Preparation of Poly(Aniline-co-p-Nitro Aniline) by Spin-Coating and Study of the Effect of Thickness on Energy Gap

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Abstract

Thin films of a copolymer of aniline with p-nitro aniline were prepared from a dimethyl sulfoxide solution (DMSO) by spin-coating. The solution of the polymer was spread on cover glass and at room temperature. The optical properties of the poly(aniline-co-p-nitro aniline) were investigated at room temperature. An absorbance, transmission and reflectance were determined from UV-visible measurements. The absorption coefficients and bang gap of films material were developed. The thickness of the poly(aniline-co-p-nitro aniline) thin layer on the glass was determined at the range from 1055 to 2033 nm.

Keywords: Copolymer, aniline, p-nitro aniline, spin-coating optical properties, UV-visible

Introduction

In the past few years, the increasing activity in nanotechnology has fascinated the re-examination of observations on organic polymers. In 2000 the Nobel Prize in chemistry recognized the discovery of conducting polymers [1,2]. Optical methods are very useful for the quantitative determination of the electronic band structure of solids. Experiments on optical reflectivity, transmission and refraction provide the way to determine the dielectric constant of the solid, which is related to the band structure. Optical characterization of thin films gives information about other physical properties, e.g. band gap energy and band structure, optically active defects etc., and therefore may be of permanent interest for several different applications. Considerable differences between optical constants of bulk material and thin films or those of films prepared under varying growth characteristics are often reported. Therefore determination of optical constants for each individual film by a non-destructive method is highly recommended. Generally, the optical band gap (E_g) and absorption coefficient α could be evaluated from transmittance or absorbance spectra. Swanepoel [3] has improved this method to determine more accurately the thickness (t), absorption coefficient (α), etc. There are several reports on this method [4-6].

In another conventional method, the reflectance (R) and transmittance (T) spectra are used to determine α. Since α is related to the extinction coefficient k, which is defined as the imaginary part of the complex refractive index, where n is the real part of refractive index, an accurate determination of n and k is possible. But this often becomes difficult due to the presence of multiple solutions. It is necessary to have a rough idea about the thickness t and refractive index n to start with, and by a judicious adjustment of the magnitude of thickness it is possible to secure a continuous solution of n and k throughout the whole spectral range. Therefore, in this paper, the copolymer was prepared by a chemical method. The effect of thickness on the optical energy gap of the material is presented then the optical properties of thin films of a copolymer of aniline with p-nitroaniline which have different thicknesses have been studied for the first time.

Materials and methods

Experimental

Double distilled water was used to prepare all the solutions. Aniline was purified by single distillation under reduced pressure when received from Aldrich. Nitroaniline from (Merck, Mumbai, India) was recrystallized with acetone-ethanol mixture. The ammonium persulfate is used as received from Merck Chemicals. Initially 1.0 M of aniline dissolved in an aqueous solution of 0.5 M HCl. 1.0 M solution of p-nitroaniline each mixed with aniline in a separate reaction. Ammonium persulfate (APS) was dissolved in a 0.5 M HCl aqueous solution. The aqueous solution of ammonium persulfate was introduced to start the polymerization. The reactions were carried out in 0.5 M solution of HCl under pseudo first-order conditions with a large [amine]: [ammonium persulfate] ratio of 10:1. The reaction mixture was thoroughly mixed with a magnetic stirrer for 5 min and kept in a water bath at room temperature, a color change pattern from the light yellow to light green and then finally dark green precipitate was observed from 0 to 48 h polymerization of aniline with PNA in aqueous solution of ammonium persulfate has been used as initiator of the polymerization reaction. The polymerization system becomes more acidic during the course of the polymerization [1,10] The polymerization process for simplicity can be shown in Scheme 1. The general structure of the poly(aniline-co-p-nitro aniline) is given in **Figure 1**. The polymer powder was added to DMS solvent and mixed under constant stirring at room temperature. After completing the mixing process, the polymer was filtered under vacuum, then the mixture was deposited on glass substrates as a thin films using spin coating. The thickness of the thin film can be calculated by spectroscopic ellipsometry (VASEC) Woolam M-2000TM.
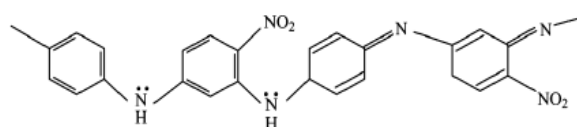
Poly (aniline-co-*p*-nitroaniline) 1:1

SCH. 1.

Figure 1 The general structure of the poly(aniline-co-p-nitro aniline).

Results and discussion

The FT-IR spectrum of poly(aniline-co-p-nitro aniline) is verified by **Figure 2**. The copolymer shows characteristic bands corresponding to the benzenoid stretching vibration at 1591 cm^{-1}. There is also a possibility of the overlap of bands due to asymmetric N-O stretching vibration at 1353 cm^{-1}. The bands in the region 744 - 1130 cm^{-1} are due to tri-substitution in the benzene ring. The band at 1533 cm^{-1} is assigned to a C-H bending vibration.
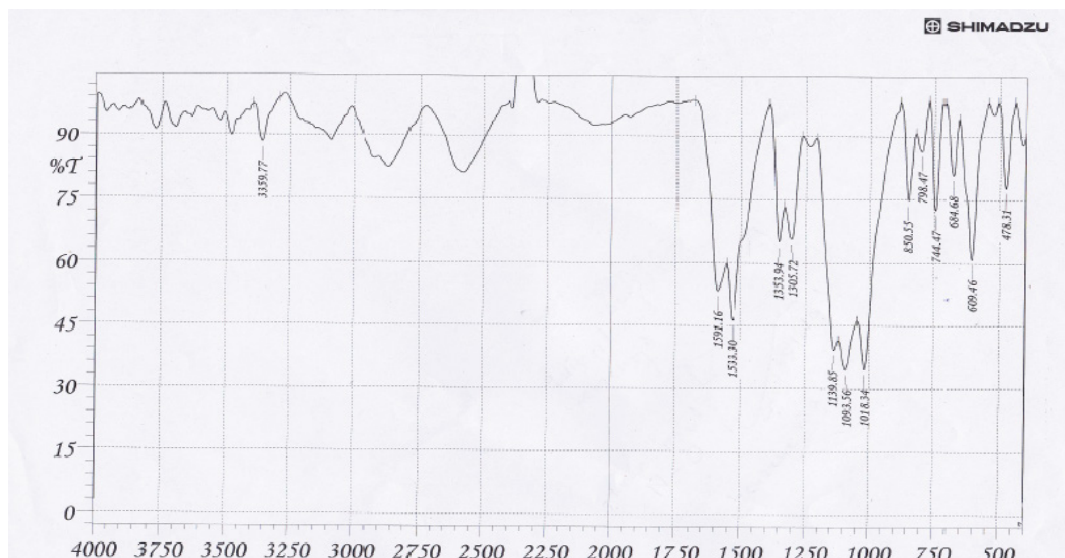
Figure 2 FT-IR spectrum of poly(aniline-co-p-nitro aniline).

The optical absorption spectra of the crystallites were measured using a UV-Vis spectrophotometer (USB- CECIL CE3055 Refro Spectrometer UK). The poly(aniline-co-p-nitro aniline) films have been recorded at room temperature over the range of 280 - 1080 nm at different thickness (1055, 1285, 1420 and 2033 nm) as shown in **Figure 3**. It is clear from the absorption spectra of these samples that all four samples have absorption peak at wavelength from 350 to 380 nm. All samples show small shifts of the absorption edges due to different samples thicknesses.
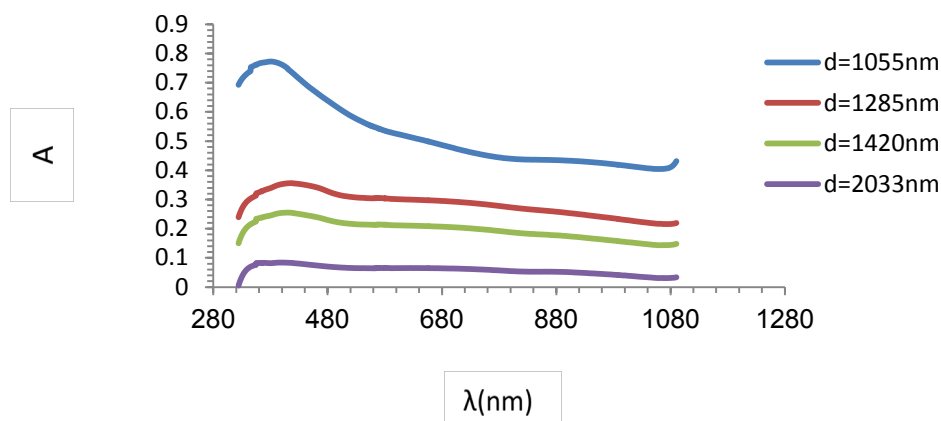

Figure 3 Absorption spectra of copolymer aniline with p-nitro aniline.

The optical data were analyzed from the classical relation for near edge optical absorption in semiconductors [7,8].

$$\alpha = A \left[\frac{(hv - E_g)\tau}{hv} \right] \tag{1}$$

where v is the incident frequency, h is Planck constant and τ is the (½, 3/2, 2 and 3) for transitions (direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively). A is a constant and Eg is defined as the optical energy band gap between the valence band (V.B) and the conduction band (C.B).

The type of transition depends on the absorption coefficient value. When α value is larger than 10^4 cm^{-1}, the transition is called a direct transition, where the electron moves from the V.B to C.B with the different wave vector (k), the energy and momentum are conserved. While, indirect transition occurs when the value of absorption coefficient is less than 10^4 cm^{-1} [9], where the electrons are transferred from V.B to C.B at the same wave vector (k). The momentum and energy must be conserved with phonon assistant [9].

Figures 4a - d show the relationship between the absorption coefficient and photon energy for the copolymer aniline with p-nitro aniline. The value of absorption coefficient plays an important role in the limitation of the type of transition. From the above figures the value of the (α) was greater than 10^4 cm^{-1} indicating that the transition was direct electron transmission.
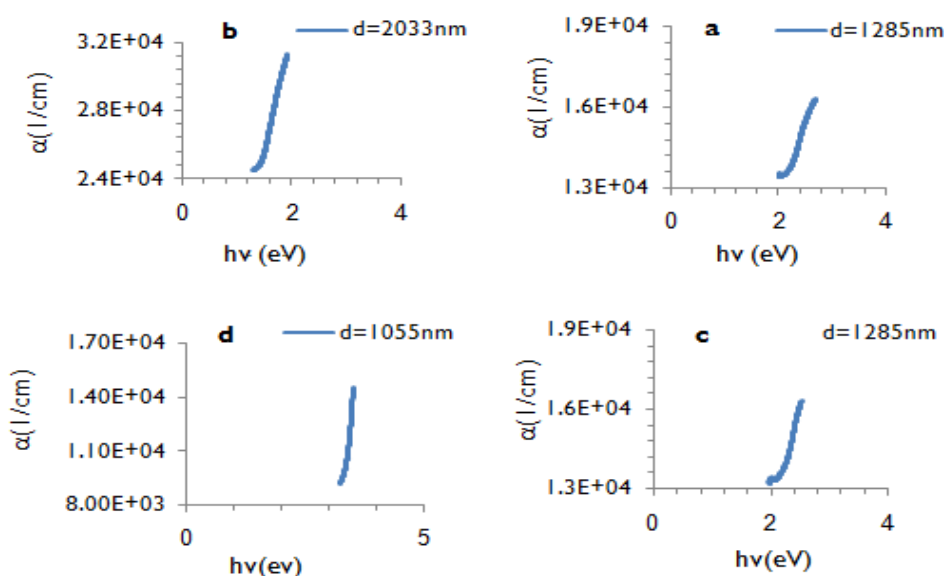

Figure 4 The relationship between absorption coefficients versus Photon energy at different thickness (a-1055, b-1285, c-1420 and d-2033 nm) for poly(aniline-co-p-nitro aniline).

According to Eq. (1) the optical band gap determined, from the plot of $(\alpha hv)^2$ versus photon energy is shown in **Figures 5a - d**. The value of the energy gap is obtained by extrapolating the linear region of the plot $(\alpha hv)^2 = 0$. The allowed direct transition optical gap is found (1.19, 1.96, 2.1 and 2.6 eV) for thickness (2033, 1420, 1285 and 1055 nm) of poly(aniline-co-p-nitro aniline) as shown in **Table 1**. The optical band gap decreases with thickness of quantum size effect [10] The quantum size effect appears in semiconductors and semi- metal films, when the thickness of the films is found to be comparable with the mean free path effective de-Broglie wavelength of the carries. The transverse component of the quasi momentum of the carriers is quantized due to the finite size of the thickness. The transverse components of the electron states assume quasi-discrete energy values in thin films. Due to this quantisiation, the

bottom of the conduction and top of the valence band are separated by an additional amount (ΔE) which is given by [11];

$$\Delta E = (h^2/8m^*d^2) \tag{2}$$

Table 1 The relationship between thickness and optical band gap.

d (nm)	1055	1285	1420	2033
E_g (eV)	2.6	2.1	1.96	1.19

where d is the thickness of the film and m* is the effective mass of the carrier. Therefore, the increase in the band gap in the present case may be due to the additional contribution of the energy band because of the quantization effect the band gap in case of poly(aniline-co-p-nitro aniline) thin film decrease with film thickness [12]. Svorcik *et al.* [13] studied the relationship between thickness and energy gap. They also observed that the optical energy gap increases with decreasing thickness. Thus the optical energy gap (E_g) decreases from 6.1 - 5.2 eV when the thickness increases from 500 - 1500 nm.
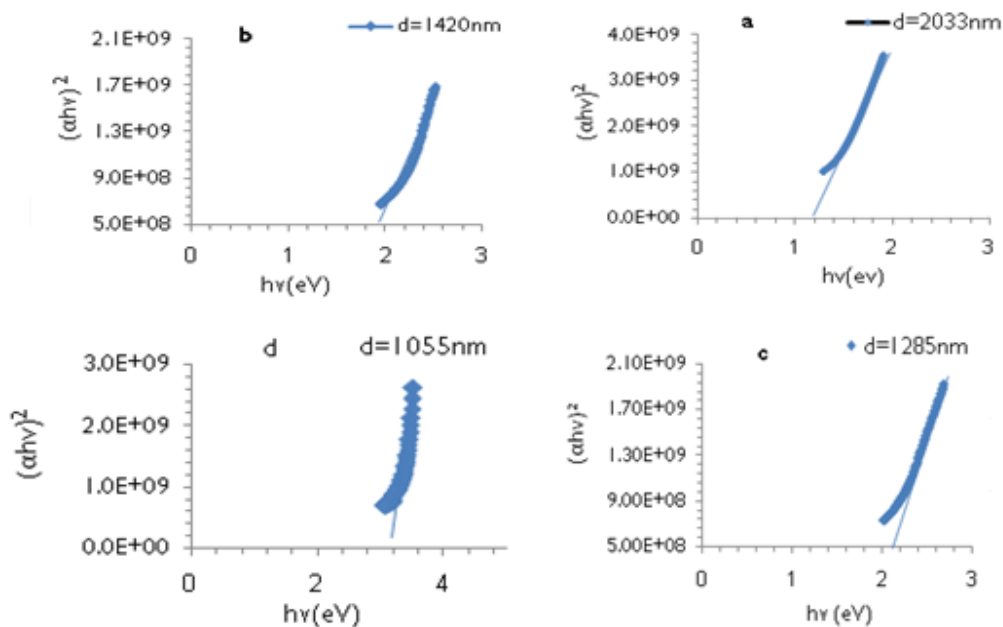

Figure 5 The relationship between $(\alpha h\nu)^2$ versus photon energy at different thickness (a-2033, b-1420, c-1285 and d-1055 nm) for poly(aniline-co-p-nitro aniline).

The optical band gap decreases with the increase in the thickness of the films. The variation is due to the quantum size effect occurring in the semiconducting thin films. This is verified in this study by **Figure 6** which shows a straight line with inverse square of thickness versus an optical band gap.
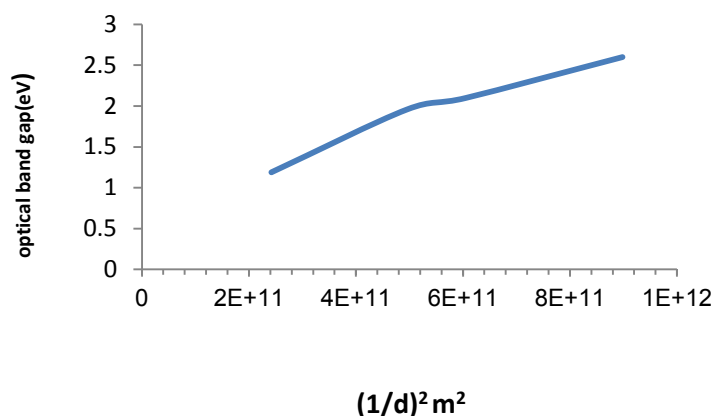
(1/d)² m²

Figure 6 Variation of optical band gap with $(1/d)^2$

Optical transmission spectrum and photon energy of the layer films is observed in **Figure 7**. The variation of transmission with photon energy at different thickness (1055, 1285, 1420 and 2033 nm) as we see there is a dependence of transmittance on the thickness of films, its reaches about (100 %) for the lower thickness 1055 nm and about (10 %) for the higher thickness 2033 nm. The increase in transmittance with increasing photon energy and then decreases the transmission of light because of an increase in the absorption in the films
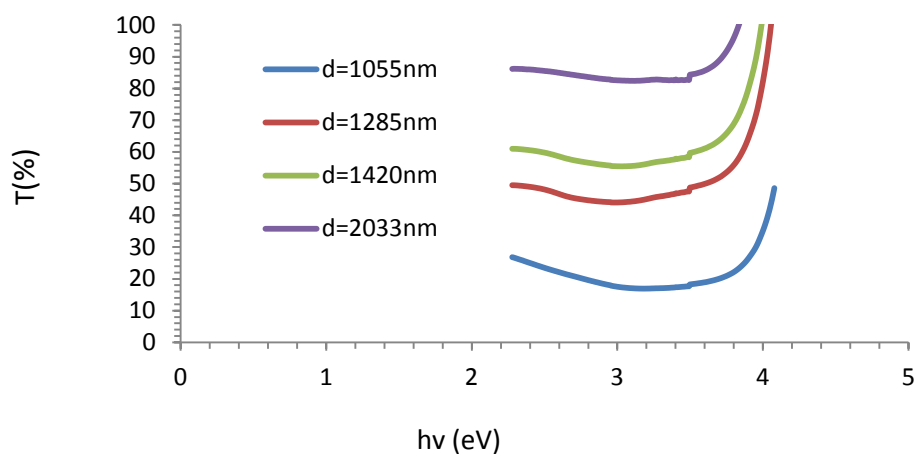

Figure 7 Variation of Transmittance (T) with photon energy at difference thickness (1055, 1285, 1420 and 2033 nm) for poly(aniline-co-p-nitro aniline).

Conclusions

The present study include the preparation of poly(aniline-co-p-nitro aniline), by chemical polymerization. The polymer solution was deposited on glass by the use of spin coating in order to study optical properties. The polymer thin films (1055, 1285, 1420 and 2033 nm) prepared were analysed by the use of (FT-IR) to determine the functional groups of the chemical bonds. The optical properties of the thin films prepared were studied including recording the absorption spectroscopy for wavelengths of 300 - 900 nm. The absorption coefficient and the forbidden energy gap to transmission.

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