Synthesis and investigation of Linear Optical Properties of Novel Azo Dye Polymer Films

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Abstract

The optical properties of an azo dye Poly(4-((3,5-bis(3-ethyl-2-hydroxybenzyl) -4-hydroxybenzyl) diazenyl) benzoic acid) films have been investigated by absorption and transition spectra at wavelength range (300-900 nm) at normal condition . The linear optical parameter includes calculation of (refractive index, extraction coefficient, absorption coefficient, Real and Imaginary part of dielectric constant, optical conductivity). Urbarch energy(E_u), indirect energy gap E_g^{ind} and phonon energy E_{Phonon} are equals 0.41497 eV, 2.3059 eV and 147.35 eV, respectively have also studied.

Keywords: Azo dye polymer, optical properties, optical energy gap, Urbarch energy.

1- Introduction

Azo dye has received great attention due to its environmental stability, ease of preparation and its optical and electrical properties. Much work has been done on the molecular design, synthesis, and assembly of structures with desired properties [1-5]. The discovery of diazo compounds occurred around the year 1858, which parallels the beginning of what is considered the starting point of modern organic chemistry [6,7]. Studies on polymers with different optical properties have attracted more attention due to their applications in the optical [8]. We can classify The Novolac 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[9].

The study of optical absorption transition of azo dye, particularly, the absorption edge has proved to be very useful for the elucidation of the application electronic structure of these materials. It is possible to determine the indirect and direct transition occurring in the band gap of the materials by the optical absorption spectra.

The transmittance data can be analyzed to determine the optical constants such as refractive index, absorption index and the dielectric constant. This paper reports the synthesis of the noval azo dye polymer and the linear optical constants of the azo dye (Poly (4-((3,5-bis(3- ethyl-2-hydroxybenzyl)-4-hydroxybenzyl)diazenyl)) benzoic acid) film of thickness ($15\mu m$) in the wave length range (300-900 nm) through an optical spectral analysis.

2- Experimental Details
2-1 Synthesis of the azo dye

The azo dyes compound Poly (4-((3,5-bis(3- ethyl-2-hydroxybenzyl)-4-hydroxybenzyl)diazenyl) benzoic acid) prepared using the Fox method [10,11] (0.685 gm ,0.005 mole) of 4-amino bezoic acid 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 the mixing

of novolac (0.538 gm , 0.005 mole) in ethanol /water ratio (1:3) with sodium hydroxide (2 gm) dissolved 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 . 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 were given in Tables (1,2).

Fig.(1) shows the chemical Structure of the compound

Table (1)

Compound	No.mol.	Molecular formula	M. wt	Wt.
Novolac	0.005 mol	/	106 g/mol	0.53g
4-aminobenzoic acide	0.005 mol	$C_7H_7NO_2$	137.14g/mol	0.685g

Table (2)

Compound	M. P (^{0}C)	Compound State	Colour	Yield %
4-aminobenzoic acide	Over 250C	Powder	red	75%

2-2 Preparation of the Film

The dye solution was prepared on glass substrate that has dimension (1.4×2) cm^2 by using spin coating method with 2500 r/min . The thickness of azo dye film found to be   15 µm . which measured by digital micrometers(photo detector fed to the power meter) . Finally , the film was heated at 80 ^{0}C for   1hr to evaporate the solvent used .

3- **Results and Discussion**

A UV-spectrophotometer CE-7200 (in comp. Aquarius) has been used to characterize the azo dye polymer in the spectral range (300-900 nm), the spectra curve of absorption(A) of film is shown in the fig.(1), The value of absorption coefficient (α) was obtained directly from the adsorption spectra   using Beer – Lambert Law ($\alpha = \dfrac{2.303}{d} \times A$) [12]where (A) is the absorbance and (d) is the thickness of the film . The analysis of optical transmission spectra is one of the most productive tools for understanding and

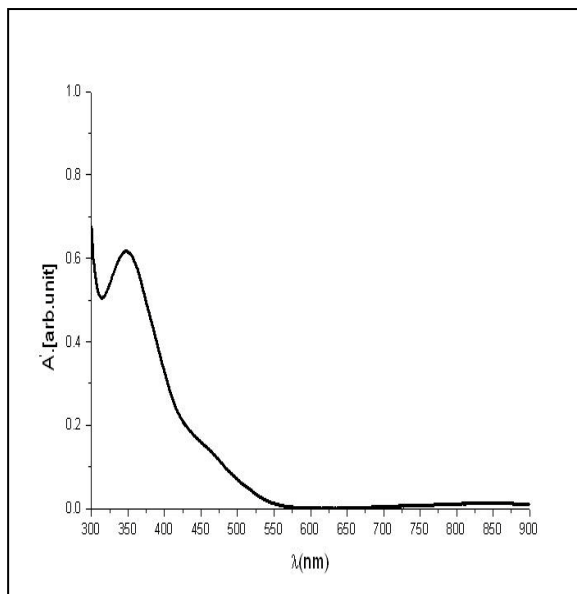developing the band structure and energy band gap of materials . The spectral dependence on transmittance (T) and reflectance (R) for azo dye is shown the fig.(2) . Reflectance R of thin films was calculated from the equation (1) [13] :

$$R = 1 - \sqrt{\frac{T}{\exp(-A)}} \qquad (1)$$

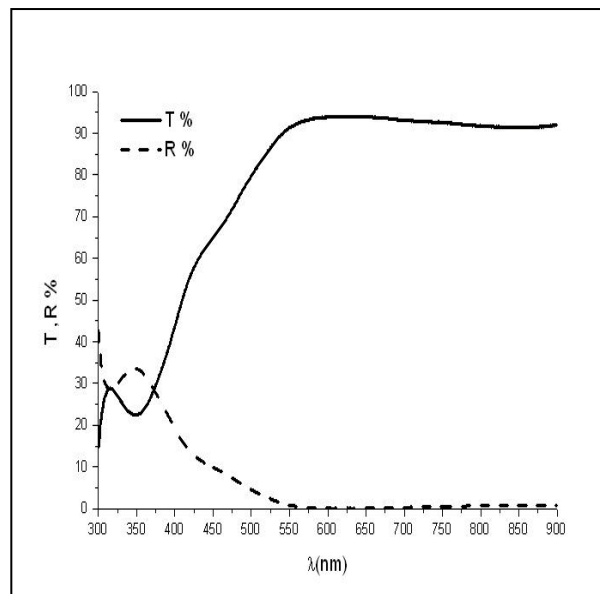**Fig. (1) the absorbance as a function of wavelength**

Fig. (2) the transmittance (T) , the Reflectance(R), as a function of wavelength

From the transmittance and reflectance spectra of azo dye it was observed that at a large wavelength ($\lambda > 550$ nm) the azo dye shows high transmission . The quality (R+T < 1) at wavelength ($\lambda < 550$ nm) implies the existence of absorption , i.e. an absorbing region .

The excitation coefficient relates with absorption coefficient by the relation ($K = \alpha\lambda / 4\pi$) , it is presented in fig (3) , and the refraction index (n) and the extinction coefficient (K) are related by the equation (2) [14]

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

Where λ is the wavelength.

The version of the refractive index as a function of wavelength is shown in the fig. (4).
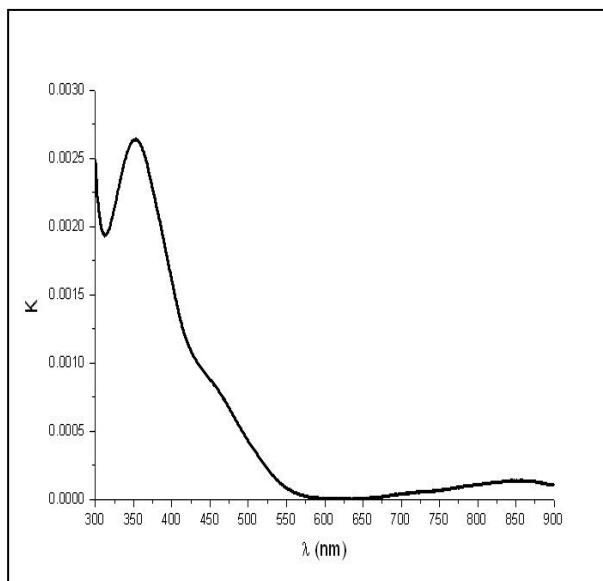
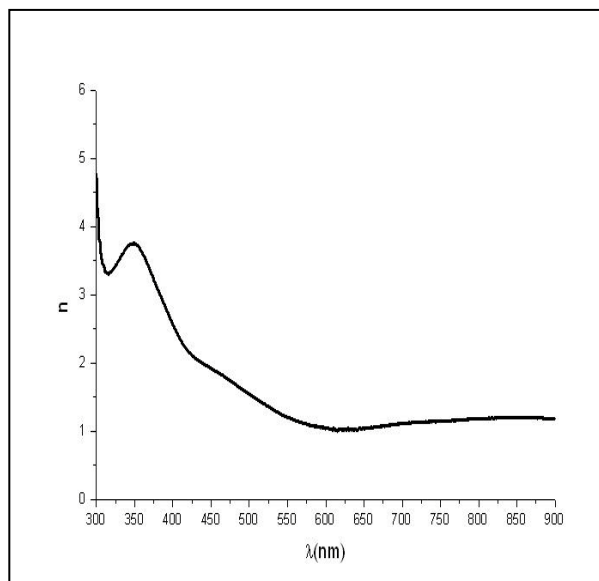**Fig.(3) extinction coefficient (k) as a function of wavelength**

Fig.(4) Refractive index (n) as a function of wavelength

The version of the absorption coefficient α as a function of photon energy is shown in the fig.(5),

In this fig. the electronic transitions are deduced (in addition to $\pi \rightarrow \pi^*$) at 3.5 eV.

The film has high extinction along the wavelength (350- 550 nm), this denotes the light at his value of wavelength which causes more extinction for electrons and atoms of the material, and the refractive index is noted that in the wavelength range ($\lambda > 350$ nm) , the refractive index has high values and then changed a smoothly, in the high wavelength ($\lambda > 550$ nm) . The refractive index is less significant.

The optical band gap was determined from the analysis of the spectral dependence of absorption near the absorption edge .The absorption coefficient α relates to the incident photon energy $(h\nu)$ of by the relation (3) [15].

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

Where B is constant , $h\nu$ photon energy , E_g is a value optical band gap between the valence band and the conduction band , r is parameter that gives the type of electron transition. Specifically, r is 1/2 ,3/2,2 and 3 for transition direct allowed, direct forbidding , indirect allowed and indirect forbidding respectively [16].

The indirect energy gap is calculated plot $(\alpha h\nu)^{0.5}$ as a function to photon energy (hv) for the film as shown in fig. (6) .The indirect transition, requires phonon assistance, the absorption coefficient has the following dependence on photon energy [17, 18] .

$$\alpha h\nu = A(hv - E_g + E_p)^2 + B(hv - E_g - E_p)^2$$
$$(4)$$

Where E_p is the energy of the phonon associated with the transition, A and B are constants depending on the band structure. The obtained values of the energy band gap are equal to 2.3059 eV and the phonon assistance to 147.35 meV .
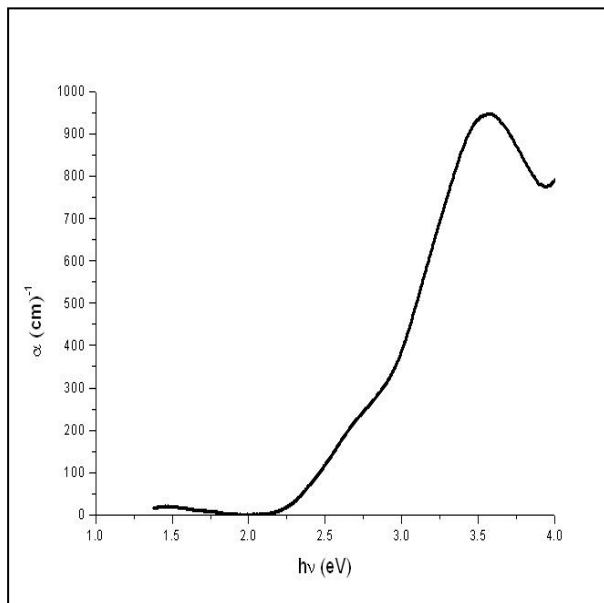
Fig .(5)The version of absorption coefficient α as a function of photon energy (hv)

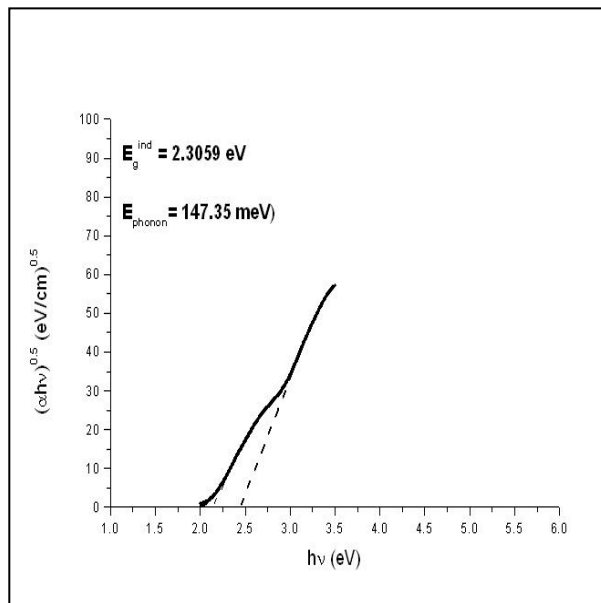**fig.(6) The plot $(\alpha hv)^{0.5}$ as a function of photon energy (hv)**

Fig.(7) shows the variation of lnα as a function of photon energy and the relation given by[19]

$$\alpha = \alpha_0 . \exp(\frac{hv}{E_u}) \qquad (5)$$

Where E_u is the Urbarch energy, it can be evaluated by the reciprocal of the slope yields the magnitude of the (E_u), the value of E_u was found ($E_u = 0.41497$ ev).

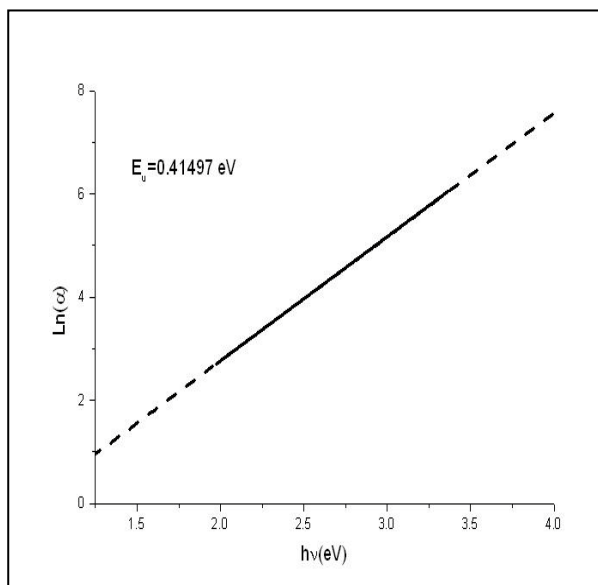**Fig.(7) Ln of absorption coefficient (α) as A function photon energy (hv)**

The complex dielectric constant ($\epsilon_{complex} = \epsilon_1 + i\epsilon_2 = (n + iK)^2$), where real part ϵ_1 and imaginary of the part ϵ_2 dielectric constant are given [20] .

$$\epsilon_1 = n^2 - K^2 \quad , \quad \epsilon_2 = 2\,n\,K \qquad (6)$$

Fig.(8) The variation of the real part of the dielectric constant as a function of photon energy , and fig.(9)shows the variation of imaginary part of the dielectric constant as a function of photon energy.

Fig.(8) the real part ϵ_1 of the dielectric constant as a function of photon energy (hv)
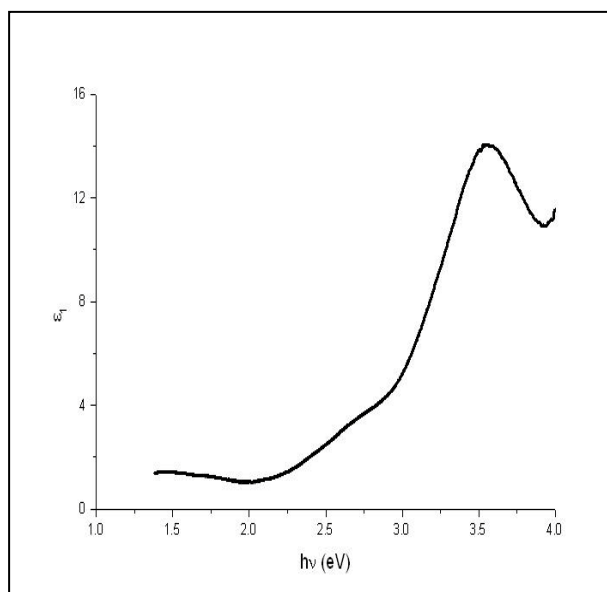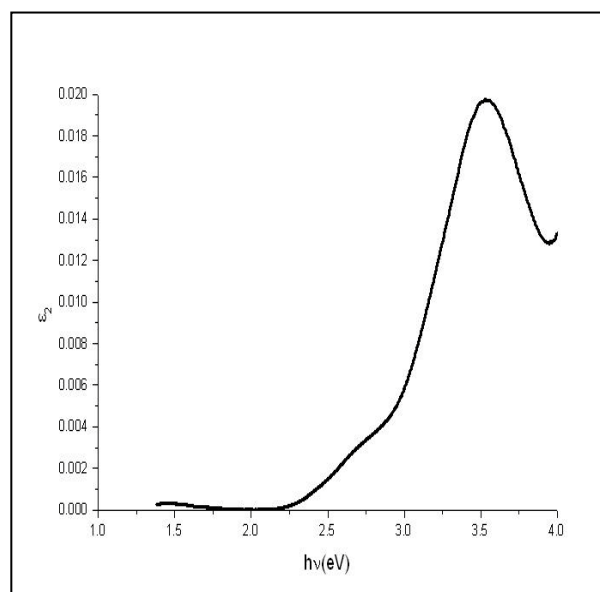

Fig.(9) the imaginary part ϵ_2 of the dielectric constant as a function of photon energy (hv)

In general, the real and imaginary parts of the dielectric increases with increasing photon energy. This behavior leads to increase the extinction and the electronic transfers through the material from valence band to the conduction band .The random electronic transfers occurs electronic collisions elastic . It leads to increase the dielectric constant .

The variation of optical conductivity σ_{op} as a function of photon energy (hv) is shown in fig.(9) . And they determined using thee relations (7) [21]

$$\sigma_{op} = \alpha n c / 4\pi \qquad (7)$$

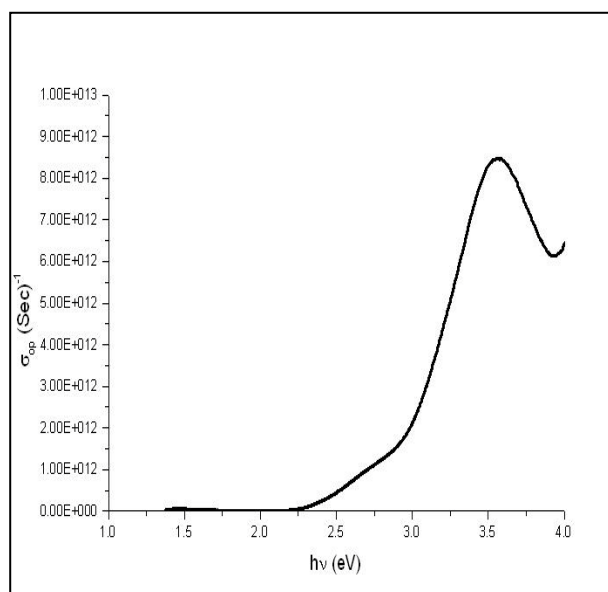where c:the velocity of light , n : refractive index

Fig.(9) Optical conductivity σ$_{op}$ as a function of Photon energy (hv)

The optical conductivity increases with the photon energy in the range (hν >3.5 eV) ,but decreases in the range (3.5 – 4 eV) .

4- Conclusion

Azo dye polymer compounds have been synthesized from 4-aminobanzoic acid with Novolac. The azo dyes were investigated optical transmission and the absorption spectrum are used to calculate the optical absorption coefficient, refractive index , extinction coefficient , optical band gap. The UV-visible spectroscopic studies shows that the novel azo dye polymer compound has high refractive index and the energy gap is equal to 2.45325 eV. The novel compound has specifications semiconductor high conductivity that can be used in the electronics industry.

5- References

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الخلاصة

تم في هذا البحث تحضير مركب ازو جديد من 4–amino bezoic acid ومن بوليمر novolac حيث تم الحصول على صبغة ازو بوليمرية جديدة , بعد ذلك اختبرت الثوابت الضوئية لفلم صبغة الازو (3,5–)–(4)Poly (bis(3–ethyl–2–hydroxybenzyl)–4–hydroxybenzyl)diazenyl بالاعتماد على منحنى طيف الامتصاصية والنفاذية عند الطوال الموجي (900–300 nm) عند درجة حرارة الغرفة . تضمنت المعاملات الضوئية الخطية حساب (معامل الانكسار , معامل التوهين, معامل الامتصاص , ثابت العزل الكهربائي بجزئيـة الحقيقي والخيـالي , التوصـيلية الضوئية وكذلك طاقة Urbrach تساوي eV 0.41497 وكذلك فجوة الطاقة للانتقال غير المباشر تساوي eV 2.3059 وطاقة الفوتون المساعد 147.35 meV.