect forbidden transition, respectively [19].

The optical energy gap can be obtained by plotting $(\alpha h v)^2$ versus $(h v)$ in the high absorption range followed by extra plotting the linear region of the plots to $(\alpha h v)^2 = 0$. Fig.(8) shows the plots of $(\alpha h v)^2$ versus photon energy for PHPP film. The obtained value of the E_g^{opt} is shown in Table (2).
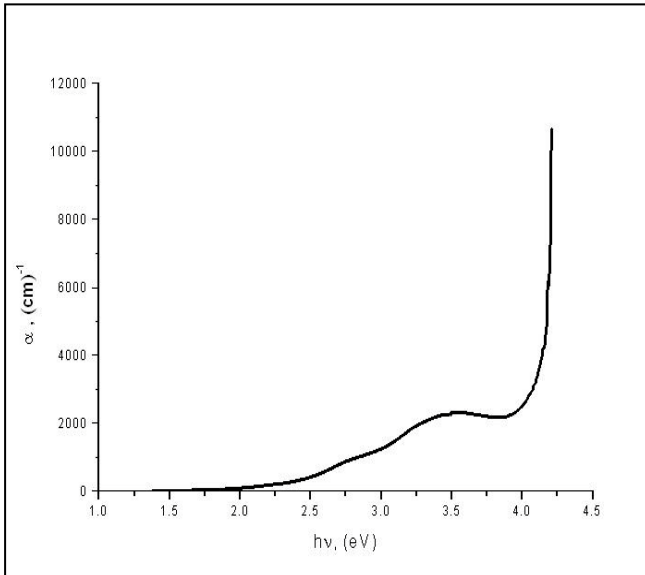

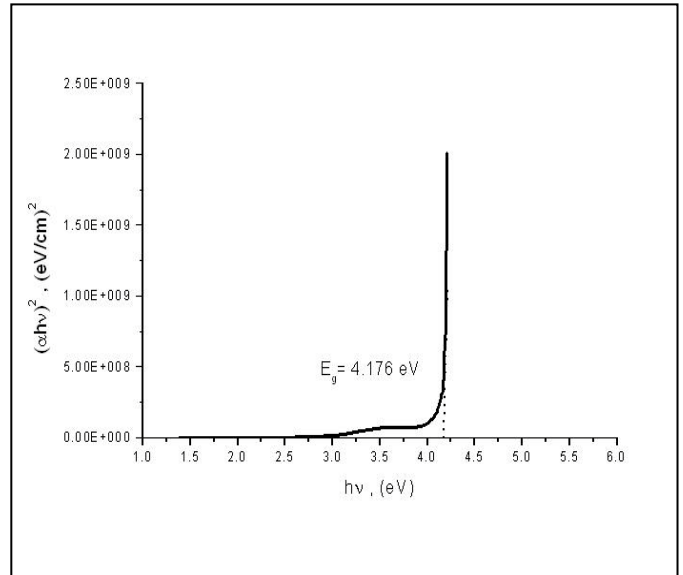**Fig.(7) Absorption coefficient as a function of photon energy for PHPP film.**

Fig.(8) Dependence of $(\alpha h v)^2$ on the photon energy for PHPP film.

3-3 Complex Dielectric Constant of PHPP Film

The frequency dispersion of ε characterizes completely the propagation, reflection and loss of light in multilayer structures. It provides us an information about the electronic quantity for the design of the highly efficient optoelectronic devices [20]. The complex dielectric constant is described by :

$$\varepsilon = \varepsilon_1(v) - \varepsilon_2(v) \qquad (4)$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric constant, respectively. It is well known that polarizabiltiy of any solid is proportional to its dielectric constant. The real and imaginary parts of the complex dielectric constant are expressed [20-22] as :

$$\varepsilon_1 = n^2 - k^2 \qquad (5)$$
$$\varepsilon_2 = 2nk$$

The dependences of ε_1 and ε_2 on the photon energy are shown in Fig. (9) and (10) respectively The real and imaginary parts follow the same pattern and the values of the real part are higher than the imaginary part. The variation of the dielectric constant with photon energy indicates that some interactions between photons and electrons in the films are produced in this energy range. These interactions are observed on the shapes of the real and imaginary parts of the dielectric constant .They cause formation of peaks in the dielectric spectra which depends on the material type [20]. Quantitative optical properties are playing an increase important role in electronic structure studies of materials [23,24]. All optical properties can be derived from the complex dielectric function $\varepsilon(v)$.This function is therefore of prime importance, and can be determined in many ways, using either incident photons or electrons. In general, the real and imaginary parts of the dielectric increases with increasing photon energy, this behavior led to increase extinction and electronic

transfers through the material from valence to conduction band. The random electronic transfers makes electronic collisions elastic and inelastic lead to increase the dielectric constant.
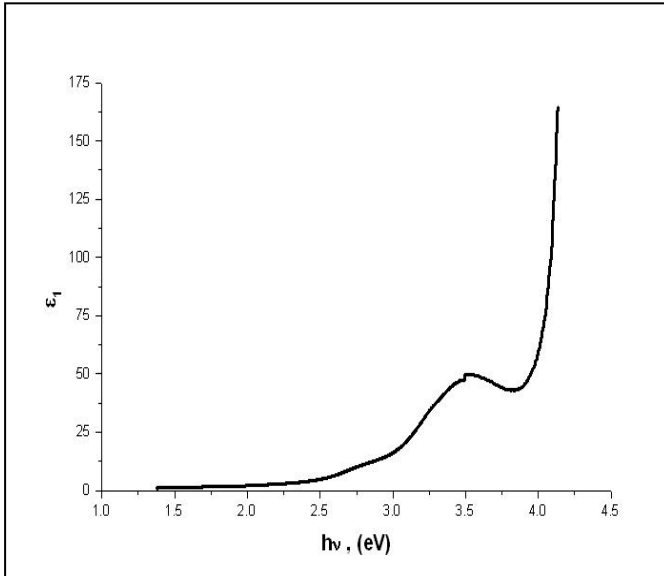

Fig.(9)T he real part(ε_1) of the dielectric constant as a dielectric function of photon energy of PHPP film. PHPP film.
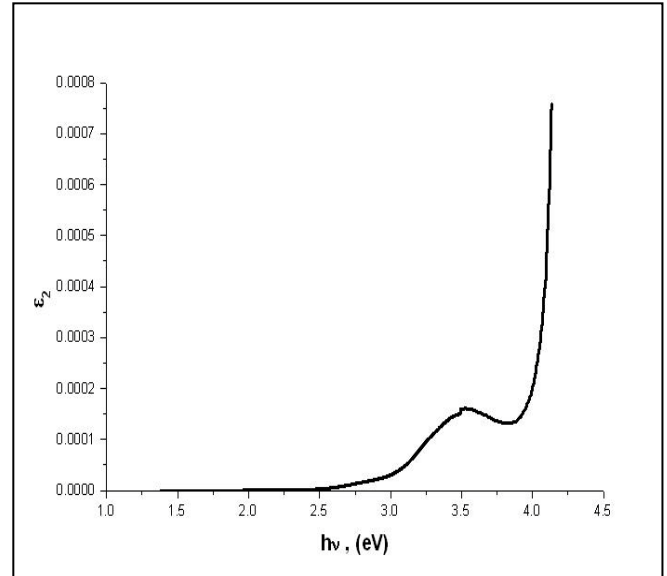
Fig.(10) The imaginary part (ε_2) of the dielectric constant as a function of photon energy of

Interband transition strength

From the real and imaginary parts of the dielectric constant the complex interband

$$J_{cv} = J_{cv1} + J_{cv2} = \frac{m_o^2\, 4\pi^2}{e^2 h^2}\, \frac{(h\nu)^2}{2}\, (\varepsilon_2 + i\, \varepsilon_1) \qquad (6)$$

where m_o is the mass of the electron, h is Plank's constant , e is the charge of electron and $(h\nu)$ is the photon energy . The real part of interband transition strength J_{cv1} is proportional to the imaginary part of the dielectric function . the imaginary part of interband transition strength J_{cv2} is proportional to the real part of the dielectric

transition strength [25] can be calculated as :

function ε For computational convenience we take the prefactor $(\frac{m_o^2\, 4\pi^2}{e^2\, h^2})$ in Eq.(6) , whose value in cgs units is $8.289 \times 10^{-6}\, g\, cm^{-3} eV^{-2}$, therefore, the J_{cv} calculated from is Eq.(6) is shown in the Figs.(11) and (12).
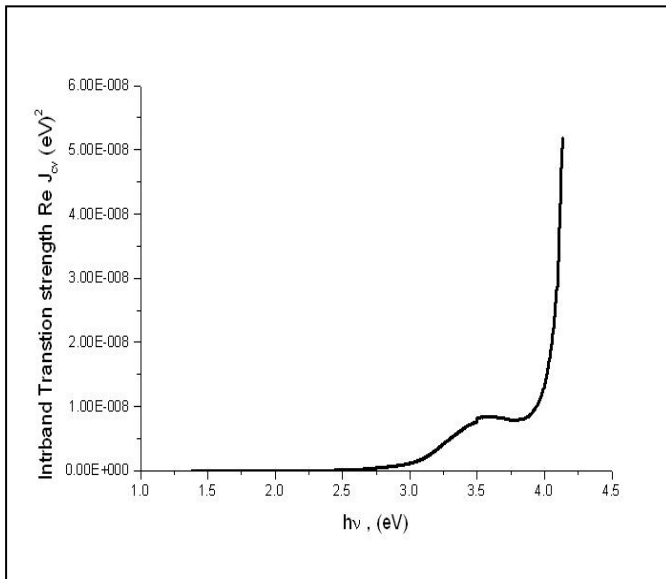
Fig.(11) The real part J_{cv} as a function of photon energy of PHPP film.

Fig.(12) The imaginary part J_{cv} as a function of photon energy of PHPP film.

In these figs. Illustrated Interband transition strength J_{cv} as a function of the photon energy. It increases with increasing photon energy and this denotes that the probability of electronic transition makes increase with increasing photon energy. These Figures also show that the interband
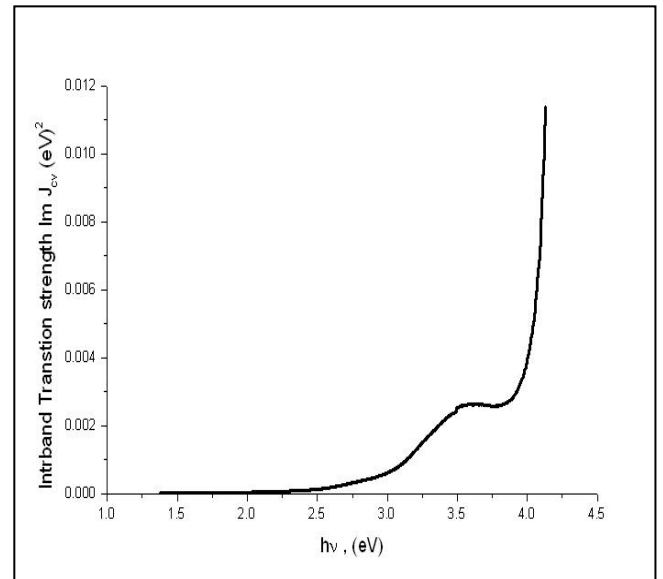
Surface and Volume Energy Loss Function

It is also possible to calculate the surface $-Im\left(\frac{1}{1+\varepsilon}\right)$ and volume (bulk) $-Im\left(\frac{1}{\varepsilon}\right)$ energy loss functions (SELF and VELF) related to the real and imaginary parts of the dielectric constant as [26,27]:

$$Surface - Im\left(\frac{1}{1+\varepsilon}\right) = \frac{\varepsilon_2}{((\varepsilon_1+1)^2+\varepsilon_2^2)} (7)$$

$$Volume - Im\left(\frac{1}{\varepsilon}\right) = \frac{\varepsilon_2}{(\varepsilon_1+\varepsilon_2)^2}$$

The behavior of both surface and volume energy loss function as a function of photon energy is shown in the Fig.(13). It is clear

transition strength J_{cv} grows significantly when the photon energy is higher than 3eV . This means that most of the high absorption happens which increases the excitation of the electrons and moving it from the valence band to the conduction band.

that the volume energy loss is greater than surface energy loss at incident photon energies. It is also clear that the maximum of SELF and VELF correspond to the absorption energy due to the interband transition that occurs at [2.75 eV (451 *nm*)for SELF] and [2.65 eV (468 *nm*] for VELF). Roth the energy losses are when the fast single electrons traverses from valance band to conduction band in the PHPP film.
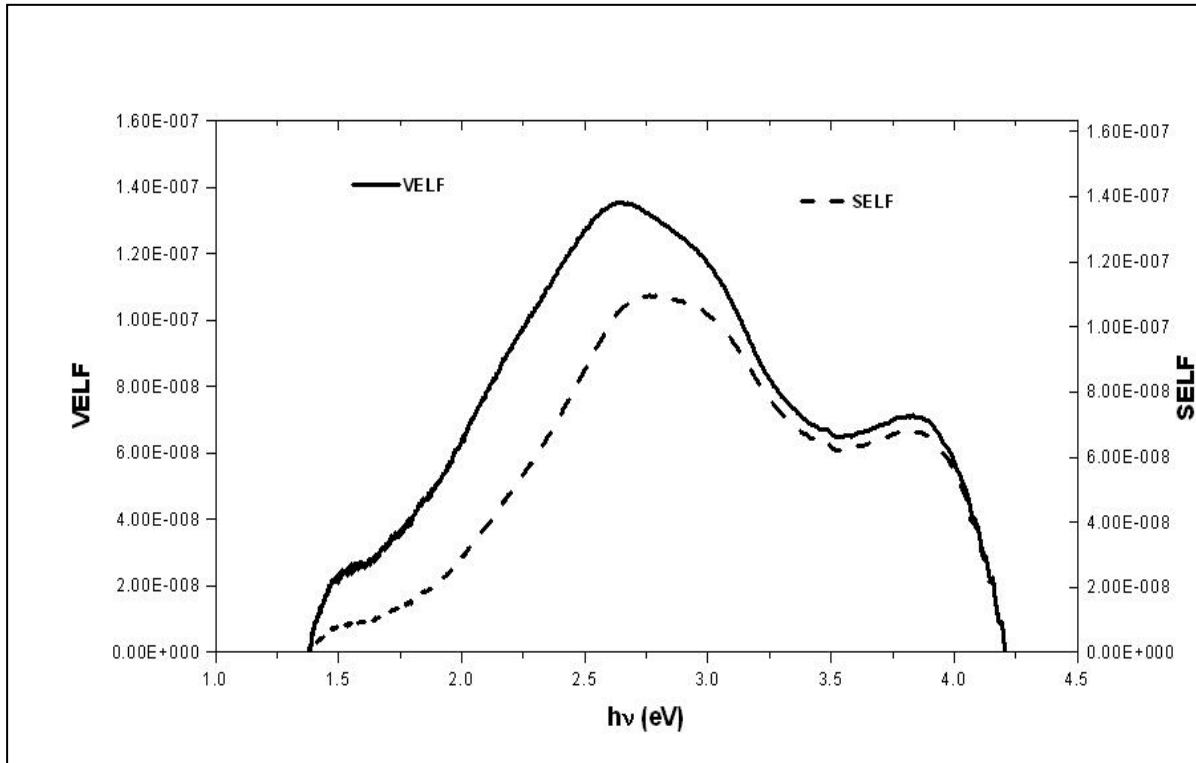
Fig.(13) Surface and Volume energy loss functions of PHPP as a function photon energy .

4- Conclusion

In this paper, azo dye polymer materials were synthesized from aniline with Novolac by Fox 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 in the azo dye polymer PHPP film is direct allowed transition. The interband transition strength of PHPP film found active when the photon energy for > 3eV. Bath surface, volume energy loss function have been obtained by depending on real and imaginary parts of dielectric constant, it has maximum peak at energy (2.75eV and 2.65 eV) .This leads to single electron excitation process that occurs in the PHPP film.

Table (2) Parameters of the PHPP film

Quantity	Value
N	12.8
K	2.9×10^{-5}
$E_g^{opt}(eV)$	4.176
ε_1	160.8
ε_2	7.33×10^{-4}
$Re\, J_{cv1}(eV)^2$	5.18×10^{-8}
$Im\, J_{cv2}(eV)^2$	0.0113
SELF	1.09×10^{-7}
VELF	1.35×10^{-7}

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الخلاصة :

في هذا البحث, تم تحضير صبغة ازو بوليمرية من الانلين و بوليمر النوفولاك بطريقة فوكس. درست الخصائص البصرية لأنموذج PHPP المحضر بطريقة الطلاء بأستخدام تقنية البرم المغناطيسي وبسمك 5µm. بالاعتماد على طيف الامتصاص والانتقال ضمن الطول الموجي *(nm* 900 − 300) عند درجة حرارة الغرفة. وكانت فجوة الطاقة (4.176 eV) . وبالنهاية, تم حساب طول الانتقال الداخلي و دالة فقد الطاقة السطحية والحجمية بالاعتماد على ثابت العزل لأنموذج .