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Analysis of the optical constants of spun cast polystyrene thin film

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Transmission spectra was used to analyze the basic optical properties and optical constants of spun cast polystyrene thin film.Thin film of polystyrene was prepared by spin coating technique at 2000 rpm for 30s.Thin film was characterized by X-ray diffraction technique to check its amorphous nature. The related parameters viz. oscilllator strength E_o, dispersion energy E_d were determined by the Wemple-Didomenico method.The refractive index (*n*) , extinction coefficient (*k*) and dielectric constant of thin film were calculated. The optical band gap E_g was calculated using transmission spectra.

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1. Introduction

Polymers are emerging as an important class of materials, which offers challenging opportunities for both fundamental research and new technological applications. The important advantage of polymers lies in their structural flexibility both at molecular and bulk levels. Polymer thin film coatings on solid substrates are of high technological importance due to their increasing potential of applications in electronics, sensors etc. These coatings are commonly used to optically match the refractive index of lenses and minimize reflections in optical components. In order for these coatings to be effective it is important to determine their optical constants with high accuracy. It is well established that stress can effect the optical properties of polymer thin films. Previous studies by Prest [1,2] and coworkers[3,4], have shown that spinning and solvent casting processes can induce stress in polymer thin films.

Polystyrene is chemically inert and resistant to oxidizing and reducing agents. It has excellent optical properties like color, chirality and high refractive index (1.60). These properties led us to fabricate polystyrene thin film that can be used as optical wave-guides with low propagation losses. In the field of optical devices polymers are very effective for creating complex integrated optical devices. The optical study to calculate refractive index (*n*) and extinction coefficient (*k*) was performed for polystyrene thin film by analyzing transmission spectrum using envelop method proposed by Swanpoel[5]. So, the aim of present study is to determine the basic optical properties and optical constants of spun cast polystyrene thin film.

2. Experimental details

2.1 Preparation of polystyrene thin film

In this study polystyrene was prepared as follows: Styrene monomer was taken and polymerized by bulk polymerization technique. 50 mg of freshly recrystallized dry initiator benzoyl peroxide (BPO) was taken, and 10 ml of styrene monomer was added to it in a conical flask. The flask was stirred gently till the BPO got fully dissolved in the monomer. Another 40 ml of styrene and 500 mg of dodecyl merceptane (DDM) chain modifier were then added to the flask and the contents were flushed with oxygen free dry nitrogen for about 15 minutes. A water condenser was then fitted to the flask and the flask was then fitted placed in a constant temperature bath maintained at 70°C. The flask was then stirred after every five minutes. Then the viscosity increase was constantly observed and the flask was removed from the bath when the contents attained high viscosity. These were then emptied from the flask in 250 ml of toluene taken in a beaker. The contents of the beaker were now stirred for some time with a glass rod; till a homogeneous solution was formed. Polystyrene formed was now in the form of a solution in a mixture of toluene and the remaining styrene monomer. The polystyrene so formed was recovered by pouring the solution slowly into 2 liters of methanol under constant agitation. Polymer then precipitated as white fluffy solid. The solid polymer was then again washed with methanol and dried at 60°C. The film of polystyrene was prepared from viscous saturated solution analar grade toluene and casted on borosilicate substrate (microscopic glass slide) using spin coating technique for thin film fabrication, by spinning the substrate at 2000 rpm for 30 second. Then the film was dried in air. The film was then dried at 40°C for three hours. From the optical spectral curves, the average thichness of the film was calculated [6] and was found to be 100 nm. The properties related to structure were studied by using microscopic (SEM, NMR) methods.

2.2 Measurements

[1]H NMR, SEM analysis was performed to get an idea about the configuration, conformation, sequence distribution and tacticity of polystyrene chains. The UV-Visible spectra of the polystyrene thin film was recorded by Perkin Elmer Lamda 750 UV/Visible/NIR spectrophotometer at room temperature. The optical transmission spectrum was analyzed to calculate the optical constants such as refractive index (*n*) and extinction coefficient *k*. Analysis of absorption coefficient was also carried out to determine optical band gap of the polystyrene thin film.

2.3 Characterization studies

Scanning electron microscopy and [1]H NMR spectroscopy were used to characterize the configuration, conformation, sequence distribution and tacticity of polystyrene chains. In the [1]H NMR spectra the doublets at 5.77 & 5.71 and 5.25 & 5.25 were due to unsaturated chain ends present in the polymer chain. The two broad peaks at 1.63 and 1.42 correspond to the protons of CH and CH_2 of polystyrene. Up field peak having high relative intensity is ascribed to CH_2 and down field with low relative intensity is due to former. In the extended spectra of polystyrene in the region between 5.0 and 7.6, two peaks one at 7.03 and other at 6.57 were found due to the fact that the ortho-protons of benzene are in different environment and other protons were in different one that explains splitting of the signal.

NMR of PS was compared with literature reference and it is similar to the reported spectra of isotactic PS implying that the PS under investigation in the present work has high tacticity with isotactic and syndotactic conformations of phenyl ring.

3. Results and discussion

3.1 Refractive index and extinction coefficient

Using the experimental data of optical transmittance of the polystyrene thin film, the refractive index and extinction coefficient are calculated using this spectrum. The homogeneous polystyrene film has thickness (*d*) and complex refractive index $n^* = n - ik$, where *n* is the refractive index and *k* is the extinction coefficient. The thickness of the substrate is several times the thickness of the film. Fig.1 shows the oscillating curves which indicates that the thickness of the film is constant.

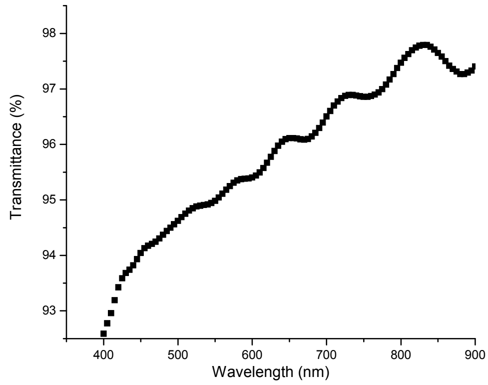

Fig. 1. Transmission spectrum of polystyrene thin film.

The optical parameters were obtained from the fitting pattern in transmittance spectrum. According to Swanepoel [5] the value of refractive index can be calculated as follows:

$$n = \left[N + (N^2 - s^2)^{\frac{1}{2}}\right]^{\frac{1}{2}} \tag{1}$$

where

$$\frac{2s}{T_m} - \frac{(s^2+1)}{2} \tag{2}$$

and T_m is the envelope function of minimum transmittance and *s* is the refractive index of the substrate.

In the weak region where α ≠ 0 the transmittance decreases due to influence of α and refractive index is given by

$$n = \left[M + (M^2 - s^2)^{\frac{1}{2}}\right]^{\frac{1}{2}} \tag{3}$$

Where

$$M = 2s\frac{T_M - T_m}{T_M T_m} + \frac{(s^2+1)}{2} \tag{4}$$

and T_M is the envelope function of maximum transmittance. Refractive index can be calculated by extrapolating the envelops corresponding to $T_M \text{ and } T_m$.

The extinction coefficient *k* can be calculated using the relation

$$k = \frac{\alpha\lambda}{4\pi} \tag{5}$$

where α is the absorption coefficient.

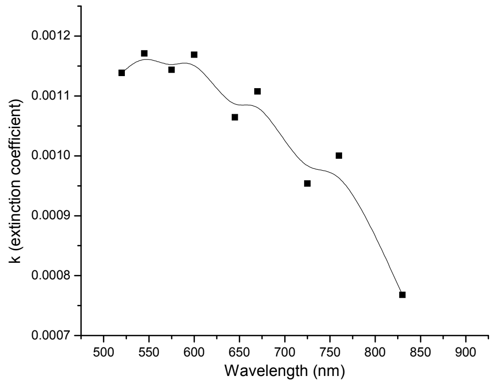

Fig. 2. The variation of extinction coefficient with the wavelength.

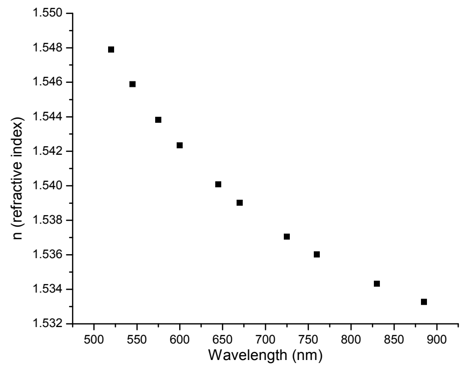

Fig. 3. The variation of refractive index with the wavelength.

The spectral distributions of refractive index n and extinction coefficient are shown in Fig. 2 and Fig. 3. Both refractive index and extinction coefficient were found to decrease with increase of wavelength for thin film under investigation. The values of refractive index show that the compound is transmitting. The variation of n and k values in investigated frequency shows that some interaction take place between photon and electrons [7]. The refractive index changes with the variation of wavelength of incident beam due to these interactions. The refractive index dispersion of the thin film is expressed as [8-10]:

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

where n is the refractive index, h is Planck's constant, υ is the frequency, $h\upsilon$ is the photon energy, E_o is the average excitation energy for electronic transitions and E_d is the dispersion energy which is a measure of strength of interband optical transitions. The dielectric response for transitions below the optical gap is described by this model. E_d and E_o [9] values were calculated from the slope and intercept on the vertical axis of plot of $(n^2-1)^{-1}$ versus $(h\nu)^2$ (Fig. 4) and are given in the Table 1.

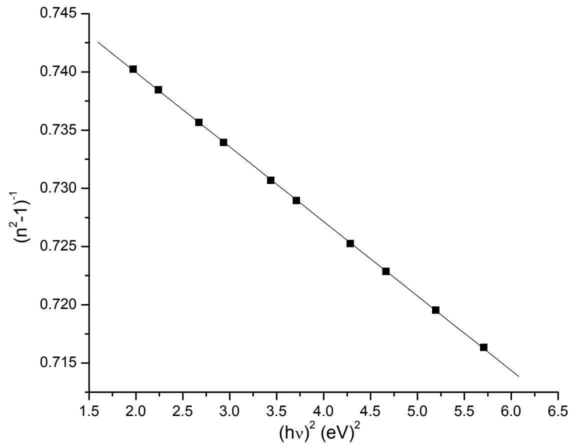

Fig. 4. Plot of $(n^2-1)^{-1}$ vs. $(h\nu)^2(eV)^2$ for polystyrene thin films.

3.2 Determination of optical band gap

To determine the nature of the optical transitions, the optical transmission study was performed for the thin films. In the region of high absorption from which optical band gap is determined, the absorption is characterized by Tauc's relation [11]

$$\alpha h\nu = B\left(h\nu - E_g\right)^n \tag{7}$$

where $h\nu$, E_g and B denotes the photon energy, the optical gap and band tailing parameter respectively and n is a constant which determines the type of transition (n = ½ and 3/2 for direct allowed and forbidden transitions respectively, n = 2 and 3 for indirect allowed and forbidden transitions respectively). The value of n was calculated from the curve of $\ln(\alpha h\nu)$ versus $\ln\left[\left(h\nu - E_g\right)\right]$ and was found to be 2, which indicates an indirect transition. More precise value was obtained from the linear part of $(\alpha h\nu)^{0.5}$ versus $h\nu$ curve (Fig.5) and is given in Table 1.

Table 1. Optical parameters of polystyrene thin film.

E_g Optical band gap [eV]	E_o Oscillator strength [eV]	E_d Dispersion energy [eV]
1.19	10.93	14.54

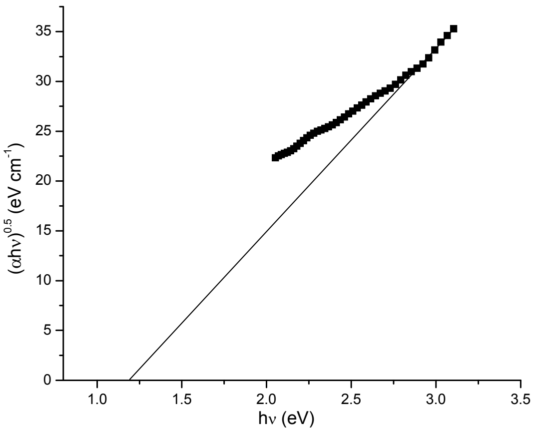

Fig. 5. Plot of $(\alpha h\nu)^{0.5}$ vs. photon energy for polystyrene thin films.

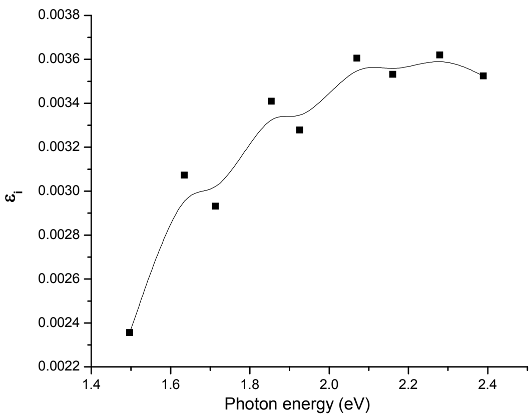

Fig. 6. Plot of ε_i vs. photon energy for polystyrene thin film.

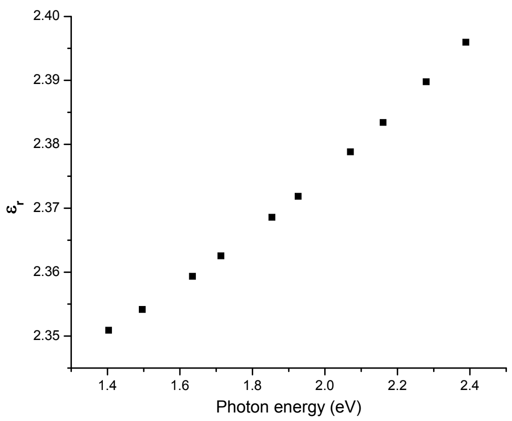

Fig. 7. Plot of ε_i vs. photon energy for polystyrene thin film.

3.3 Complex dielectric function

The complex dielectric constant $\varepsilon^* = \varepsilon_r + i\varepsilon_i$ characterizes the optical properties of a solid material. The real and imaginary parts of dielectric constant were also calculated by the following relation [12]:

$$\varepsilon_r = n^2 - k^2 \tag{8}$$

And

$$\varepsilon_i = 2nk \tag{9}$$

The real and imaginary parts of the dielectric constant were calculated by using eqn. (8) and (9) are shown in Figs. 6 and 7. It is seen that real and imaginary parts of the dielectric constant increases with increase in photon energy. The real part of dielectric constant is much higher than the imaginary part.

4. Conclusions

The transmission spectrum of polystyrene thin film was analyzed to calculate the optical parameters.Refractive index and extinction coefficient both decrease with increase in wavelength. The optical band gap was calculated by Tauc's extrapolation and is 1.19 eV for the polystyrene thin film. The oscillator energy E_o, dispersion energy E_d and other parameters were determined by Wemple-Dedomenico method. The optical band gap calculated by the optical transmission spectrum show that the transition is indirect transition.

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