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A Study of Some Optical Properties of PHMNP Thin Film

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Abstract

In the present work the refractive index spectra of Poly(2,2'-oxybis(methylene)bis(4-(hydroxyl(4-hydroxymethyl)naphthalene-1-yl)(phenyl)methyl)naphthalene-l-ol) (PHMNP) thin film have been studied at room temperature. The transmission and reflectance spectra, at normal incidence of PHMNP thin film were obtained in the range of (200 - 900 nm). The refractive index dispersion parameters such as oscillator energy E_o, dispersion energy E_d, long wavelength refractive index n_∞, oscillator length strength S_o were calculated to be about 4.18 eV, 11.95 eV, 1.96, 10.024×10^{13} m^{-2}, respectively. The optical moments M_{-1} and M_{-3}, nonlinear optical susceptibility (X^3) and nonlinear refractive index ($n_2(0)$) were found to be $2.85(eV)^{-2}$, $0.1633(eV)^{-2}$, 4.45×10^{-13} esu and 8.64×10^{-12} esu, respectively. The low reflectance and low refractive index of PHMNP thin film in the UV-Visible region make the material a prominent one for antireflection coating in solar thermal devices.

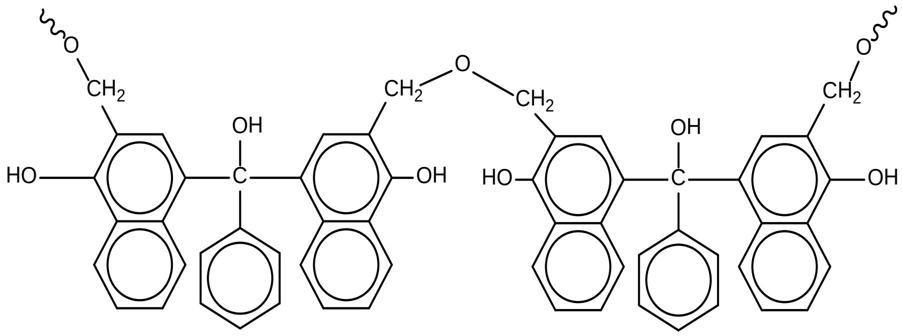
Keywords: Refractive index dispersion, optical constants, nonlinear optical susceptibility

Introduction

Polymers have received a great deal of attention due to their environmental stability, ease of preparation, and tunable optical and electrical properties. Much work has been done on the molecular design, synthesis and assembly of structures with desired properties [1]. Phenol resins are polymers used in a wide variety of applications in different areas such as construction, electronics etc. [2]. Some of the most common uses are as adhesives, coatings, moldings, laminate or plastic products [3]. Phenolic resins are obtained by the condensation of phenol and an aldehyde, commonly formaldehyde, in a batch reactor, in acid or basic media, followed by vacuum distillation to give phenolic products [4]. Information about the spectral dependence of optical parameters such as refractive index, dielectric constant, reflectivity and absorption coefficients are essential in characterizing materials that are used in the fabrication of optoelectronic devices [5-8]. In the present paper, we present the results of the transmission and reflection measurements performed on the polymer in order to derive the refractive index. The refractive index dispersion data were analyzed using the Wemple-DiDomenico single-effective - oscillator model. The determination of the optical constant is expected to expand the available physical information.

Experimental

A thin film of PHMNP was prepared at room temperature using cast method on glass 1.4 × 2 cm in size. Measurement of the spectral transmittance (T) and reflectance (R) were recorded using a CE3055 Reflectance Spectrophotometer in the wavelength range of (200 - 900 nm). The Chemical Structure of PHMNP is shown in **Figure 1**.



2,2'-oxybis(methylene)bis(4-(hydroxyl(4-hydroxy-3-(methoxymethyl)naphthalene-l-yl)(phenyl)methyl)naphthalene-l-ol)

Figure 1 Chemical structure of PHMNP.

Results and discussion

The spectral distributions of transmittance (T) and reflectance (R) were studied for PHMNP and are illustrated in **Figures 2** and **3**.

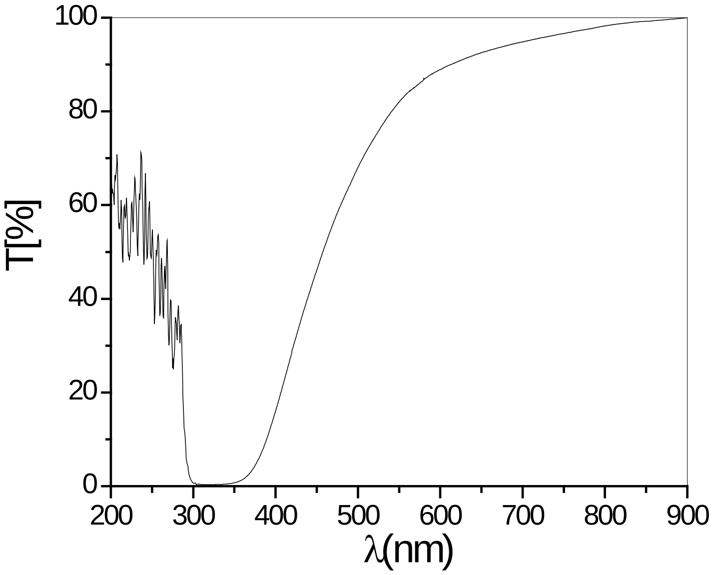


Figure 2 Spectral transmittance (T) as a function of wavelength for a PHMNP thin film.

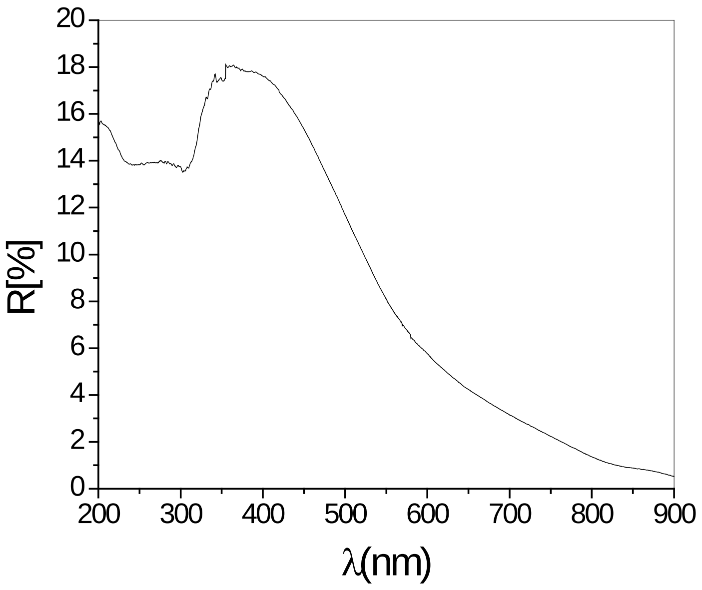


Figure 3 Reflectance (R) as a function of wavelength for a PHMNP thin film.

It should be noted from transmittance and reflectance distributions of the PHMNP thin film, in **Figures 2** and **3**, that at longer wavelengths ($\lambda > 550$ nm) the film becomes transparent. The inequality $(R + T) < 1$ at shorter wavelengths ($\lambda < 550$ nm) is due to absorption (absorbing region).

The refractive index (*n*) of the film can be determined using the following equation [9].

$$n = (\frac{1+\sqrt{R}}{1-\sqrt{R}}) \quad (1)$$

The extinction coefficient (*k*) can be calculated using the equation:

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

Figures 4 and **5** show the variation of the refractive index (*n*) and extinction coefficient (*k*) as a function of wavelength.

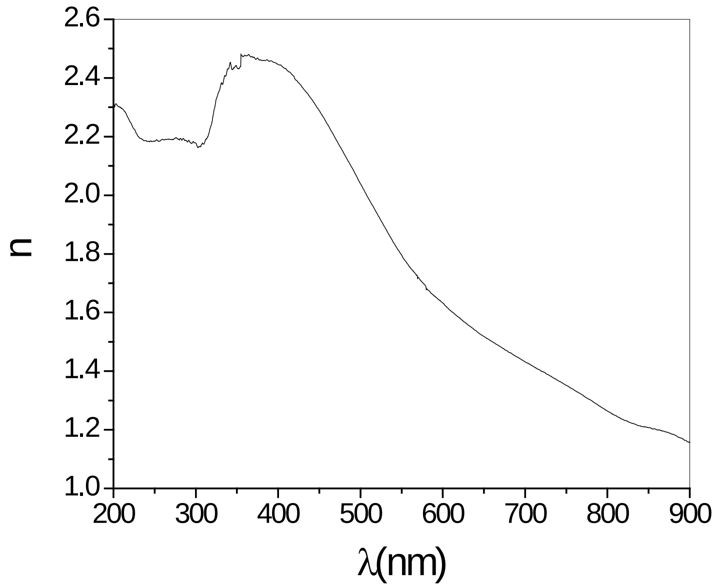


Figure 4 Refractive index (*n*) as a function of wavelength for a PHMNP thin film.

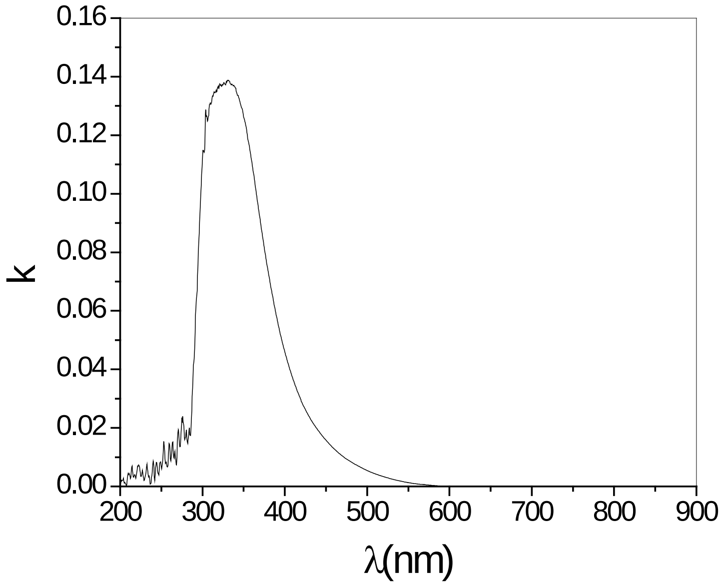


Figure 5 Extinction coefficient (*k*) as a function of wavelength for a PHMNP thin film.

From **Figures 4** and **5** we can see that the values of the refractive index (n) and extinction coefficient (k) are decreasing with the increase in wavelength. In the region 200 - 350 nm it is clear that the values of (n) and (k) sharply decrease with increasing wavelength. At wavelength values > 350 nm the values of (n) and (k) smoothly decrease.

The refractive index, n was obtained according to the single effective oscillator equation used by Wemple and DiDomenico [10,11].

$$(n^2 - 1) = \frac{E_d E_\circ}{(E_\circ^2 - E^2)} \tag{3}$$

where E_o is the single oscillator energy and E_d is the dispersion energy. Values of the parameters (E_o, E_d) can be evaluated by plotting $(n^2\text{-}1)^{-1}$ versus $(h\nu)^2$ and the linear regression was taken as shown in **Figure 6**.

The statically refractive index n_o is evaluated from Eq. (3), $n_o^2 = 1 + (E_d/E_o)$. The value of E_o and E_d are calculated from the slope of plotting $(n^2\text{-}1)^{-1}$ verses $(h\nu)^2$ as shown in **Figure 10**. From the fitting we found that the values are 11.95 and 4.18 eV, respectively. The values of static dielectric constant, $\varepsilon_s = n^2(0)$, and static refractive index are also calculated using Eq. (3), The value of $n(0)$ is found to be 1.96.

The moments of the optical dispersion spectra M_{-1} and M_{-3}, can be evaluated using the relationships [10]:

$$E_\circ^2 = \frac{M_{-1}}{M_{-3}} \tag{4}$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \tag{5}$$

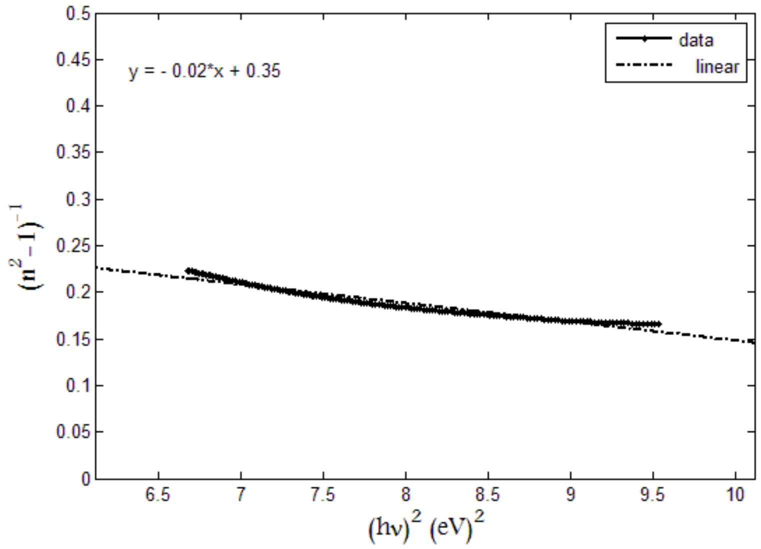


Figure 6 Variation of $(n^2\text{-}1)^{-1}$ versus $(h\nu)^2$ for a PHMNP thin film.

The values of dispersion parameters and the optical moments of the films are presented in **Table 1**.

The relationship between the real part of optical dielectric constant ε_1 and the square of wavelength λ^2 is given by [12]

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_\infty - \frac{e^2}{4\pi^2 c^2 \varepsilon_o} \frac{N}{m^*} \lambda^2 \qquad (6)$$

$$A = \frac{e^2}{4\pi^2 c^2 \varepsilon_o} \frac{N}{m^*} \qquad (7)$$

where ε_∞ is the infinite high frequency dielectric constant, e is the electronic charge, ε_o is the permittivity of free space (8.85×10^{-12} F/m), C is the speed of light, and N/m* is the ratio of carrier concentration to the effective mass. The high frequency dielectric constant ε_∞ can be obtained from plotting n^2 as a function of λ^2 as shown in **Figure 7**. It is observed to be linear at large wavelengths. Extrapolating the linear part of this dependence to zero wavelength gives a value of ε(∞) and from the slope the values of N/m* were calculated according to Eq. (6). The obtained values of ε_∞ and N/m* are given in the **Table 1**.

Table 1 Optical constants of PHMNP thin film.

Quantity	Value	Quantity	Value
$E_o(eV)$	4.18	$N/m^*(m^3.kg)^{-1}$	23.55×10^{30}
$E_d(eV)$	11.95	$\lambda_o(nm)$	167.33
$M_{-1}(eV)^2$	2.85	$S_o(m^{-2})$	10.204×10^{13}
$M_{-3}(eV)^2$	0.1633	$\chi^3(0)(esu)$	4.45×10^{-13}
n_o	1.96	$n_2(0)(esu)$	8.64×10^{-12}
ε_o	3.85		

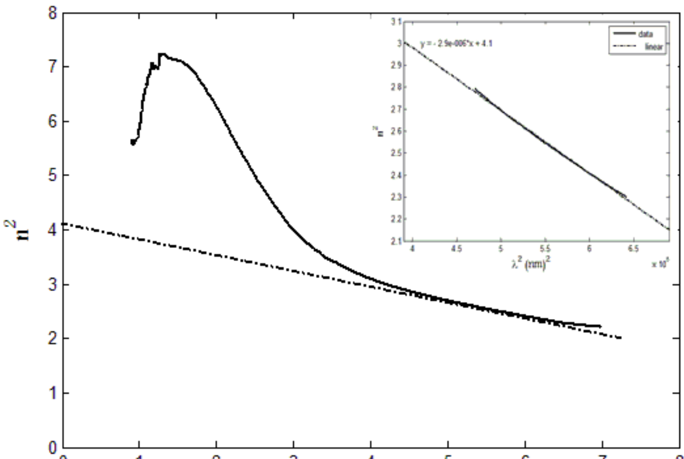


Figure 7 Plot of n^2 as a function of λ^2 for a PHMNP thin film.

The average inter-band oscillator wavelength λ_o can be calculated by the following equation [13]

$$\frac{n_\circ^2 - 1}{n^2 - 1} = 1 - (\frac{\lambda_\circ}{\lambda})^2 \quad (8)$$

where n_o is the refractive index at infinite wavelength λ_o. The plotting $(n^2\text{-}1)^{-1}$ verses λ^{-2} shows a linear part below the absorption edge as shown in **Figure 8**.

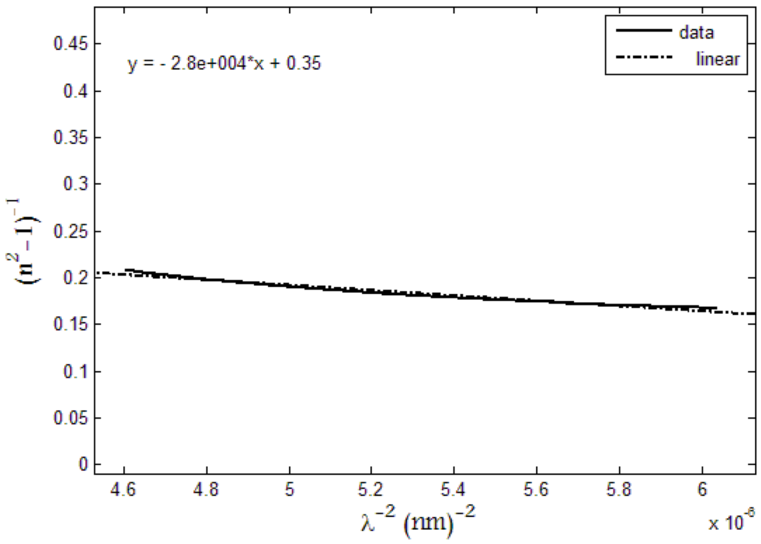


Figure 8 Plot of $(n^2\text{-}1)^{-1}$ against λ^{-2} for PHMNP thin film.

The intersection with $(n^2\text{-}1)^{-1}$ axis is $(n^2\text{-}1)^{-1}$ and hence, n_o^2 at λ_o is equal to ε_∞. The average oscillator strength is given by,

$$s_\circ = \frac{n_\circ^2 - 1}{\lambda_o^{\ 2}} \quad (9)$$

The optical conductivity is a measure of the frequency response of the material when irradiated with light and it is determined from the following relationship [14],

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

where c is speed of light. The electrical conductivity can be estimated by using the following relationship [14].

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

The high magnitude of the optical conductivity (10^{14} sec^{-1}) confirms the very high photo response of the film. The increasing optical conductivity at high photon energies is due to the high absorbance of PHMNP thin film and may be due to electron excitation by photon energy. The optical and electrical conductivities have different profiles with increasing photon energy with optical conductivity higher than electrical as shown in **Figure 9**.

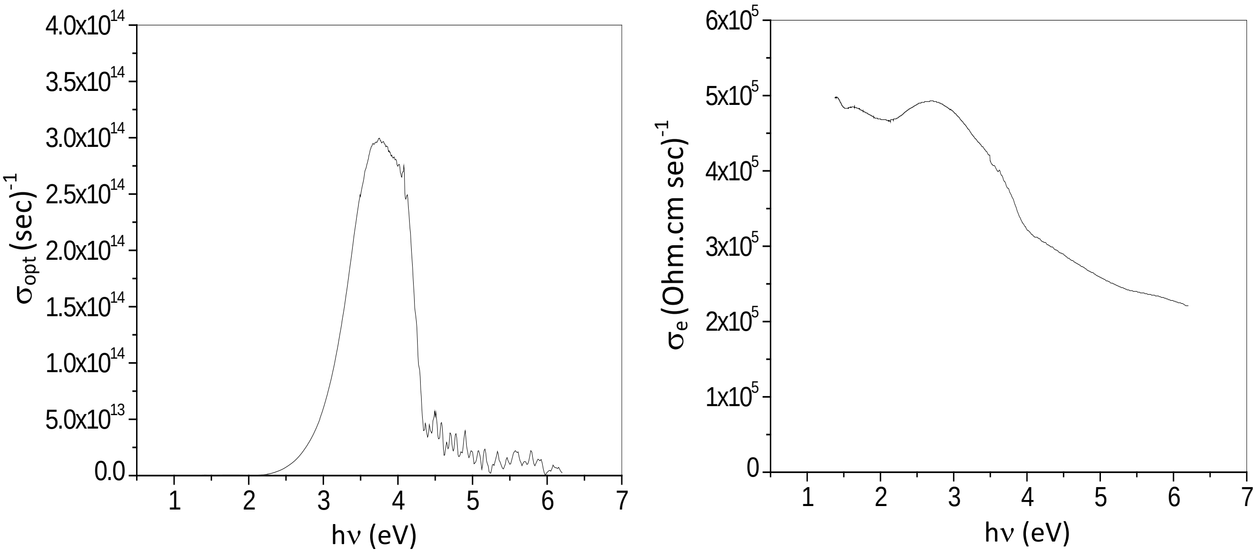


Figure 9 Plots of (a) optical conductivity σ_{opt} and (b) electrical conductivity σ_e as a function of wavelength for a PHMNP thin film.

According to Frumer, the Miller rule is very convenient for visible and near infrared frequencies. It relates the third- order of nonlinear polarizability ($\chi^{(3)}$) parameter, and the linear optical susceptibility $\chi^{(1)}$ are related by the following equation [15,16]:

$$\chi^{(3)} = A(\chi^{(1)})^4$$
$$= A[E_o E_d / 4\pi(E_o^2 - (h\nu)^2]^4 \quad (12)$$
$$= A/(4\pi)^4 (n^2 - 1)^4$$

where A is a constant of value 1.7×10^{-10}. The covalency and ionicity of chemical bonds strongly influence the magnitude of the non linearity.

The values of nonlinear refractive index (n_2) are calculated from the semi-empirical relationship [16].

$$n_2(esu) = 2.6\times10^{-13} \frac{(n^2 - 1)^4}{n} \quad (13)$$

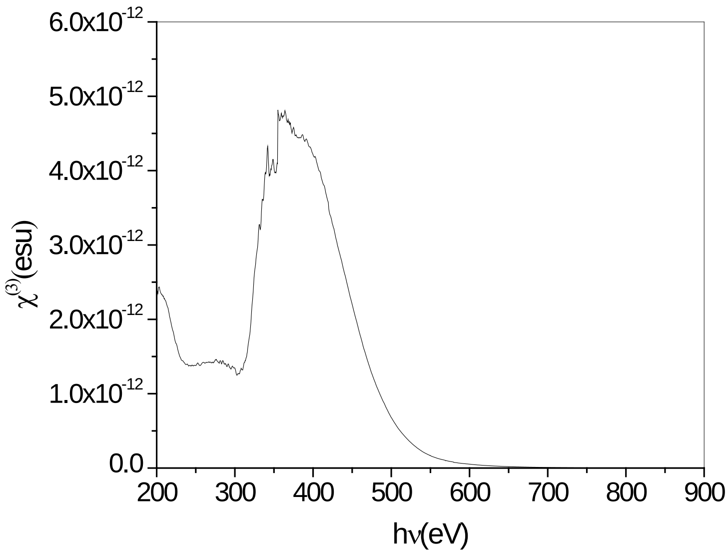


Figure 10 Plot of nonlinear optical susceptibility ($\chi^{(3)}$) as a function of wavelength for a PHMNP thin film.

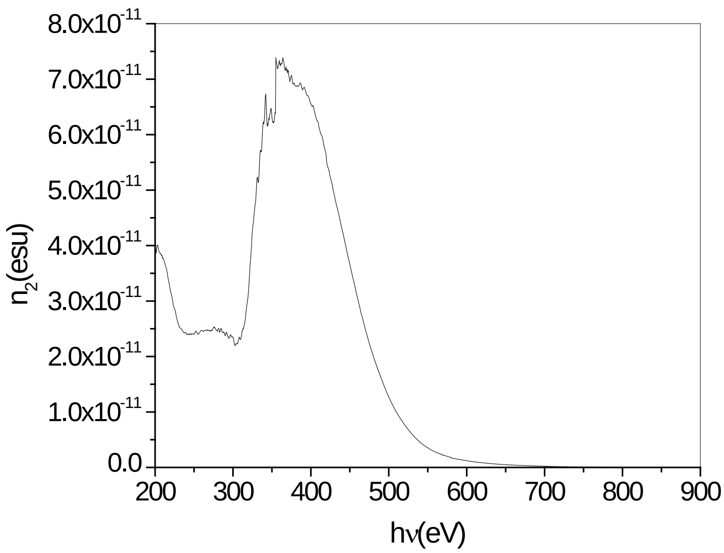


Figure 11 Plot nonlinear refractive index (n_2) as a function of wavelength for a PHMNP thin film.

The variation of nonlinear optical susceptibility ($\chi^{(3)}$) and nonlinear refractive index (n_2) as a function of photon energy are shown in **Figures 10** and **11** respectively. It is clear from **Figures 10** and **11** that the values of third-order nonlinear susceptibility $\chi^{(3)}$ and the nonlinear refractive index n_2 are decreased as the wavelength increases.

Conclusions

The optical transmission spectrum is used to calculate the optical, electric and dielectric properties (i.e. the refractive index, extinction coefficient, optical and electrical conductivity), for PHMNP thin films. The optical conductivity $\sigma_{Opt.}$ was increased with increasing photon energy. The PHMNP thin film exhibited more transmittance at higher wavelength. The high transmission, low reflectance and low refractive index of PHMNP thin films in the UV-Visible region make the materials a prominent one for antireflection coatings in solar thermal devices. The high extinction coefficient value (10^{-1}) and electric conductivity (10^{5} $(\lambda\ cm)^{-1}$) confirm the semi-insulating behavior of the material. The high magnitude of the optical conductivity (10^{14} s^{-1}) confirms the very high photo responsiveness of the material.

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