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Optical Properties of Poly(2-thioacetate) Thin Films Prepared By Spin-Coating Method

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Abstract

Poly(2-thioacetate) has been prepared and characterized by infrared spectroscopy (IR). A thin film of new Polythioacetate been prepared by spin-coating technique and its optical properties were studied . Transmittance measurements in the wavelength range (300-900 nm) were used to calculate the refractive index *n* and extinction coefficient *k*. The optical band gap E_g , optical conductivity σ_{opt}, electrical conductivity σ_e , real dielectric constant, complex dielectric constant, relaxation time τ and dissipation factor tan δ were determined. The analysis of the optical absorption data indicated that the optical band gap *Eg* was governed indirect transitions. According to Wemple and Didomenico method, the optical dispersion parameters E_o (average excitation energy for electronic) and E_d(dispersion energy) were determined.

Introduction

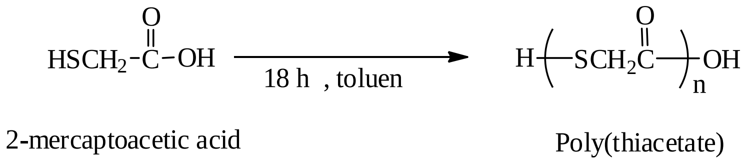
In recent years, polymers with different optical properties have attracted much attentions due to their applications in the sensors [1], light-emitting diodes [2–4], anti-reflection maritals and others [5,6]. The optical properties of these materials can be easily tuned by controlling contents of the different concentrations. Though excellent works have been reported on such materials [7–9], it is still meaningful to extend researches on these polymers. Optical properties, such as complex refractive index ($n-ik$, where i is the unit of imaginary) for a certain range of wavelength from ultraviolet to near infrared, and optical band gap values *E*g, are becoming quite important criteria for the selection of applications of the fabricated films. The refractive index is one of the fundamental properties of materials, because it is closely related to the electronic polarizability of ions and local field inside the material. The evaluation of refractive indices of optical materials is of considerable importance for applications in integrated optic devices such as switches, filters and modulators, etc., where the refractive index of a material is the key parameter for device design [10,11].

The study of optical absorption has proved to be very useful for elucidation of the electronic structure of these materials. It is possible to determine indirect and direct transition occurring in band gap of the materials by optical absorption spectra. The data of transmittance can be analyzed to determine optical constants such as refractive index, extinction coefficient and dielectric constant. The optical constants of thin films depend on the condition of preparation such as the substrate temperature during the deposition process. These parameters have to be controlled right from the initial stages of deposition. The aim of this study is to investigate the structure and optical constants of Polythioacetate thin films such as refractive index *n*, absorption index *k*, optical band gap E_g, optical dispersion parameters E_o and E_d, complex dielectric constant, relaxation time τ, dissipation factor tanδ , optical conductivity σ_{opt}. and electrical conductivity σ_e. [12,13].

Experimental

Preparation of Polythioacetate

Poly (2-thioacetate) was prepared by simple condensation polymerization . Thioacetic acid (7.6g , 0.1mol) was dissolved in dry toluene (75ml) . The solution was refluxed for 18h . After cooling , the precipitate was collected by filtration . The crude product was washed several times with ethanol to give a white solid in 80% yield .



Scheme 1: Preparation of poly (2-thioacetate) .

Measurement

FT. IR spectra for poly (2-thioacetate) was recorded as KBr disc using a FT. IR spectrophotometer Shimadzu model 8400S in the range 4000-400 cm^{-1}. The measurements of absorbance and transmittance spectra of polythioacetate thin film in the wavelength range (300-900) nm were carried out using UV-VIS Recording Spectrophotometer (UV-CE7200-Aquarius). The optical absorption (A) and reflectance spectra(R) were analyzed to determine the optical constants such as refractive index (n), extinction coefficient (k), absorption coefficient (α), optical band gap E_g , oscillator energy E_o , optical dispersion parameters E_d, complex dielectric constant, optical conductivity (σ_{opt}). and electrical conductivity (σ_e). Analysis of the absorption coefficient was also carried out to determine the relaxation time (τ) and dissipation factor tanδ. The thickness of prepared films was measured (0.12μm).

Result and Discussion

Poly (2-thioacetate) was prepared by condensation 2-mercapto acetic acid with itself . The prepared poly(2-thioacetate) was obtained as a white solid in 80% yield . The prepared polymer was characterized by FT.IR spectroscopy , Figure 1 . The spectrum of poly(2-thioacetate) shows a broadening band centered at 3350 cm^{-1} can attributed to hydroxyl group of the carboxyl end group [14,15] . Also a strong band appeared at 1735cm^{-1} due to asymmetric stretching of carbonyl group while a symmetrical stretching band appeared at 1475cm^{-1} [14,15] , bands were appeared at 2915 and 2851 cm^{-1} due to asymmetrical and symmetrical stretching of aliphatic C-H bond respectively . Furthermore , variable bands between 1380-1300 cm^{-1} be assigned to aliphatic C-H bending [14,15] . Two strong band appeared at 1290 and 1174 cm^{-1} can be assigned for stretching band of C-S and C-O bonds [14,15] .

The study of materials by means of the optical absorption provides a simple method for explaining some features concerning the band structure and energy gap. The absorption spectra of the polythioacetate was recorded in the wavelength range of 300−900 nm and is given in Figure (2). The optical parameters related to the spectrum are given in table 1.

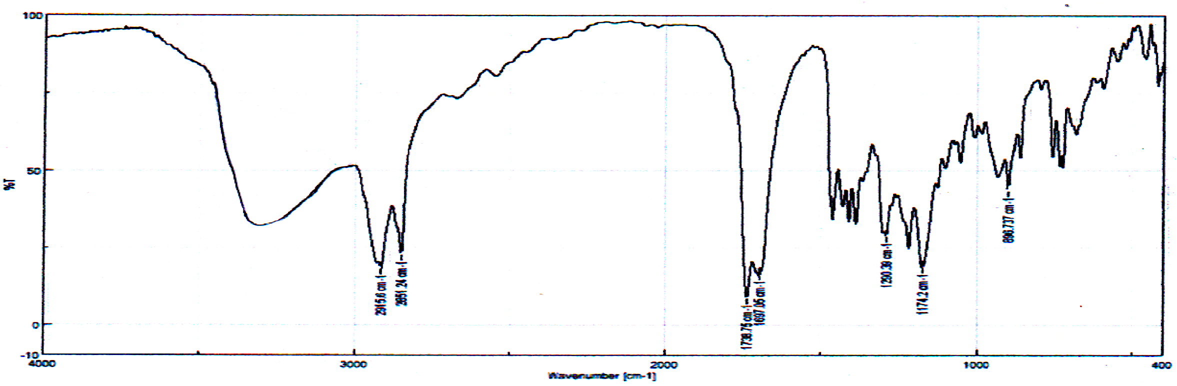


Fig 1 : IR Spectrum of Poly (2-thioacetate)

Table 1. optical parameters of the polythioacetate thin film.

Quantity	Value
$E_g^{in}\,(eV)$	3.55
$E_{opt.}^{WD}\,(eV)$	5.69
$B_{in}\quad (cm.eV)^{-1}$	27
$E_{Phonon}\,(meV)$	558
$\alpha_o\ cm^{-1}$	1.95
$E_{Urbach}\,(eV)$	2.9
$E_{\circ}\,(eV)$	11.38
$E_d\,(eV)$	19.96
$n_{\circ}$	1.65
$\varepsilon_{\circ}$	2.75
ε_{∞}	2.8
$N/m^*(m^3.kg)^{-1}$	5.36×10^{29}
So, m^{-2}	7.45×10^{13}
$\lambda_{\circ}\,(nm)$	226.2
M_{-1}	1.75
$M_{-3}(eV)^2$	0.0135

The absorption coefficient (α) can be calculated from observed absorbance data using Beer Lambert's formula $(\alpha = 2.303(A/d))$, where A is the optical absorbance and d is the film thickness. The extinction coefficient can be obtained from the relation $(k = \alpha\lambda/4\pi)$, where λ is the wavelength of the light. The reflection can be determined by using the following relation [16]:

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \qquad \ldots\ldots\ldots\ldots (1)$$

Where T is the transmittance, R the reflectance and d is the film's thickness. Fig. (2) Shows the variation of absorption coefficient as a function of wavelength of the light in the rang (300-900) nm. It is clear that, the absorption coefficient (α) decrease as the wavelength increases. This is due to an increase Permeability class in the range of wavelength. Figure (3) show the dependence of the optical transmission and reflection, on wavelength respectively. The data from transmission and reflection spectrum are used to calculate absorption coefficient by using equation (1).

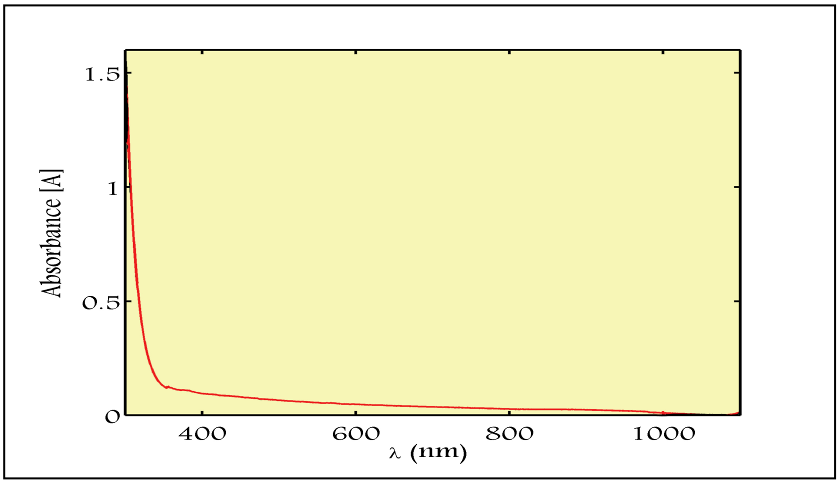


Figure (2) Absorbance as a function of wavelength for polythioacetate.

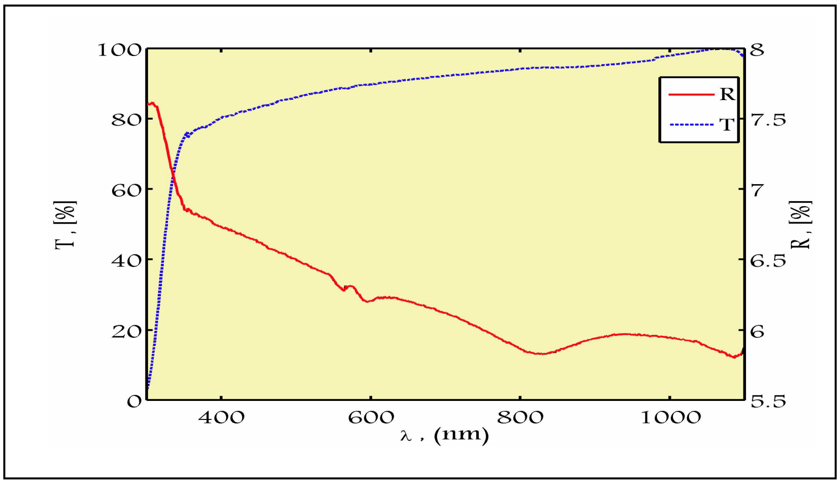


Figure (3) Optical transmittance and reflectance spectra as a function of wavelength polythioacetate.

The extinction coefficient represents the amount of attenuation of an electromagnetic wave that is traveling in material, where it values depends on the density of free electrons in the material and also on the structure nature. The values of extinction coefficient are directly related to the absorption of light. It can be noticed that there is a decrease of extinction coefficient with increasing wave length. Figure (4) shows the extinction coefficient (*k*) for polythioacetate thin films as a function of wavelength in the rang (300-900) nm [17].

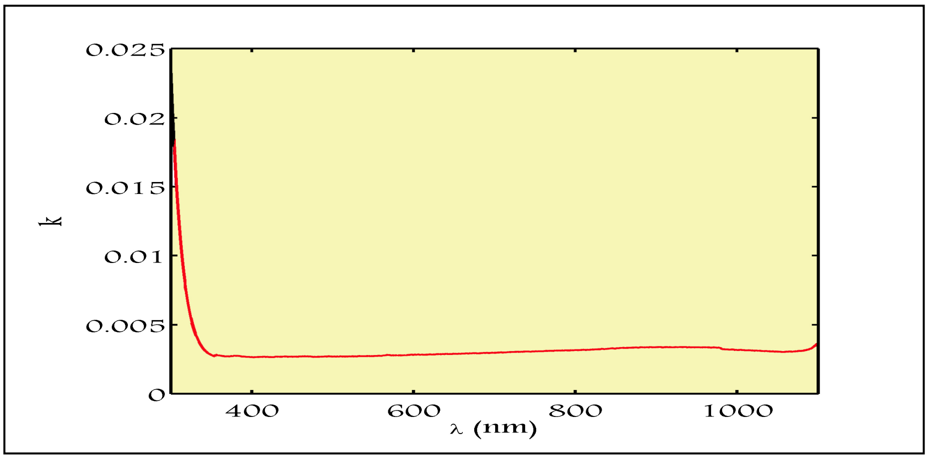


Figure (4) Extinction coefficient (*k*) as a function of wavelength polythioacetate.

The refractive index (n) {n = [(1+√R)/(1-√R)]+√(4R/(1-R)^2-K^2) *where* R } is reflectance of polythioacetate thin film as functions of wavelength is shown in Figure (5). It can be seen that refractive index decreases with the increasing of wavelength. The decrease obtained in the value (n) is due to that some interactions take places between photons and electrons. The refractive index changes with the variation of the wavelength of the incident light beam due to these interactions, in another word, one is the optical loss caused by absorption and scattering, which decreases the amplitudes of the transmission intensity oscillations at shorter wavelengths, in this work it can be neglected because of the highly transparent of polythioacetate thin film. In the determination of refractive indices for the polythioacetate thin film, the main loss arises from the transmission measurement procedures, such as small difference of light spot sizes and apertures [11].

The relation between the absorption coefficient α, and optical band gap *Eg,* is given by the following relation [12].

$$\alpha = \frac{B(h\nu - E_g)^r}{h\nu} \quad \text{……….. (2)}$$

Where B is an energy-independent constant (hν) is the photon energy, The absorption coefficient (α) identifies the type of the transitions between the electronic levels. The transition is direct if α greater than 10^4 cm^{-1} or it's indirect if (α) less than10^4 cm^{-1}. According to Tauc law the relation between (αhα)$^{1/r}$ and photon energy (hv) was examined for different value of the parameter r (where r=1/2, 3/2, 2 and 3) to determine the type of the optical transition. The parameter r is an index depending on the nature of the electronic transition responsible for the absorption r =1/2 for allowed direct transition, r = 3/2 for forbidden direct transition and r =3 for forbidden indirect transition, with r =2 refers to indirect allowed transitions. The optical absorption spectra studies reveal that the absorption mechanism is an indirect allowed transition , it has been found that the value of E_g equal 3.55ev [13].

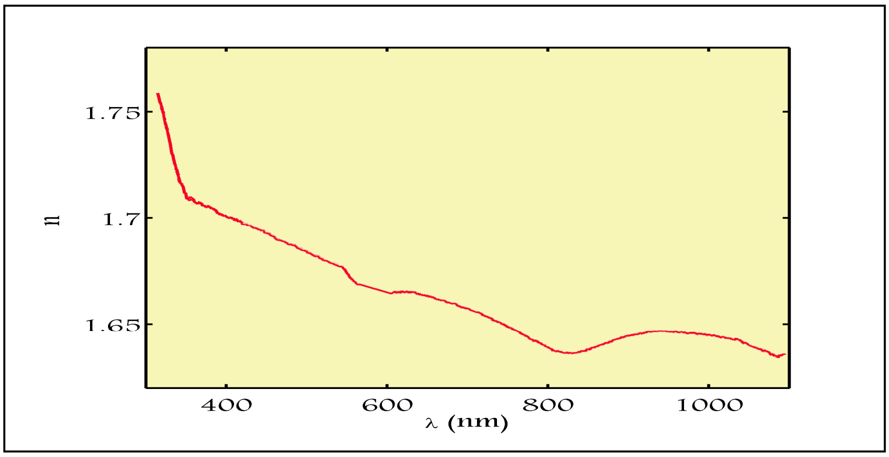


Figure (5) The variation of the refractive index (n) vs. photon energy for polythioacetate.

The energy gap values depends in general on the film crystal structure, the arrangement and distribution of atoms in the crystal lattice, also it is affected by crystal regularity. The energy gap (Eg) value is calculated by extrapolation of the straight line of the plot of (αhv)$^{1/2}$ versus photon energy(hν) as shown in Figure (6). The optical absorption coefficient near the fundamental absorption edge is found to be exponentially dependent on the incident photon energy and obeys the empirical Urbach rule [16].

$$\alpha = \alpha_{\circ} \exp(hv / E_u) \quad \text{……… (3)}$$

Where $\alpha_\circ$ is constant and E_u is the Urbach energy and it can be evaluated as the width of the localized states.

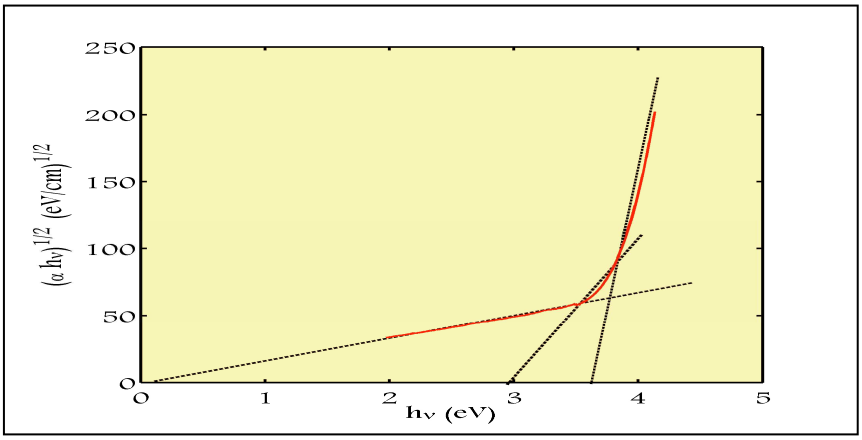


Figure (6) Plot of $(\alpha h\nu)^{1/2}$ vs photon energy ($h\nu$) near the absorption edge for polythioacetate

A plot of α as a function of photon energy $h\nu$ for polythioacetate thin film illustrated in figure (7). The exponential dependence of α on photon energy for the compound indicates that it obeys Urbach's energy equation. An electronic transition between localized states in the band edge tails is valid in this compound. The exponential dependence of the optical absorption coefficient with photon energy may arise from the electronic transitions between the localized states, which tail off in the band gap [17]. Figure (8) shows the variation of the (lnα) against the photon energy ($h\nu$) for polythioacetate.

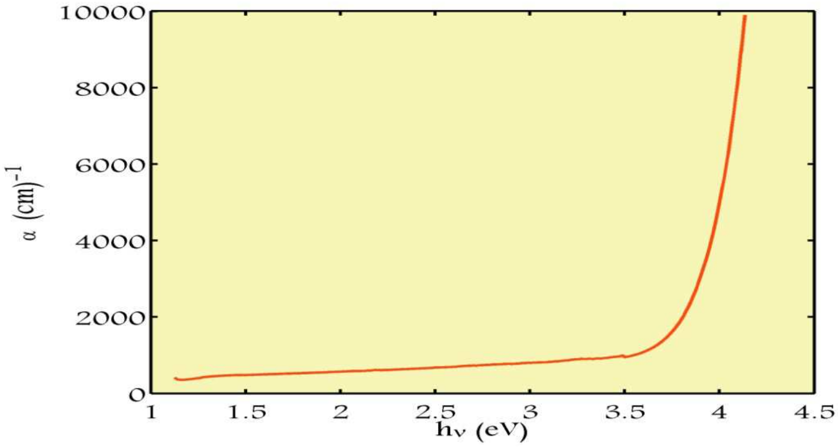


Figure (7) Variation of the absorption coefficient (α) against the photon energy ($\hbar\omega$) for polythioacetate.

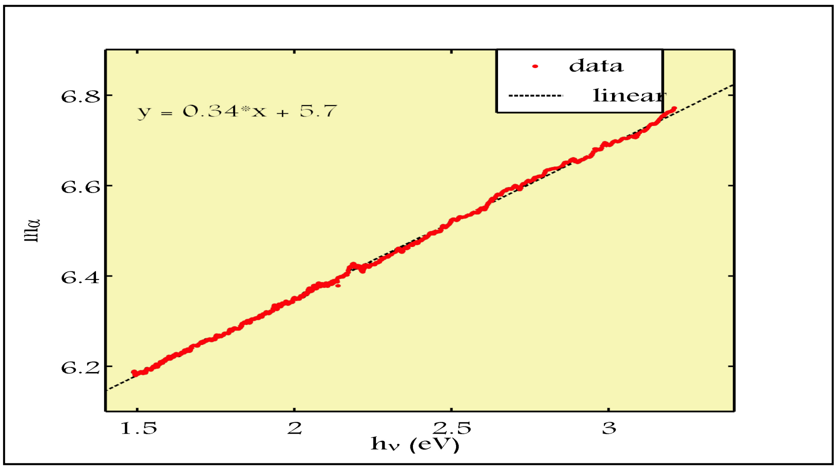


Figure (8) Variation of the (lnα) against the photon energy ($h\nu$) polythioacetate

The relation between the refractive index n, and the single oscillator strength below the band gap is given by the expression [18,19]:

$$n^2 = 1 + \frac{E_d E_\circ}{E_\circ^2 - (h\upsilon^2)} \quad \ldots\ldots\ldots \quad (4)$$

where E_d and E_o are single-oscillator constants, E_o is the energy of the effective dispersion oscillator, E_d the so-called dispersion energy, which measures the average strength of interband optical transitions.

Experimental verification of Eq. (4) can be obtained by plotting $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ as illustrated in figure (9) for polythioacetate thin films, which yields a straight line for normal behavior having the slope $(E_oE_d)^{-1}$ and the intercept with the vertical axis equal to (E_o/E_d). But the obtained curves in figure (9), show positive deviation from linearity. A positive curvature deviation [19] from linearity at longer wavelength is usually observed due to the negative contribution of lattice vibrations on the refractive index. [19].

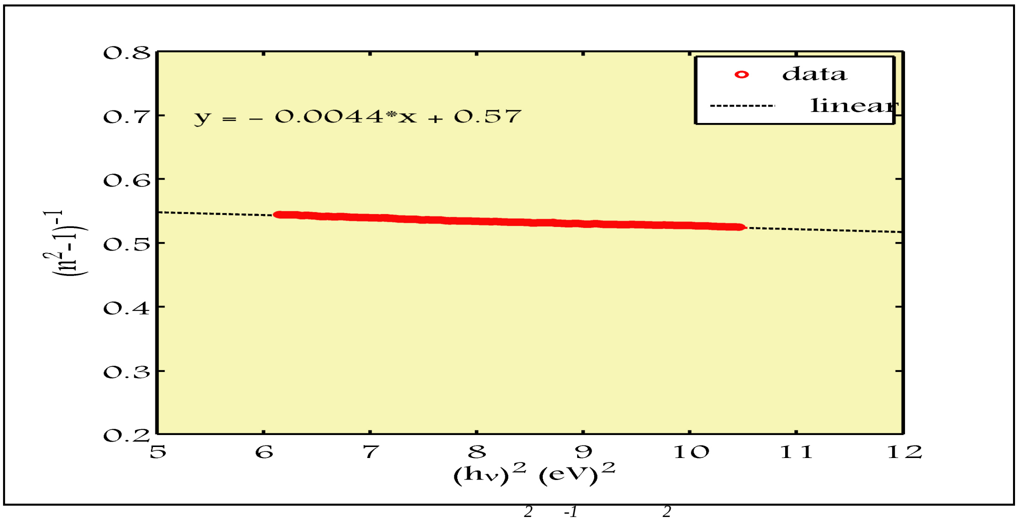


Figure (9) The plots of the variations of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ for polythioacetate.

The obtained data of refractive index n can be analyzed to obtain the high frequency dielectric constant via two procedures [20]: the first procedure describes the contribution of the free carriers and the lattice vibration modes of the dispersion. The second procedure, however, is based upon the dispersion arising from the bound carriers in an empty lattice. To obtain a reliable value for the high frequency dielectric constant ε_∞, we employed both procedures.

The first procedure. The following equation can be used to obtain the high frequency dielectric constant [20]:

$\varepsilon_1 = \varepsilon_\infty(1) - B\lambda^2$,

where

$B = e^2N/4\pi^2c^2\varepsilon o m^*$ .... (5)

where ε_1 is the real part of dielectric constant, ε_∞ (1) the lattice dielectric constant or (the high frequency dielectric constant) according to first procedure, λ the wavelength, N the free charge carrier concentration, ε_o the permittivity of free space (8.854×10−12 F/m), m^* the effective mass of the charge carrier and c the velocity of light. The real part of dielectric constants $\varepsilon_1 = n^2$ was calculated at different values of λ. Then, the obtained values of ε_1 are plotted as a function of λ^2 as shown in Figure 10. It is observed that the dependence of ε_1 on λ^2 is linear at longer wavelengths. Extrapolating the linear part of this dependence to zero wavelength gives the value of $\varepsilon_\infty(1)$ and from the slopes of these lines, values of N/m^* for the investigated oxides were calculated according to the Eq. (5) of the constant B. The obtained values of ε_∞ (1) and N/m^* are given in Table 1.

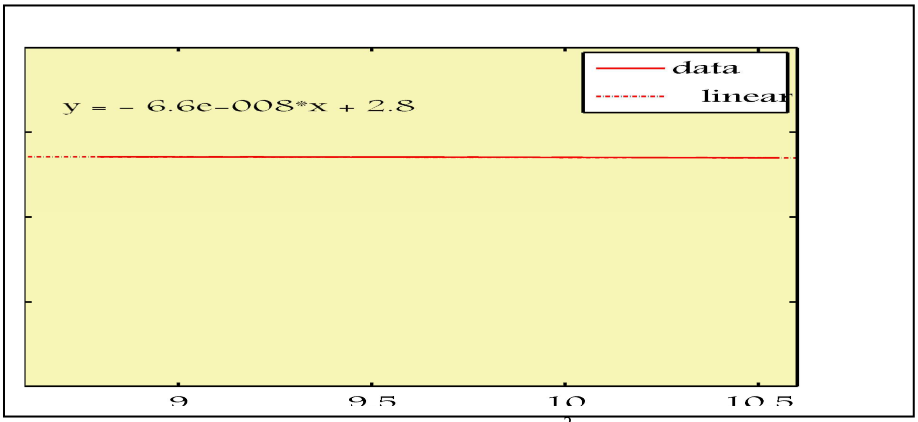


Figure (10) the plots of the variations of (n^2) vs λ^2 polythioacetate

The second procedure. The dielectric constant of a material could be calculated using the dispersion relation of incident photon. The refractive index was also fitted using a function for extrapolation towards shorter wavelengths. The model of Moss [21], which stated that the free carriers contribution to dispersion are relatively small. This means that data corresponding to the wavelength range lying below the absorption edge of the material are to be used. In such a case, so, one can apply the next relation. The properties of the investigated polythioacetate could be treated as a single oscillator at wavelength λ_o at high frequency. The high frequency dielectric constant can be calculated by applying the following simple classical dispersion relation [20]:

$$\frac{n_\circ^2-1}{n^2-1}=1-\left(\frac{\lambda_\circ}{\lambda}\right)^2 \quad \ldots\ldots\ldots \ (6)$$

where n_o is the refractive index at infinite wavelength λ_o (average interband oscillator wavelength), n the refractive index and λ the wavelength of the incident photon. Plotting $(n^2-1)^{-1}$ against λ^{-2} which showed linear part, was below the absorption edge as shown in Figure 11. The intersection with $(n^2-1)^{-1}$ axis is $(n^2_o-1)^{-1}$ and hence, n^2_o at λ_o equal to $\varepsilon_\infty(2)$ (high frequency dielectric constant). Values of $\varepsilon_\infty(2)$ for polythioacetate thin films are given in Table 1. [22]. The average oscillator strength is given by ,

$$s_\circ = \frac{n_\circ^2 - 1}{\lambda_o^2} \quad \ldots\ldots\ldots\ldots \ (7)$$

The real part of the permittivity ε_1 and the imaginary part of the permittivity ε_2 can be calculated by the following relations [20,21]:

$$\varepsilon_1 = n^2 - k^2 \quad \ldots\ldots\ldots\ldots \ (8)$$

$$\varepsilon_2 = 2nk \quad \ldots\ldots\ldots\ldots\ldots\ldots \ (9)$$

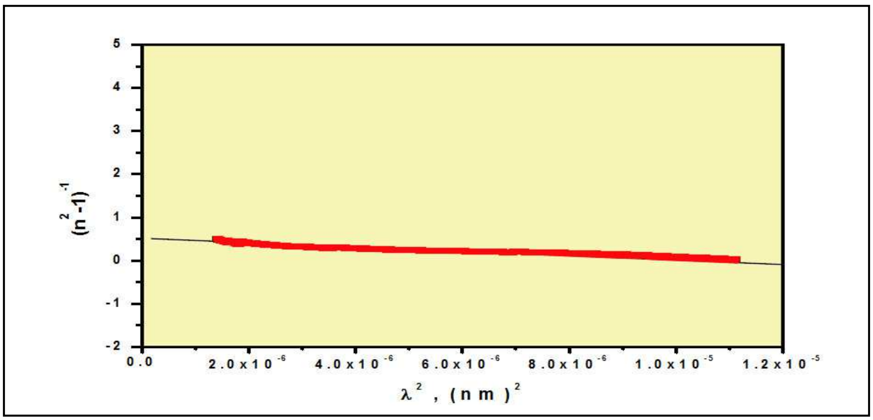


Figure (11) the plots of the variations of $(n^2-1)^{-1}$ vs λ^{-2} for polythioacetate.

Figures (12&13) show the relation between $\varepsilon_1, \varepsilon_2$ and photon energy. Figure (14) shows the variation of optical conductivity with incident photon energy. The optical conductivity is determined by using the relation [23]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \quad \text{........ (10)}$$

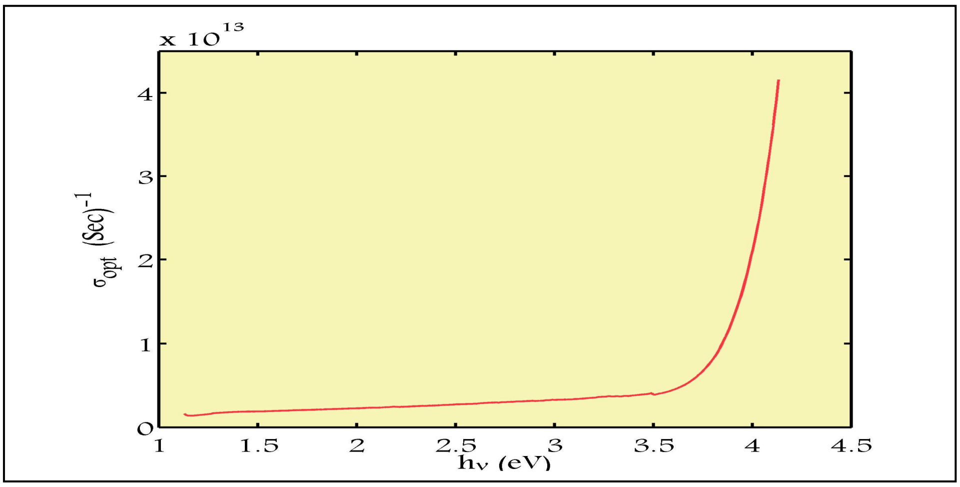


Figure (11) the plots of the variations of $(n^{2}-1)^{-1}$ vs λ^{-2} for polythioacetate.

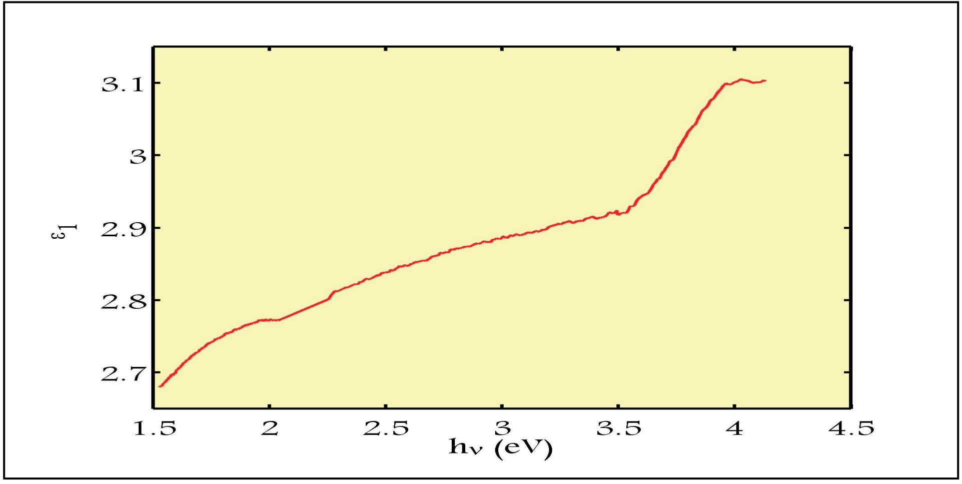


Figure (12) the plots of the variations ε_1 vs $h\nu$ for polythioacetate.

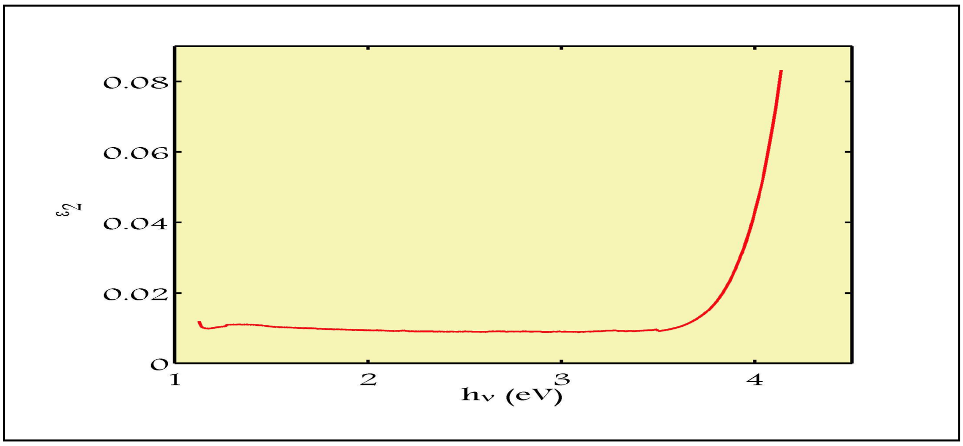


Figure (13) the plots of the variations ε_2 vs $h\nu$ for polythioacetate

The optical conductivity directly depends on the absorption coefficient and was found to increase sharply for higher energy values due to the large absorption coefficient for these values. Figure (15) shows the variation of electrical conductivity with incident photon energy. the electrical conductivity is can be also estimated by using the fallowing relation [24] .

$$\sigma_e = \frac{2\lambda\sigma_{opt}}{\alpha} \qquad (11)$$

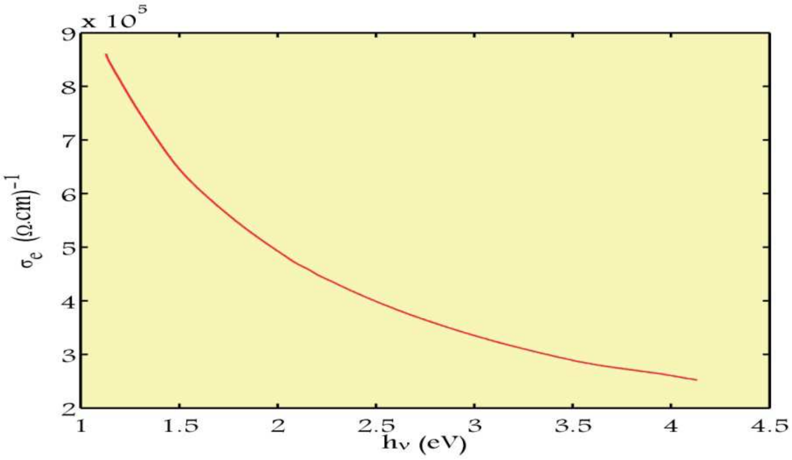


Figure (15) the plots of the variations electrical Conductivity vs *hν* for polythioacetate.

The dielectric relaxation time τ can be evaluated by using the relation [25,26]:

$$\tau = \varepsilon_\infty - \varepsilon_1 / \omega\varepsilon_2 \qquad (12)$$

Figure(16) indicates the dielectric relaxation time τ as a function of photon energy *hν* for polythioacetate. This figure showed that the relaxation time increases with increasing the photon energy. The dissipation factor (tan δ) is a measure of loss-rate of power of a mechanical mode. The dissipation factor tan δ can be calculated according to the following equation [27]:

$$\tan\delta = \varepsilon_2 / \varepsilon_1 \qquad (13)$$

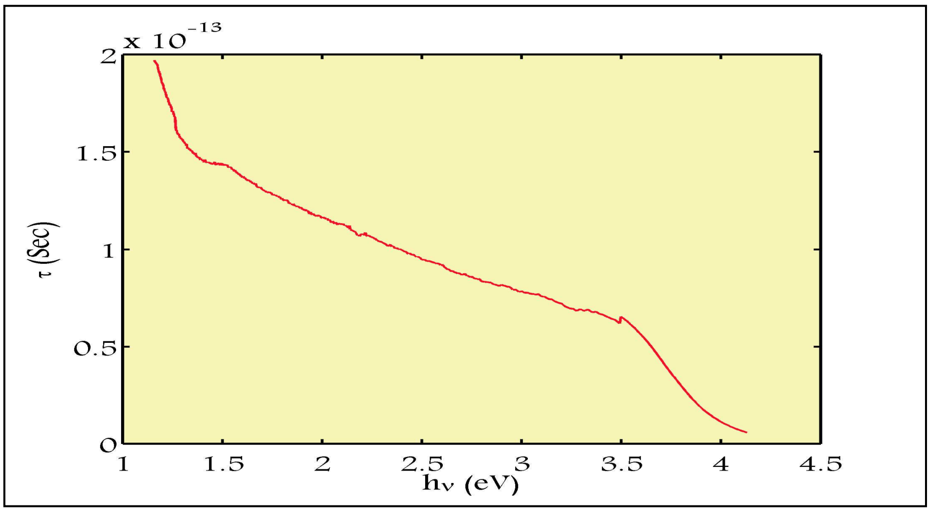


Figure (16) Dependence of relaxation time τ on the photon energy *hν* for polythioacetate.

The variation of dissipation factor of the investigated films with frequency *f* is shown in figure (17). It is found that the dissipation factor increases with increasing photon energy in the absorption region. Figures(18)show the relation between the ln(α hν) vs photon energy ln(hν -E$_g$) for polythioacetate thin film. The moments of optical dispersion spectra M_{-1} and M_{-3} ,can be evaluated using the relationships (Table 1.)[18].

$$E_\infty^2=\frac{M_{-1}}{M_{-3}} \quad \ldots\ldots\ldots\ldots (14)$$

$$E_d^2=\frac{M_{-1}^3}{M_{-3}} \quad \ldots\ldots\ldots\ldots (15)$$

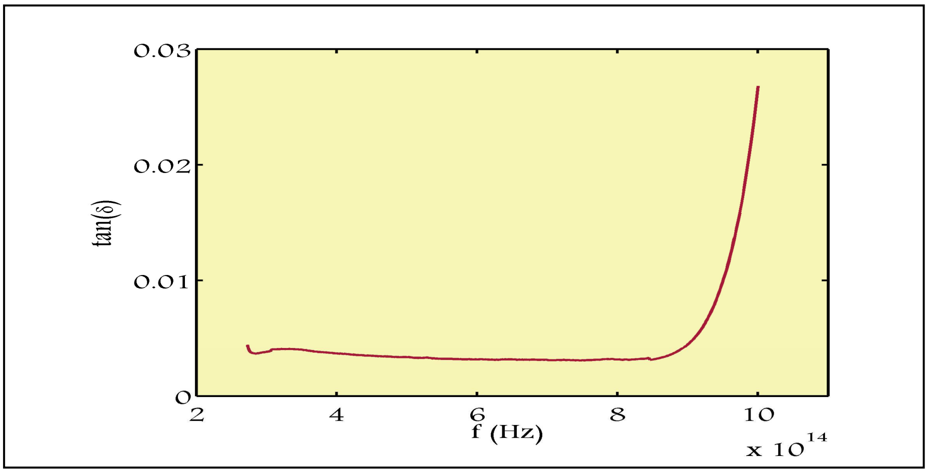


Figure (17) Dependence of dissipation factor tan *δ* on the photon energy *hv* for polythioacetate.

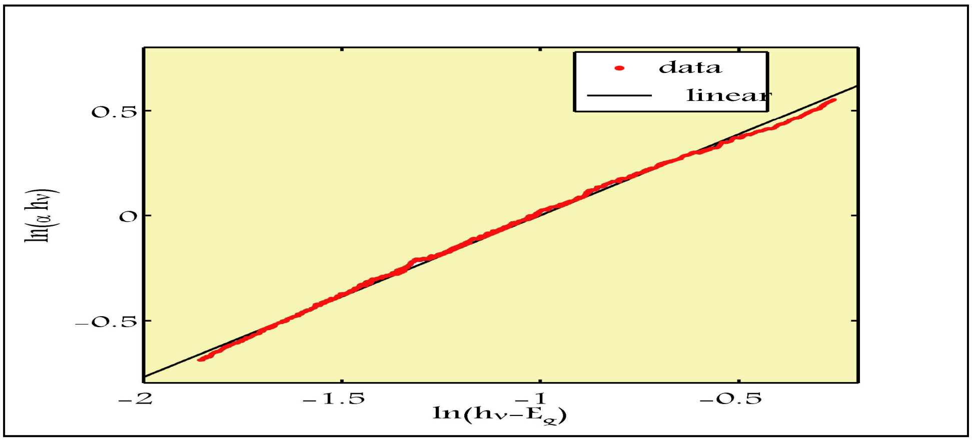


Figure (18) Variation of the ln(α hν) vs photon energy ln(hν -E$_g$) for polythioacetate.

Conclusions

The dependence of the absorption coefficient (α) on photon energy (hν) was determined in the spectral range from (300–900 nm). The variation of the absorption coefficient and the optical gap are reported. The allowed indirect transitions were found to be responsible for interband transitions. The type of optical transition responsible for optical absorption was indirect transitions. Values of real part of the dielectric constant are higher than imaginary part. The relaxation time *τ*, the dissipation factor tan *δ*, the electrical conductivity and the optical conductivity (σopt) were increased with increasing the photon energy.

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