Optical Properties of the Poly(*N*-benzylaniline) Thin Film

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Received: August 26, 2005; In Final Form: October 31, 2005

The optical properties of the poly(*N*-benzylaniline) thin film were investigated by optical characterization. The optical constants such as refractive index and dielectric constant were determined from the transmittance and reflectance spectra of the film. The refractive index dispersion was analyzed by the Wemple−DiDomenico model. The n_∞ values changed from 6.37 to 5.71 and these values did not show any certain trend with annealing temperatures. The average oscillator parameter S_o value, which is the strength of the individual dipole oscillator, was found to be in the range of 1.15×10^{13} to 1.03×10^{13} m^{-2}. The optical band was determined from the direct optical transitions in *K* space. The optical band E_g of the film decreases from 2.089 to 2.046 eV with increasing annealing temperatures while the Urbach energy E_u called the width of localized states in the optical band gap increases from 0.544 to 0.598 eV. Consequently, the optical constants and optical band gap of the poly(*N*-benzylaniline) change with the annealing temperatures.

Introduction

Conjugated polymers are materials for fabrication of solid-state devices.[1] The potential applications of conducting polymers in organic electronic devices, chemical sensors, electrochromic displays, and valuable optical properties have encouraged scientists to synthesize new materials.[2]

Polyaniline is very popular conductive material and has great scientific and industrial interest because of its technological applications in electrical devices. And it also has great thermal and environmental stability.[3,4] Polyaniline has great interest as an organic magnet due to the potentially strong exchange interactions occurring through the π-conjugated backbone.[5] Potential applications of polyaniline are as an antistatic agent for plastics, conductive rubbers and plastics composites, microelectronic devices, a component of electrochemical batteries, optical waveguides, catalysts for chemical reactions, an antioxidant for rubbers and plastics, and a key component in gas sensing devices.[6] However, for such applications, materials must be soluble in common solvents or melt processable, and polyaniline does not satisfy this requirement. Substitution or addition of side chain polyaniline provides solubility and processability.[7−9] The refractive index and optical band gap are the fundamental parameters of an optical material, because these are closely related to the electronics of the material. The evaluation of the refractive index and absorption edge of optical materials are of considerable importance for applications in integrated optic devices such as switches, filters, and modulators, etc., where the refractive index of an optical material is the key parameter for device design.[10]

In the present work, we investigate the optical properties of the poly(*N*-benzylaniline) thin film to show the effect of the thermal annealing on optical parameters. This information will help researchers in applying this material in optical communication and optical devices. The determination of the optical constants has also proved to be very useful for elucidation of the optical properties of poly(*N*-benzylaniline).

Experimental Section

The Preparation of *N*-Benzylaniline. *N*-Benzylaniline was prepared according to ref 11. A 100-mL two-necked flask was equipped with a separatory funnel, a mechanical stirrer, and a reflux condenser. Pure sodium carbonate (3.5 g), water (3.5 mL), and freshly distilled aniline (3.2 g, 3 mL) were placed in the flask and benzyl chloride (4.2 g, 3.8 mL) was placed in the separatory funnel protected by a calcium chloride guard-tube. The flask was heated to 90−95 °C and the contents was stirred vigorously and run in the benzyl chloride slowly (about half hour). The heating and stirring were continued for an additional 3 h. The solution was allowed to cool to room temperature and filtered with suction, then the organic layer was separated from the filtrate, washed with 25 mL of saturated salt solution, and extracted with dichloromethane. The solution was then dried with magnesium sulfate and filtered. Solvent was evaporated. Unreacted aniline was distilled under reduced pressure.

The Preparation of Poly(*N*-benzylaniline). Poly(*N*-benzylaniline) was chemically prepared from *N*-benzylaniline in aqueous HCl (Merck) solution. To 0.46 g of *N*-benzylaniline in 20 mL of 2 M aqueous HCl solution in a 100-mL one-necked flask maintained at 0 °C was added dropwise over 30 min 0.6 g of $(NH_4)_2S_2O_8$ (Fluka) in 5 mL of 2 M aqueous HCl solution. After the complete addition of the oxidizing agent, the mixture was stirred at 0 °C for 5 h and then overnight at room temperature. The final polymer was washed several times with distilled water and acetonitrile (Merck) to remove oligomers as well as any other impurities. The polymer was treated with 1.0 M NH_4OH solution (Merck) for 2 h at 70 °C for deprotonation and then washed again with distilled water several times. The polymer was then dried in an oven. Benzyl groups are electron donating groups which increase the electron density

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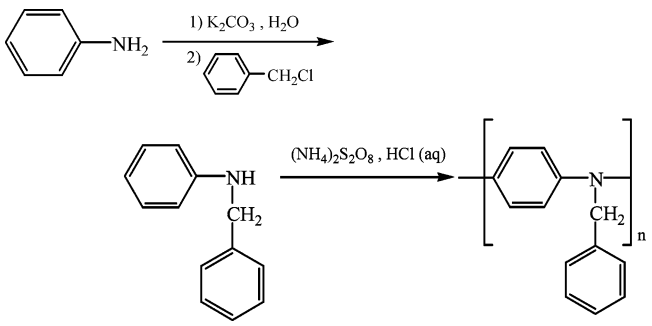
10.1021/jp054844m CCC: $33.50
Published on Web 12/08/2005

along the conjugated polymeric chain. The reaction scheme for the synthesis of poly(*N*-benzylaniline) is shown below.



The Preparation of Poly(*N*-benzylaniline) Thin Film. Poly(*N*-benzylaniline) was dissolved in THF (Merck) at room temperature. The film of the poly(*N*-benzylaniline) was prepared by evaporating the solvent from a solution of the compound with subsequent drying of the film deposited on quartz substrate. The poly(*N*-benzylaniline) solution was homogenized for 4 h and then rotated for homogeneous mixing.[12−14] The film prepared was left to dry at 25 °C for 48 h. The film thickness was obtained as ∼110 nm.[12−14] For the annealing processes of the film, a proper annealing atmosphere was selected. The film was annealed at various temperatures (55, 115, and 145 °C) in atmosphere with use of a furnace for 30 min. The UV−visible spectra of the film prepared and annealed thin film were recorded by a Shimadzu UV-2401 PC UV−visible recording spectrophotometer at room temperature. Experiments such as infrared spectra and optical observations were performed to observe the influence of annealing temperature and time on the film structure. These experiments show that the optical properties of the film can be discussed with respect to annealing temperature.

Results and Discussion

The Refractive Index Dispersion and Optical Constants. Figure 1 shows the transmittance (*T*) and reflectance (*R*) spectra of the film. The optical properties of the film are characterized by *T* and *R* spectra. The dispersion plays an important role in the research for optical materials because it is a significant factor in optical communication and in designing devices for spectral dispersion. The complex refractive index of the film is expressed as,

$$\hat{n} = n(\omega) + ik(\omega) \tag{1}$$

where n is the real part and k is the imaginary part of the complex refractive index. The refractive index of the film can be obtained from the following equation,[15,16]

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{2}$$

The refractive index of the film was calculated with eq 2. The refractive index dependence of wavelength was plotted. As seen in the plotted figure of refractive index, the refractive index decreases with photon energy, shows a peak, and then increases. The change in the refractive index is a result of the thermal changes in the film. The refractive index decreases with increasing annealing temperatures up to 500 nm, and afterward it does not indicate a certain trend with annealing temperatures. The decrease in the refractive index is associated with the fundamental band gap absorption. The changes in the refractive

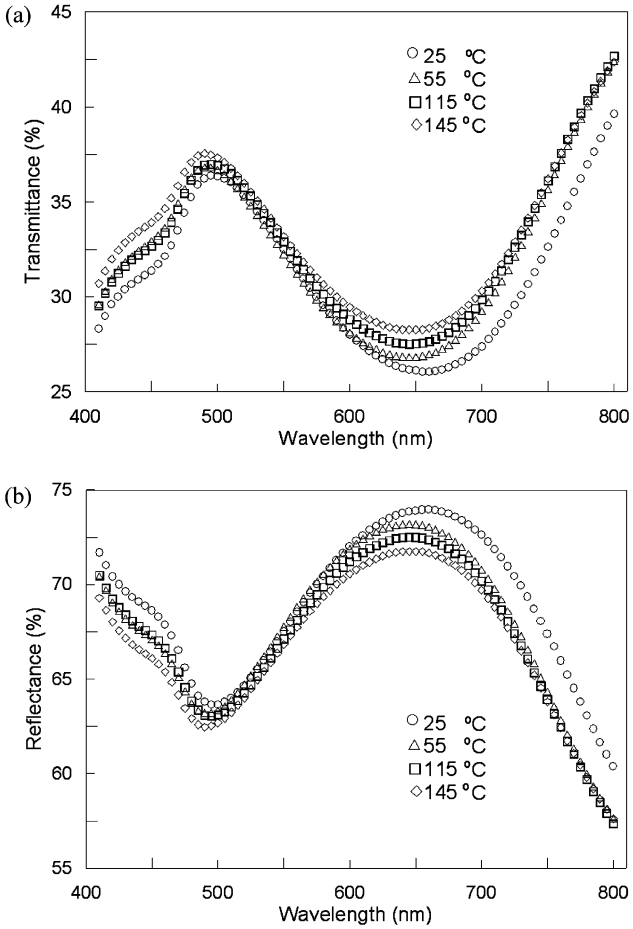


Figure 1. Transmittance and reflectance spectra of the film at room temperature (25 °C) and various annealing temperatures.

index indicate that some interactions take place between photon and electrons in the thin film. It is clearly evident that a peak appears in the refractive index, which shifts with annealing temperatures. This shift confirms the change in the optical band gap. To obtain refractive index dispersion parameters of the poly(*N*-benzylaniline), the refractive index of the film can be analyzed by using the Wemple−DiDomenico model[16−19]

$$\frac{(n_\infty^2 - 1)}{(n^2 - 1)} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \tag{3}$$

where n_∞ is the long wavelength refractive index and λ_o is the average interband oscillator wavelength. Figure 2 shows the plots of $1/(n^2 - 1)$ vs λ^{-2} at various annealing temperatures. The n_∞ values were calculated from the curves of Figure 2 and are given in Table 1. Equation 3 can also written as,

$$n^2 - 1 = \frac{(S_o \lambda_o^2)}{(1 - \lambda_o^2/\lambda^2)} \tag{4}$$

where $S_o = (n_\infty^2 - 1)/\lambda_o^2$ is the average oscillator parameter, which is the strength of the individual dipole oscillator. The S_o values were obtained by using the above equation and are given in Table 1. It is seen in Table 1 that n_∞ and S_o values change with the annealing temperatures. S_o values are of the same order for different materials.[16,19]

The complex dielectric constant is expressed as,

$$\epsilon^* = \epsilon_r + i\epsilon_i \tag{5}$$

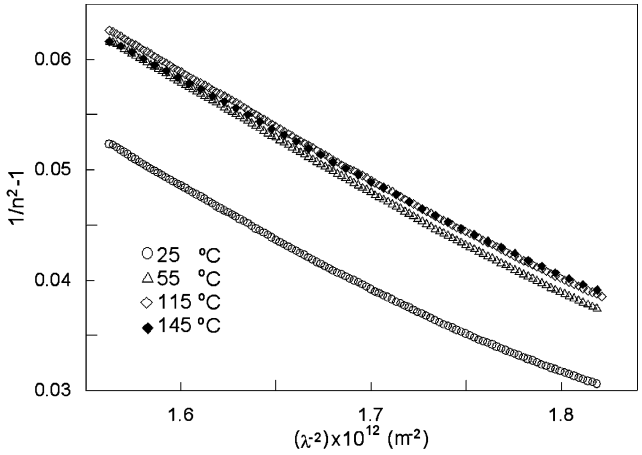


Figure 2. Plot of $(1/n^2 - 1)$ vs λ^{-2} at room temperature (25 °C) and various annealing temperatures.

TABLE 1: Optical Band Gap and Optical Constant Values of the Thin Film at Room Temperature (25 °C) and Annealing Temperatures

T (°C)	E_g (eV)	E_u (eV)	n_∞	S_o (m^{-2})
25	2.09 ± 0.12	0.54 ± 0.03	6.37 ± 0.12	$(1.15 \pm 0.1) \times 10^{13}$
55	2.08 ± 0.09	0.55 ± 0.02	5.71 ± 0.04	$(1.03 \pm 0.12) \times 10^{13}$
115	2.07 ± 0.11	0.58 ± 0.05	5.76 ± 0.07	$(1.05 \pm 0.06) \times 10^{13}$
145	2.05 ± 0.05	0.60 ± 0.08	5.95 ± 0.11	$(1.11 \pm 0.11) \times 10^{13}$

where ϵ_r is the real part and ϵ_i is the imaginary part of the dielectric constant. The imaginary and real parts of the dielectric constant of the film were also determined by the following relations,[20]

$$\epsilon_r = n^2 - k^2 \tag{6}$$

and

$$\epsilon_i = 2nk \tag{7}$$

We calculated the imaginary and real parts of the dielectric constant. The dependence on photon energy of the real and imaginary parts is shown in Figure 3a,b. Both the real part and the imaginary part of the dielectric constant change with increasing photon energy and show a peak and then increase. The real part of the dielectric constant is higher than that of the imaginary part of the dielectric constant. As seen in Figure 3, the real part of the dielectric constant shows a peak. It is seen that the position and height of the peak change with the annealing temperatures. The height of the peak decreases with increasing annealing temperatures, whereas after 500 nm, the dielectric constant does not show a certain trend with annealing temperatures. At the same time, the imaginary part of the dielectric constant shows the same results with the real part of the dielectric constant.

Determination of the Optical Band Gap and Width of Localized States. The optical band and width of localized states play an important role in the research for optical materials as these are significant factors in optical communication and in designing devices for spectral dispersion. In the absence of interference fringes the measured transmission is given by

$$T = \frac{(1-R)^2 + 4R\sin^2\varphi}{e^{\alpha d} - R^2 e^{-\alpha d}} \tag{8}$$

In infrared the term $4R \sin^2 \varphi$ is negligible with regard to

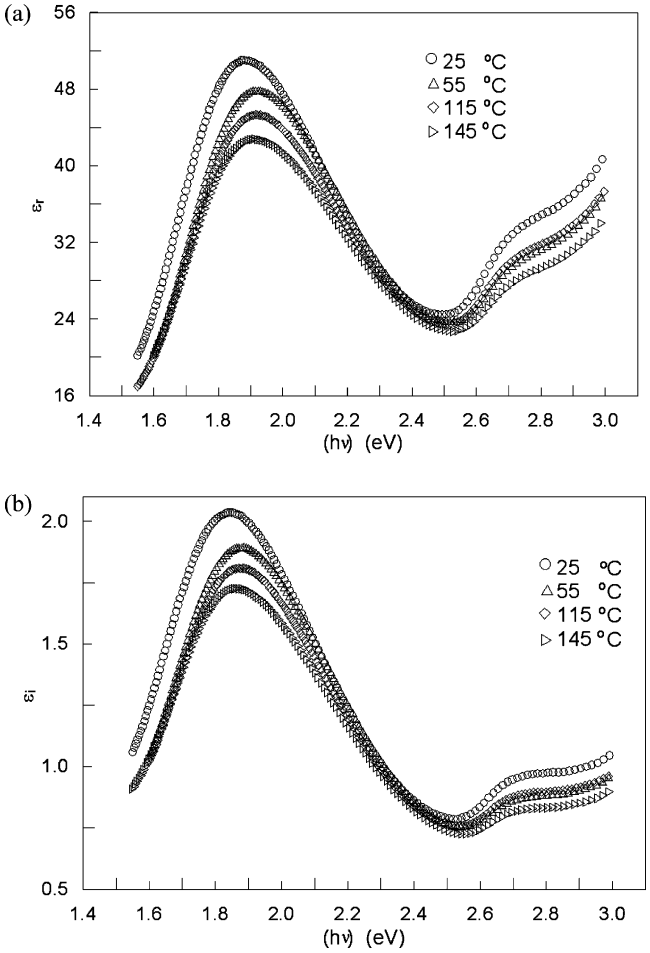


Figure 3. The complex dielectric spectra of the film at room temperature (25 °C) and various annealing temperatures: (a) real part and (b) imaginary part.

$(1 - R)^2$, whence it follows that[21]

$$T = \frac{(1-R)^2}{e^{\alpha d} - R^2 e^{-\alpha d}} \tag{9}$$

and the absorption coefficient for the film is expressed as,[15,21]

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{2T} + \left(\frac{(1-R)^4}{4T} + R^2\right)^{1/2}\right] \tag{10}$$

where d is the film thickness. The optical absorption spectrum is an important tool to obtain optical band gap of crystalline and amorphous materials. The band structure of the film obeys the rule of direct transition. The direct transition is expressed as,[22]

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \tag{11}$$

where A is a constant, $h\nu$ is the photon energy, and E_g is the optical band. The plots of $(\alpha h\nu)^2$ vs $h\nu$ are shown in Figure 4. The E_g values were calculated by taking the intercept on the x-axis and are given in Table 1. The optical band gap of the film decreases with increasing annealing temperatures.

In amorphous semiconductors, the absorption coefficient below the absorption edge indicates an exponential dependence on photon energy. This dependence is described as,[22]

$$\alpha(h\nu) = \alpha_o \exp(h\nu/E_u) \tag{12}$$

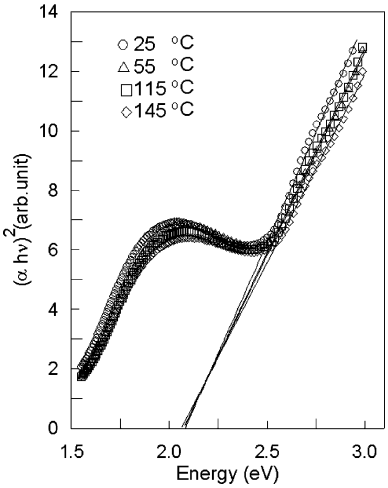


Figure 4. Plots $(\alpha h\nu)^2$ vs $h\nu$ of the thin film at room temperature (25 °C) and various annealing temperatures.

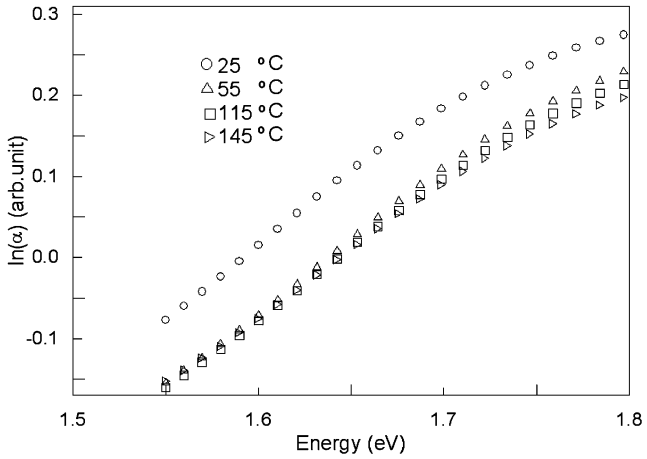


Figure 5. Curves of lnα vs $h\nu$ of the thin film at room temperature (25 °C) and various annealing temperatures.

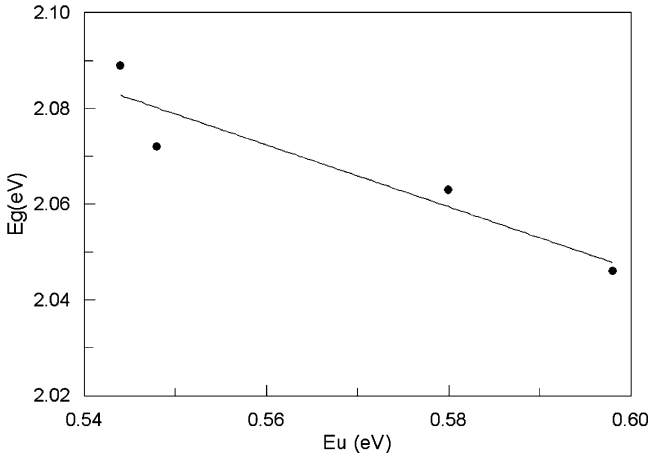


Figure 6. Variation of E_g with E_u for the thin film.

where α_o is a constant and E_u is the Urbach energy, i.e, width of localized states in the optical band gap. The curves of ln α vs $h\nu$ were plotted as shown in Figure 5. The E_u values were determined from the slope of Figure 5 and are given in Table 1. E_u values increase with increasing annealing temperatures. The increase in the values of E_u reveals the increase of width of the localized states in the optical band gap. The variation of E_g with E_u is shown in Figure 6. The decrease in the band gap can be explained on the basis of the density of states model.[23] During the thermal annealing the unsaturated defects are gradually annealed out, producing a large number of saturated bonds.[24] In turn, the density of localized state in the band gap structure expands. Consequently, the optical band gap decreases with increasing width of the localized states in the optical band gap, i.e., E_g values decrease with increase of E_u. There is a quantitative relationship[25] between the values of E_g and E_u under changes in either thermal or structural site disorder that can be expressed as follows,

$$E_g = E_f - GE_u \tag{13}$$

where G is a constant proportional to the second-order deformation potential and E_f is a constant that depends on local coordination. E_f and G values were calculated from the slope and intercept of Figure 6 and were found as $E_f = 2.43$ eV and $G = 0.64$, respectively. The linearity in Figure 6 confirms the same functional form.

Conclusions

The optical constants and optical band gap of the poly(*N*-benzylaniline) thin film were investigated by the optical characterization. The refractive index dispersion of the film obeys the Wemple−DiDomenico model. The refractive index decreases with increasing annealing temperatures up to 500 nm, and afterward it does not show a certain trend with annealing temperatures and the change in the refractive index is a result of the thermal changes in the film. The n_∞ values changed from 6.37 to 5.71 and the average oscillator parameter S_o value changed from 1.15×10^{13} to 1.11×10^{13} m^{-2}. These parameters did not show any a certain trend with temperature. The band structure of the film obeys the rule of direct transition. The direct optical band of the film decreased from 2.089 to 2.046 eV with increasing annealing temperatures while the width of localized states in the optical band gap increased from 0.544 to 0.598 eV. The increase in the values of E_u reveals the increase of width of the localized states in the optical band gap. Consequently, the annealing temperatures have an effect on optical constants and optical band gap of the poly(*N*-benzylaniline) and it is also evaluated that the optical parameters can be controlled by the applied annealing temperatures. The obtained results show that the film is suitable to changing the refractive index and the oscillator parameters by heat treatment. Moreover, the optical constants and optical band gap of the poly(*N*-benzylaniline) can be changed by various thermal annealing temperatures and various other effects. In future studies, the various studies on optical properties of the poly(*N*-benzylaniline) can be performed to control and develop the optical constants and optical band gap.

References and Notes

(1) Sayed, W. M.; Salem, T. A. *J. Appl. Polym. Sci.* **1999**, *77*, 1658.
(2) Li, J. C.; Xue, Z. Q.; Zeng, Y.; Liu, W. M.; Wu, Q. D.; Song, Y. L.; Jiang, L. *Thin Solid Film* **2000**, *374*, 59.
(3) George, V.; Young, D. J. *Polym. Commun.* **2002**, *43*, 4073.
(4) Mikheal, M. G.; Padias, A. B.; Hall, H. K. *J. Polym. Sci. Polym. Chem.* **1997**, *35*, 1673.
(5) Zaidi, N. A.; Giblin, S. R.; Terry, I.; Monkman, A. P. *Polymer* **2004**, *45*, 5683.
(6) Cataldo, F.; Maltese, P. *Eur. Polym. J.* **2002**, *38*, 1791.
(7) Goto, H.; Okuda, M.; Oohazama, T.; Akagi, K. *Synth. Met.* **1999**, *102*, 1293.
(8) Falcou, A.; Duchene, A.; Hourquebie, P.; Marsacq, D.; Longeau, A. B. *Synth. Met.* In press.
(9) Gök, A.; Sarı, B.; Talu, M. *Synth. Met.* **2004**, *142*, 41.
(10) Neumann, H.; Horig, W.; Reccius, E.; Sobotta, H.; Schumann, B.; Kuhn, G. *Thin Solid Films* **1979**, *61*, 13.

(11) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific & Technical: London, UK, 1989.

(12) Ghanashyam Krisha, M.; Pillier, J. S.; Bhattacharya, A. K. *Thin Solid Films* **1999**, *57*, 218.

(13) Yakuphanoglu, F.; Arslan, M.; Yıldız, S. Z. *Opt. Mater.* **2005**, *27*, 1153.

(14) Yakuphanoglu, F.; Sekerci, M.; Ozturk, O. F. *Opt. Commun.* **2004**, *239*, 275.

(15) Abeles, F., Ed. *Optical Properties of Solids*; North-Holland Publishing Company: London, UK, 1972.

(16) Subrahamanyam, N. A. *A textbook of Optics*, 9th ed.; Brj Laboratory: Delhi, India, 1977.

(17) Zidan, H. M.; Abu-Elnader, M. *Phys. B* (*Amsterdam, Neth.*) **2005**, *355* 308.

(18) El-Nahass, M. M.; Farag, A. M.; Abd El-Rahman, K. F.; Darwish, A. A. A. *Opt. Laser Technol.* **2005**, *37*, 513.

(19) Yakuphanoglu, F.; Cukurovali, A.; Yilmaz, I. *Phys. B* (*Amsterdam, Neth.*) **2004**, *353*, 210.

(20) Wolaton, A. K.; Moss, T. S. *Proc. R. Soc.* **1963**, *81*, 5091

(21) Fan, H. Y.; Becker, M. *Proceedings of the Reading Conference on Semiconducting Materials*; Academic Press: New York, 1951.

(22) Tauc, J. *Amorphous and Liquid Semiconductors*; Plenum Press: New York, 1974.

(23) Mott, N. F.; Davis, E. A. *Electronic Processes in Non-Crystalline Materials*; Clarendon Press: Oxford, UK, 1971

(24) Hasegawa, S.; Yazaki, S.; Shimizu, T. *Solid State Commun.* **1978**, *26*, 407.

(25) Cody, G. D.; Abeles, B.; Brooks, B.; Persans, P.; Wronski, C. R. *J. Non-Cryst. Solids* **1983**, *59*−*60*, 325.