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Optical constants of the poly vinyl alcohol grafted Rhodamine B (PVA-g-Rh B)

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Abstract

The optical constants of the prepared PVA-g-Rh B thin films have been studied. The real and imaginary part of the complex refractive index and dielectric constant of the copolymer were determined. The optical conductivity was studied. Wemple-DiDimenico was used to study the optical dispersion parameters. The volume energy loss (VELF) and the surface energy loss (SELF) functions were also investigated.

Keywords: Optical constants; Rhodamine B dye; dispersion parameters; energy loss.
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1. Introduction

During the last decades, research interests have been focused on electro-optical material [1]. Nevertheless, because of the heavy and expensive growth techniques of these inorganic compounds, research moved towards polymeric materials. Indeed, the material is suitable to low cost molecular engineering processes and very useful for specific applications. Another advantage of polymers is the possibility to achieve reliable doped thin films with customizable properties. It has been also demonstrated that by suitable doping, stable photo induced optical behavior (photorefractive effects, birefringence, dichroism, holography, etc…) can be produced and used to design new generation of optically controlled devices. Doped polymeric materials offer high optical quality and potentially large bulk nonlinear susceptibilities if the molecular hyperpolarizability of the dopant is large. Rhodamine B (Rh B) is a chromophore from a family of xanthene dyes that commonly used as an active medium in tunable lasers [2-4] due to its high fluorescence quantum yield. It has been also found in a wide range of applications in solar cell [5] as a molecular probe [6], as an electrochemical luminescence sensitizer [7], as a water – tracing agent [8], as biological stain [9]. Knowledge of optical constants of the materials (optical band gap and extinction coefficient) is vital to determine the atomic structure, electronic band structure and electrical properties. For example, the refractive index provides the information about the chemical bonding and electronic structure of the material, while the study of the optical absorption spectra provides essential information about the band structure and the energy gap in the crystalline and non-crystalline materials [10, 11]. In the

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present work, we determined the optical constants and dispersion parameters for a new copolymer polyvinyl alcohol grafted Rhodamine B, Wemple and DiDomenico relation was used to determine the refractive index, loss energy were also determined. The optical data was analyzed by using transmittance spectrum in the wavelength range of 300-800nm.

2. Experimental

2.1 Materials

Polyvinyl alcohol (PVA) (Mwt=106,000-110,000), hydroxyl content 99.9%, were provided by Aldrich. Rhodamine B dye (Rh B) was provided by Fluka without any other purification. Dimethylslfuoxide (DMSO) was used as a solvent provide by BGC company. The reaction and characterization of new copolymer was showed previously [12].

2.2 Preparation of Thin Films

Macroscopic glass substrates (1.5cm x 1.5cm) were washed by hot water and acetone were used as substrates. Thin films were prepared by using the spin-coating technique, dropping a small amount of the polymer solution PVA-g-Rh B dissolved in DMSO solvent. The transmittance (T) spectra of the prepared samples was measured at room temperature the wavelength (λ) range of 300-800 nm using a double beam spectrophotometer (Thermospectronic model HEλIOSα v 4.60).

3. Results and Discussion

3.1 Optical Transmission

Fig. 1 shows the transmission and reflectance spectrum of the prepared PVA-g-Rh B thin films. The synthesis film have three regions, first region in the wavelength $\lambda \geq$ 650nm, related to high transparency, while it had low value due to the strong absorbance in the wavelength range 500-600nm can be attributed to the S_o-S_1 transition of Rh B dye [13] and the third peak at $\lambda \leq$ 500nm related to low energy transition. The highest value of reflectance of film is 20% at 575nm.

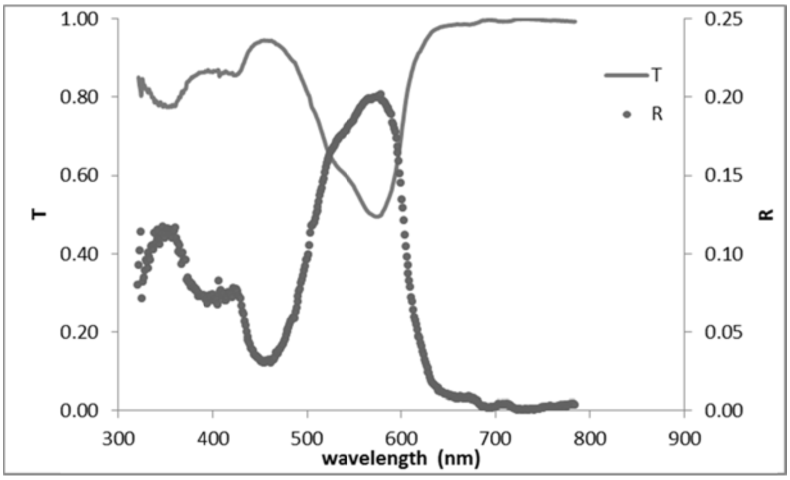

Fig. 1: The transmittance and reflectance spectrum for PVA-g-Rh B.

3.2 Determination the Extinction Coefficient

The optical absorption coefficient (α) can be calculated from transmission data as [14]:

$$\alpha = \frac{1}{d}\ln(\frac{1}{T}) \tag{1}$$

where T and d are the transmittance and thickness of the thin film, respectively. The thickness of samples was kept as 3μm, high absorption coefficient at photon energy > 2eV as shown in the Fig.2 related to the copolymer have conjugated system in pendent for Rh B dye. The extinction coefficient (k) and the refractive index (n) are calculated using the relation [14]:

$$k = \frac{\alpha\lambda}{4\pi} \tag{2}$$

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \tag{3}$$

where λ is the wavelength. The extinction coefficient (k) and refractive index (n) in the wavelength range of 300-800nm is shown in Fig. 3. Normal dispersion is observed at λ > 650nm and anomalous dispersion at λ < 650nm besides three peaks at 3.542 eV, 2.917 eV and 2.156 eV. This is due to high energy transition.

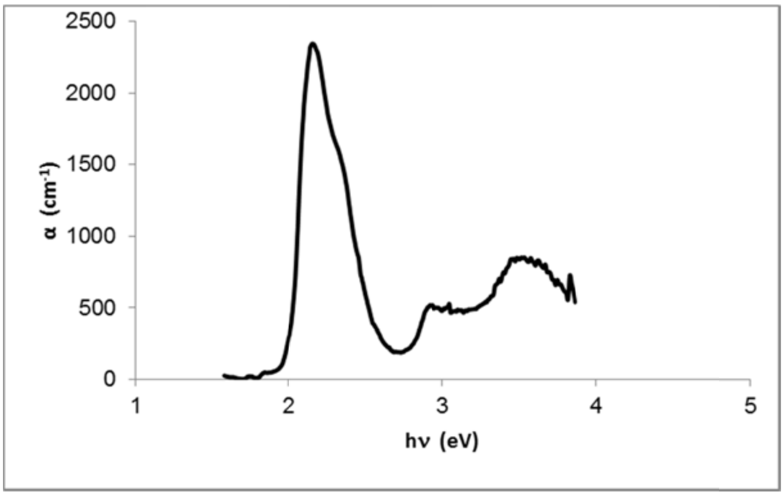

Fig. 2: The absorption coefficient vs. photon energy of PVA-g-Rh B.

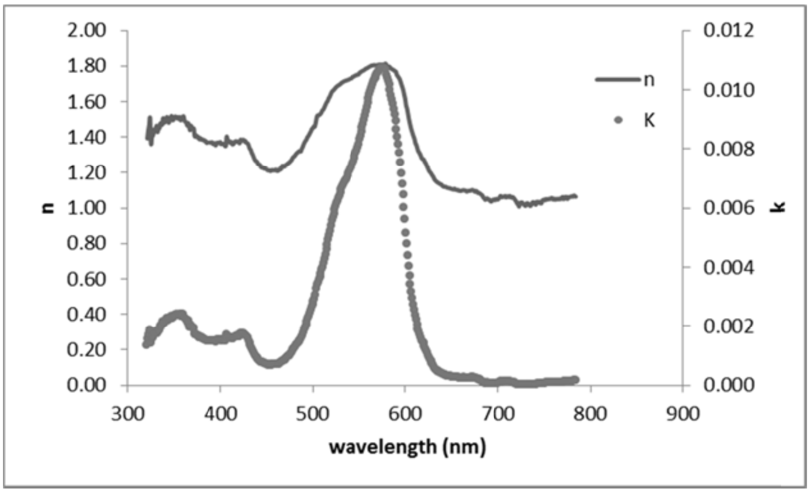

Fig. 3: The absorption index k and refractive index n dependent on the wavelength for PVA-g-Rh B.

3.3 Calculation of Optical Energy Gap

According to Tauc's relation [15, 16], the photon energy dependence of the absorption coefficient can be described by:

$$\alpha h\upsilon = B(h\upsilon - E_g{}^{opt})^{r} \quad (4)$$

where B is a parameter, depends on the transition probability, E_g is the optical energy gap and r an index and assume values 0.5, 2, 1.5 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. Fig. 4 shows the absorption coefficient in the form $(\alpha h\nu)^{1/2}$ versus hν for PVA-g-Rh B film. The intercepts of the straight lines with the photon energy axis yield the values of the optical band gap. The value of indirect allowed optical energy gap is about 1.98eV .

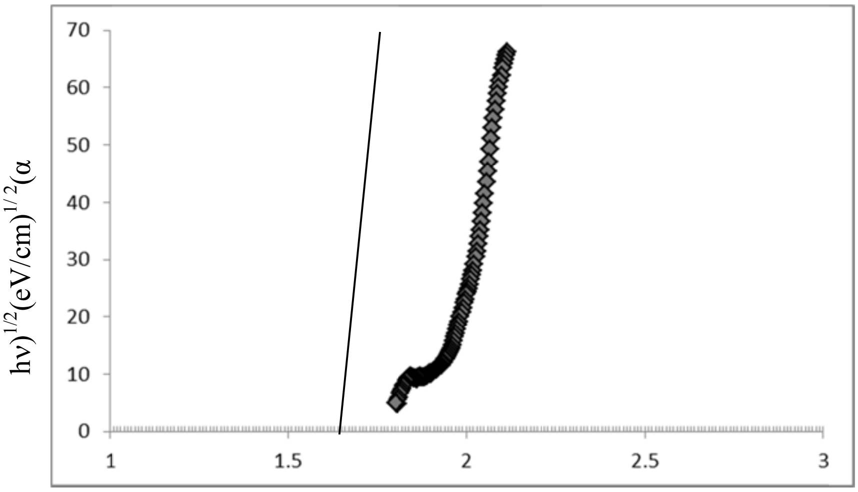

Fig. 4: The $(\alpha h\upsilon)^{1/2}$ vs. the photon energy of PVA-g-Rh B thin film.

3.4 Urbach Tail

For hν ≤ Eg there are four major absorption mechanism, the Urbach tail, defect absorption, multiphoton absorption and high scattering [17]. In case of $\alpha < 10^4$ cm^{-1}, the absorption mechanism is usually an Urbach tail [18] where α depends exponentially on photon energy as:

$$\alpha = \alpha_o e^{\frac{h\nu}{E_u}} \tag{5}$$

where α_o is a constant and E_u is the Urbach energy (related to the width of the band tail of the localized states at the conduction or valance band edge), it can be evaluated as the width of the localized states. The value of E_u is estimated from Fig. 5, by plotting lnα versus the photon energy and taking the reciprocals of the slope of the linear portion in the lower photon energy of the curve. The value of Urbach energy is 1.19eV.

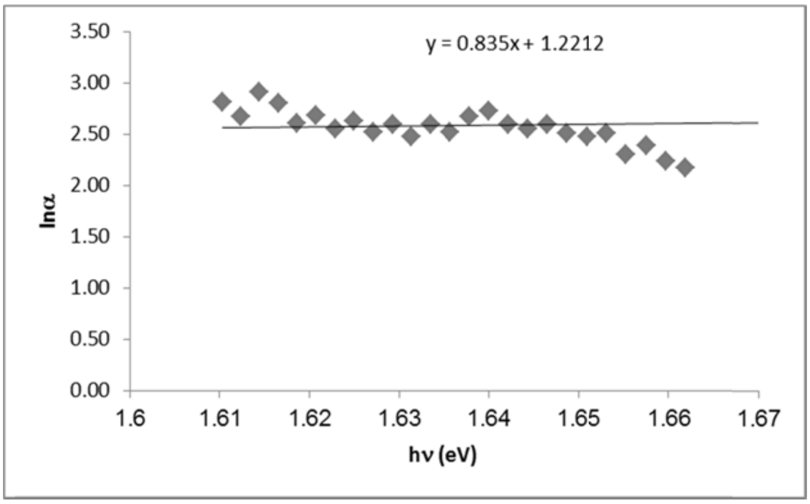

Fig. 5: The relationship between in α and photon energy for PVA-g-Rh B.

3.5 Dispersion Parameters

Wimple and DiDomenico [19, 20] developed a model where the refractive index dispersion is studied in the region of transparency below the gap, using the single oscillator approximation. Defining two parameters, the oscillation energy, E_o and the dispersion energy, E_d, the model concludes:

$$n^2 = 1 + \frac{E_o E_d}{E_o^2 + (h\nu)^2} \tag{6}$$

The relationships between the dispersion parameters and $\varepsilon_2(\omega)$ spectrum can be estimated as:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \tag{7}$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \tag{8}$$

where M_{-1}, M_{-3} are moment of optical spectrum and the -1, -3 moment are involved in computation of E_o and E_d. It is known that static dielectric constant of any substance is defined as:

$$\varepsilon_r(o) = \lim_{E \to o} n^2(E) = n_o^2 \tag{9}$$

The static dielectric constant can be written in term of dispersion parameters simply as:

$$n_o^2 = \varepsilon_r(o) = 1 + \frac{E_d}{E_o} \tag{10}$$

Plotting (n^2-1) versus $(h\nu)^2$ as illustrated in Fig. 6 for PVA-g-Rh B thin films, which yield a straight line for normal behavior having the slope $(E_oE_d)^{-1}$ and intercept with the vertical axis equal to(E_o/E_d). The value of E_o, E_d, M_{-1}, M_{-3} and n(o) are listed in Table 1.

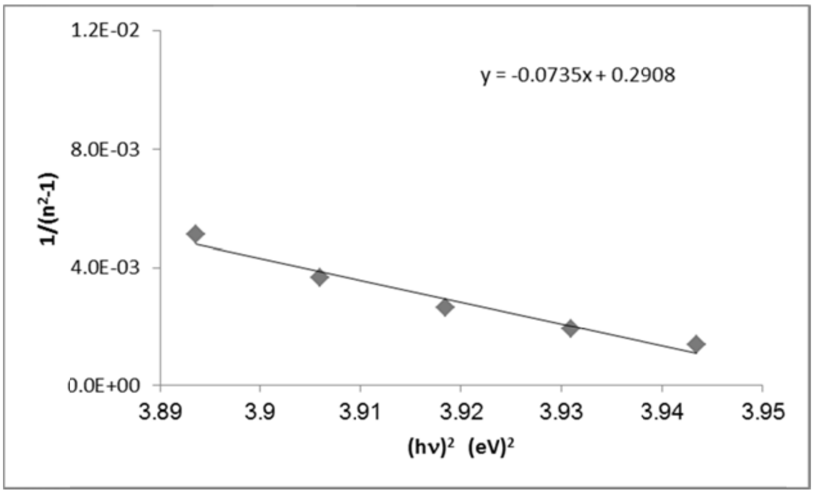

Fig. 6: Plots of $(n^2-1)^{-1}$ against $(h\upsilon)^2$ for PVA-g-Rh B.

3.6 Complex Dielectric Constant and Optical Conductivity

The real and imaginary parts of the dielectric constant can be estimated using the relation [21, 22].

$$\varepsilon_1 = n^2 - k^2 \tag{11}$$

$$\varepsilon_2 = 2nk \tag{12}$$

Fig. 7 shows the relationship between real (ε_1) and imaginary (ε_2) part and photon energy. It is clear that the variation of ε_1 mainly depended on n^2 because of small values of k^2, while ε_2 mainly depends on k values which are related to the variation of absorption coefficients.

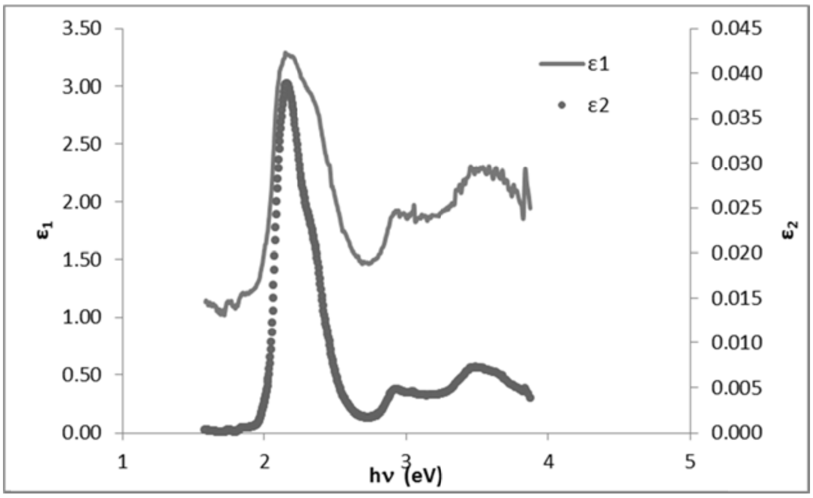

Fig. 7: The relationship between ε_1, ε_2 and photon energy of PVA-g-Rh B.

The optical response of a material is mainly studied in terms of the optical conductivity (σ_{opt}) which is given by the relation [23]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \tag{13}$$

where c is speed of light.

Fig. 8 show the relationship between optical conductivity σ_{opt} and photon energy. Optical conductivity $\sigma_{Opt.}$ were increased with increasing photon energy and at high photon energy > 2eV decreasing. This is analogue to the α spectrum. The complex dielectric constant separation of the real part and imaginary part of dielectric constant were determined from the following relation [24]:

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_\infty - B\lambda^2 \tag{14}$$

Where B:

$$B = \frac{e^2 N}{4\pi^2 c^2 \varepsilon_o m^*} \tag{15}$$

where ε_1, e, c, N/m^*, ε_∞ and ε_o are the real and imaginary part of dielectric constant, the electron charge, the velocity of light, the ratio of the free charge carrier concentration to the effective mass, the high frequency dielectric constant (the lattice dielectric constant), the permittivity of free space ($8.854\text{x}10^{-12}$ F/m). The parameters ε_∞ and N/m^* could be determined from the equation (14) by plotting n^2 ($\varepsilon_1 = n^2$) versus λ^2 as shown in Fig. 9.

It is observed that linear part at long wavelengths. Extrapolating the linear part of this dependence to zero wavelength give the value of ε_∞ and from the slope the values of N/m*. The evaluated values of the ε_∞ and N/m* were listed in Table 1.

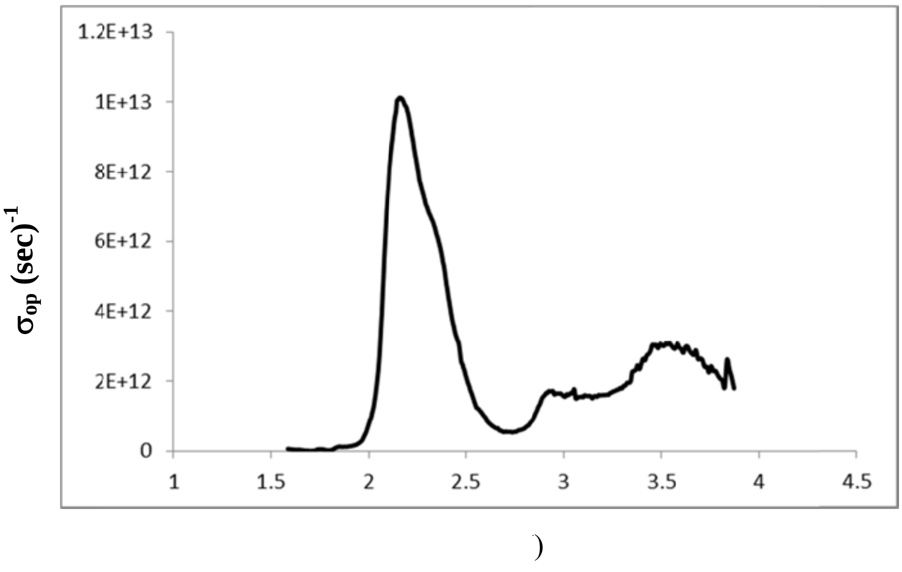

Fig. 8: Optical conductivity σ_{opt} as a function of photon energy for PVA-g-Rh B.

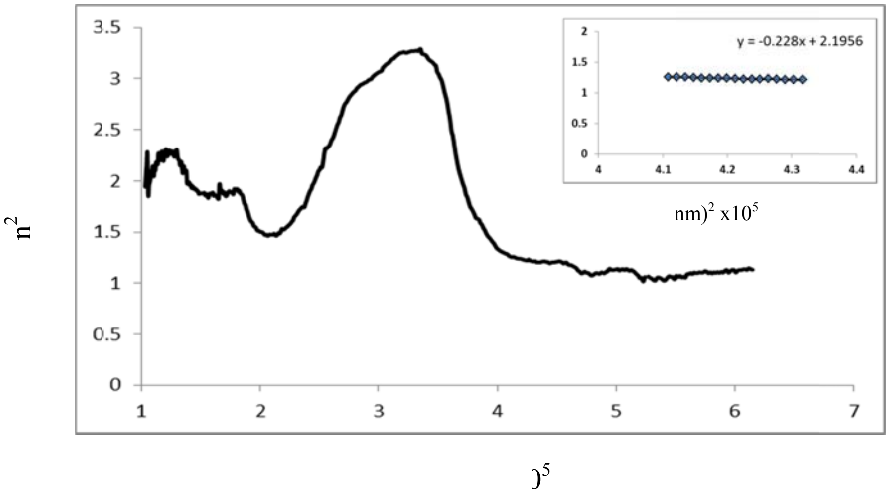

Fig. 9: n^2 as a function of square wavelength.

The average interband oscillator wavelength (λ_0) can be calculated by applying the following relation [24]:

$$\frac{n_o^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \qquad (16)$$

n_0 is the reflective index at infinite wavelength λ_0, plotting $(n^2-1)^{-1}$ versus λ^{-2} shows linear part, was below the absorption edge as shown in Fig. 10.

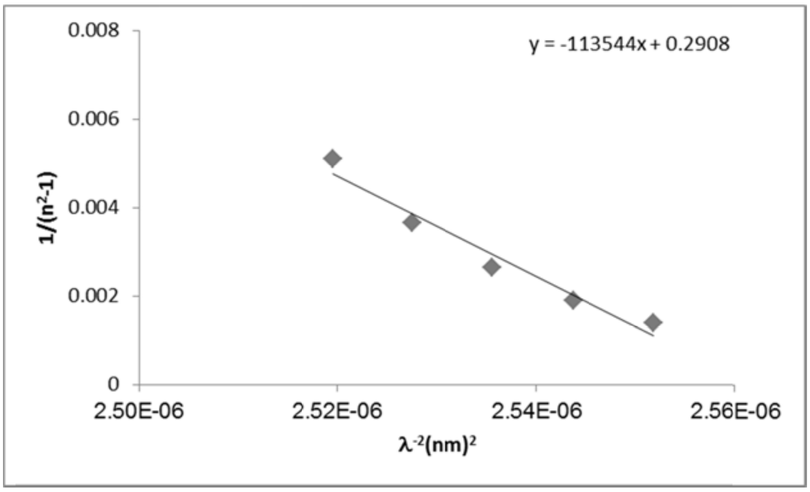

Fig. 10: $(n^2\text{-}1)^{-1}$ versus (λ^{-2}) for PVA-g-Rh B.

The average oscillator strength is given by:

$$S_o = \frac{n_o^2 - 1}{\lambda_o^2} \tag{17}$$

The value of at λ_o and S_o are listed in Table 1. According to Wagner et.el. [25], the Miller rule it is very convenient for visible, nonlinear and near infrared frequencies, which relates the third order of nonlinear polarizability parameter, $\chi^{(3)}$, the so-called nonlinear optical susceptibility and the linear optical susceptibility, $\chi^{(1)}$ can be found through the equation:

$$\chi^{(3)} = A(\chi^{(1)})^4 = A[E_oE_d / 4\pi(E_o^2 - (h\nu)^2]^4 = \frac{A}{(4\pi)^4(n^2-1)^4} \tag{18}$$

Where *A* is a constant, A=1.7×10^{-10}.

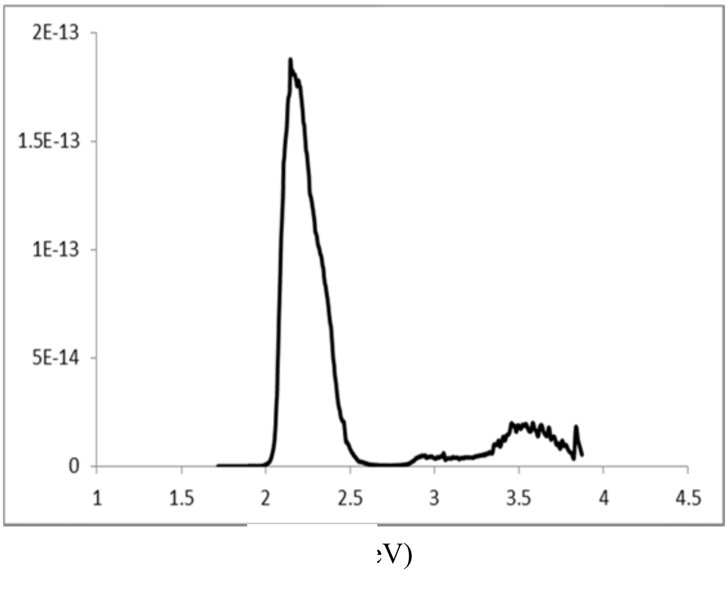

Fig. 11: The relationship between $\chi^{(3)}$ and photon energy for PVA-g-Rh B.

Fig. 11 shows the relationship between third order susceptibility and photon energy of prepared PVA-g-Rh B thin film. The covalency and iconicity of the chemical bonds strongly influence the magnitude of the non-linearity.

The volume and surface loss functions are proportional to the characteristics energy loss of the fast electrons traveling through the bulk and surface of the material, respectively. The volume energy loss function (VELF) and surface energy loss function (SELF) are related to the real and imaginary parts of the complex dielectric function [26]. The energy-loss functions are related to real and imaginary parts ε_1 and ε_2 of the complex dielectric constant by the following relations:

$$VELF = -lm[\frac{1}{\varepsilon}] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} \tag{19}$$

$$SELF = -lm[\frac{1}{\varepsilon + 1}] = \frac{\varepsilon_2}{[(\varepsilon_1 + 1)^2 + \varepsilon_2^2]} \tag{20}$$

Where (-I$_m$ [$\frac{1}{\epsilon}$]) is the volume term of energy loss and (-I$_m$[$\frac{1}{(\epsilon+1)}$]) is surface term of energy loss. The surface energy and volume energy loss functions generated from the dielectric functions (ε_1 and ε_2) are calculated and shown in Fig. 12. The two energies were computed in the energy rang from 1eV to 3.5eV, respectively a typical experimental energy range from visible to VUV. Also the surface and volume energy loss functions generated from the Lorentz oscillator dielectric functions (ε_1 and ε_2) have the same oscillator shape as seen from Fig. 7. Many optical parameters were recorded in Table 1.

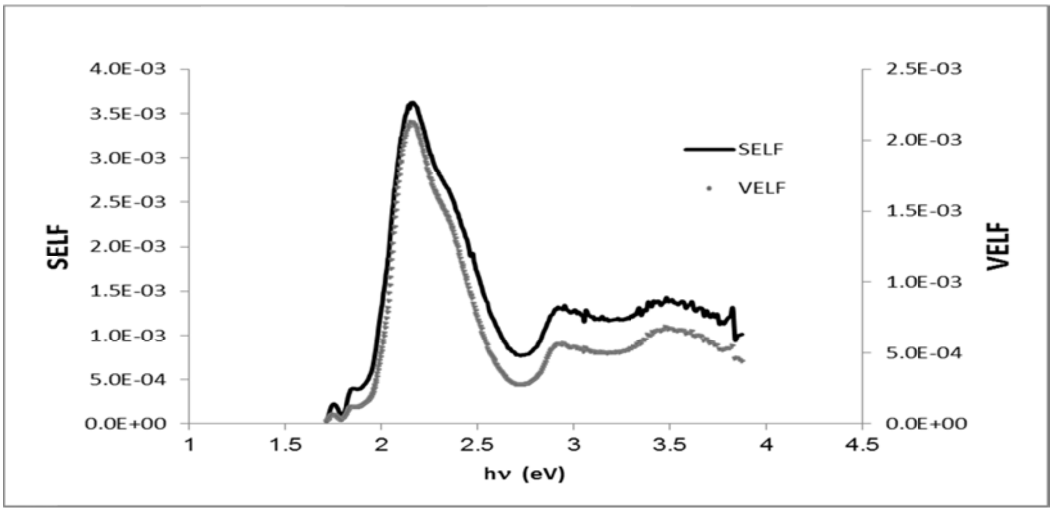

Fig. 12: The relationship between volume, surface energy and photon energy for PVA-g Rh B.

Table 1: Optical parameters of the prepared PVA-g-Rh B thin film.

Quantity	Value
$E_g^{Opt}(eV)$	1.98
$E_{Urbach}(eV)$	1.19
$E_\circ(eV)$	1.98
$E_d(eV)$	46.78
$M_{-1}(eV)^2$	23.62
$M_{-3}(eV)^2$	6.02
$n_\circ$	2.10
$\varepsilon_\circ$	4.43
$N/m^*(m^3.kg)^{-1}$	$2.79\text{x}10^{57}$
ε_∞	2.19
$\lambda_\circ(nm)$	337
$S_\circ(m^{-2})$	3.02×10^{13}
$\chi^3(0)(esu)$	$5.05\text{x}10^{-17}$

4. Conclusion

Optical transmission spectrum is used to calculate the optical and dielectric parameters for new copolymer PVA-g-Rh B thin film. The optical conductivity was increased with increasing photon energy. The refractive index dispersion curve was well fitted with Wemple DiDomenico relation and we find good agreement. Low transmission and reflective in visible range of polymeric thin film is useful to make the materials a prominent one for solar cell applications.

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