

Optical Performance of Doped Azopolyester and its Application

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Abstract

Theoretical and experimental investigations on the optical behavior of thin films mainly deal with band gap, optical reflection, transmission, absorption and their relation to the optical constants. The optical transmittance spectra are recorded from 100 to 1000nm wavelength using a Hitachi UV-VIS-NIR spectrophotometer (Model-JASCO V-570) using a doped Azopolyester thin films were observed. Unpolarized radiation at room temperature with a resolution of 2nm was used in this study. Unpolarized radiation at room temperature with a resolution of 2nm was used in this study. The measurements were made on films of typical uniform thickness of 5 μ m deposited on glass substrate. The substrate absorption was corrected by introducing an uncoated cleaned glass substrate in the reference beam. The study of optical absorption / transmittance is a useful method for the investigation of optically induced transitions which provide information on the band structure and energy gap in both crystalline and non-crystalline materials. Finally optical applications of doped Azopolyester in fiber optic cable were used in telecommunication is discussed.

Keywords: Optical Parameters, Doped Azopolyester, Band Gap, Lattice Bonding, Band Structure.

1. Introduction

Optical properties of doped Azopolyester material with a π - π transition occur in band structure. This study deals with the optical properties of doped Azopolyester thin films prepared at room temperature [1–6].

Schematic representation of electronic absorption in doped Azopolyester materials is as shown in the Figure 1. It represents, when an incident light falls on the material, due to photon interactions, the material occur vibrational states, then the photon interactions are very high, the electron move from valence band to conduction band. The gap between conduction band and valence band is called band gap. The band gap of the doped Azopolyester varies from 1.28eV–0.7eV, depending on the doping percentage of PANI in Azopolyester.

$$\text{Refractive index (n)} = \frac{\text{velocity of light in free space}}{\text{velocity in the medium}}$$

A molecule in its ground state contains two electrons of equal and opposite spin in each filled molecular orbital. On absorbing a photon of light, one of the electrons in the highest occupied molecular orbital that is the occupied π -band (or valence band) is raised from low level to high level (conduction band).

The resulting electronic state is an excited state, if the spin of the elevated electron is anti-parallel to the remaining electron. If the spin of the elevated electron is parallel to the remaining electron, an excited triplet states results (Figure 1).

Figure 2 depicts the possible electronic states of an organic molecule.

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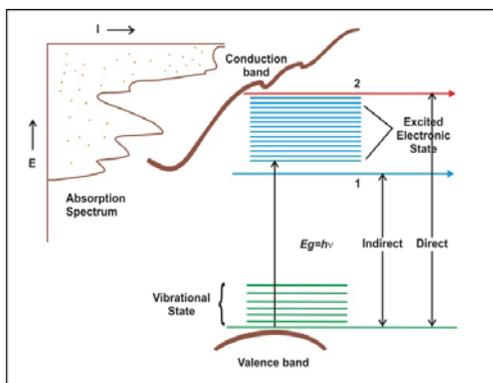


Figure 1. Schematic representation of electron absorption in organic (Doped Azopolyester) materials.

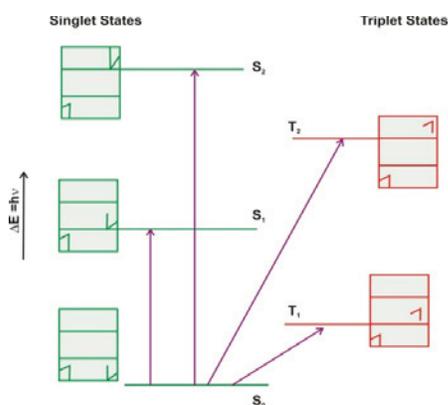


Figure 2. Possible electronic states of an organic molecule.

The optical properties of conjugated organic molecules are quite different from the non conjugated organic molecules. This is due to the fact that the π -electrons in conjugated polymer are relatively loosely bound and are in delocalized orbitals. This delocalization affects many optical properties of the conjugated polymers, especially the conjugation length, which is considered as a basic building block of the conjugated polymer system. Silbey et al. [7] has systematically carried out the studies on conjugation lengths and non-linear optical properties of organic polymers. Heeger et al. [8] developed theoretical concept of electronic excitations in conducting polymers. This has occurred a great deal of interest both theoretical and experimental aspects. Trivedi et al [9] worked on the effect of counter ion on polyani line which explains the presence of band structure and localized bound states. Rannou et al. [10] have investigated the charge carrier delocalization for pure PANI and doped Azopolyester using UV-VIS-NIR studies [11, 12].

From the detailed analysis of the available literature and data, it is necessary to carry out some more work on the optical properties of pure PANI, doped Azopolyester blend films with a typical thickness of $5\mu\text{m}$ deposited by solution casting technique. Our study the emphasis is given to the dependence of optical properties on the effect of dopant concentration of PANI in Azopolyester thin films. The absorption of light by polymer in the UV-range depends on the nature of chemical groups present in the structure. Polymers containing saturated hydrocarbon chains or saturated alkyl and polyester groups are transparent in the region $390\text{--}770\text{ nm}$. Colored polymers usually have attached chromospheres functional groups exhibiting absorption of the characteristic nature in the ultraviolet region [13, 14]. Light absorption by organic polymers in the UV-VIS range involves promotion of electrons in σ , π and n orbitals from the ground state to higher energy states. Molecular orbitals which are vacant in the ground state are known as anti-bonding orbitals. The 'n' electrons are mainly located in atomic orbitals of oxygen, sulphur, nitrogen and halogens. As the 'n' electrons do not form bonds, there are no anti-bonding orbitals associated with them. The electronic transitions involved in the ultraviolet and visible regions are shown in Figure 3.

The energy required for the transition from $\sigma\text{-}\sigma'$ is very high. Compounds contain non-bonding electrons such as oxygen, nitrogen, sulphur and halogen atoms show $n\text{-}\sigma'$ transitions. The above transition needs lower energy than $\sigma\text{-}\sigma'$ transition. Transitions to π' orbitals are usually associated with unsaturated centers in the molecule. These are of still lower energy requirement and occur at longer

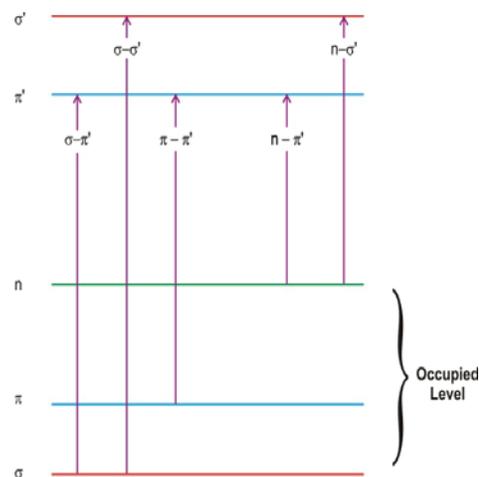


Figure 3. Schematic diagram of electronic energy level and transitions.

wavelengths. The π - π' transitions are usually between these owing to n - π' and n - σ' transitions.

The optical absorption and transmittance studies are useful for the identification of band gap, refractive index, extinction coefficient etc. The optical absorption spectra of semiconductors generally exhibit a sharp rise at a certain value of incident photon energy, which can be attributed to the excitation of electrons from the valence band to the conduction band. In the opto-electronic applications of thin films, the optical absorption studies play an important role giving an insight into the nature of transitions either direct or indirect. The absorption indices or extinction coefficient (k) can be calculated making use of Lambert's equation [15–20].

$$I = I_0 \exp \frac{(-4\pi k_d)}{\lambda} \quad (1.2)$$

where d is the distance in the medium through which the electromagnetic wave travels to change in intensity from the initial I_0 to I and λ is the wavelength of the light. Thus the value of the k can be determined from the formula

$$k = \frac{\ln \left(\frac{I_0}{I} \right) \lambda}{4\pi d} \quad (1.3)$$

In order to describe the fundamental absorption edge, the spectral dependence of absorption coefficient (α) (which is the relative rate of decrease in light intensity along its propagation path) is to be determined.

$$\alpha = \frac{4\pi k}{\lambda} \quad (1.4)$$

The electronic transitions between the valence and conduction band can be direct or indirect. In both the cases it can be permitted by transition probability (ρ) or forbidden. The transition probability is related by the following equation.

$$\alpha = A(h\nu - E_g)^P \quad (1.5)$$

where $h\nu$ and E_g are the photon energy and the optical band energy respectively. In this expression P , has discrete values like $1/2$, $3/2$, 2 or more depending on whether the transition is direct or indirect and allowed or forbidden.

In the direct and allowed cases the index $P = 1/2$ whereas for the direct, forbidden cases is $3/2$. But for the indirect and allowed cases $P = 2$ and for the forbidden it will be 3 or more. Thus, a linear graph when α^2 is drawn against $h\nu$, will suggest a direct but allowed transition whereas a linear one with $\alpha^{1/2}$ against $h\nu$ indicates an indirect transition. The

magnitude of P can also be estimated from the slope of the graph of $\log \alpha$ vs $\log h\nu$ and hence can suggest the type of transition.

The refractive index of the films can be calculated from the transmittance (T) value, defined as the ratio between the total transmitted intensity to the incident intensity when a light beam passes through a film using the relation given below

$$T = \frac{n_2}{n_0} \frac{(1 + \delta_1)^2 (1 + \delta_2)^2}{1 + (\delta_1^2 + \delta_2^2) + 2\delta_1\delta_2 \cos 2\Gamma}$$

where

$$\delta_1 = \left(\frac{n_o^2 - n_1^2}{n_o^2 + n_1^2} \right) \delta_2 = \frac{n_1^2 - n_2^2}{(n_1 + n_2)^2} \quad (1.6)$$

and $\Gamma = \frac{2\pi n_1 d}{\lambda}$

The refractive index of a material at optical frequency is mainly determined by the polarizability of the valence electrons. The analysis of wavelength dependence of the optical contents n and k is of considerable interest due to its opto-electronic applications.

2. Aim of the Study

2.1 Optical Characterization of Doped Azopolyester

The optical transmittance spectra are recorded from 100 to 1000nm wavelength using a Hitachi UV-VIS-NIR spectrophotometer (Model-JASCO V-570) using a doped Azopolyester thin films were observed. Unpolarized radiation at room temperature with a resolution of 2nm was used in this study. The measurements were made on films of typical uniform thickness of 5 μ m deposited on glass substrate. The substrate absorption is corrected by introducing an uncoated cleaned glass substrate in the reference beam. The study of optical absorption / transmittance is a useful method for the investigation of optically induced transitions which provide information on the band structure and energy gap in both crystalline and non-crystalline materials.

3. Results and Discussion

The study of optical absorption / transmittance is a useful method for the investigation of optically induced transitions which provide information on the band structure and

energy gap in doped Azopolyester materials. The optical transmittance (T) measured in the spectral region ranging from 100-1000nm for three different PANI weight ratios of 10%, 30% and 50% doped Azopolyester blend films coated on glass substrate with same thickness of ($5.0 \times 10^{-6}m$) and the transmittance spectra is shown in Figure 4.

Figure 4 shows the optical transmittance data of 10%, 30% and 50% PANI doped Azopolyester thin films. The analysis of the absorption coefficient (α) has been carried out to evaluate the optical band gap and also to study the shape of the absorption edge. The graph reveals that when PANI doping percentage increases in Azopolyester, the transmittance increases and the maximum transmittance occurs in the wavelength of 390 nm.

The frequency dependence on the absorption coefficient described by an empirical relation equation (1.4) is used to evaluate the optical band gap.

The graph (5) shows that three types of absorption edges are formed due to doping of Azopolyester. It reveals that when doping percentage of PANI increases in Azopolyester with a weight percentage ratio of 10%, 30% and 50%, there is a reduction in band gap energy of the material due to bathochromic shift between valence and conduction bands.

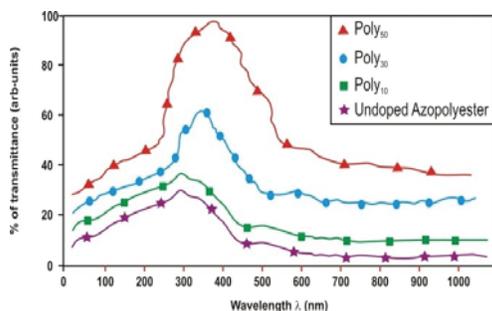


Figure 4. Transmittance spectra of doped azopolyester blend films.

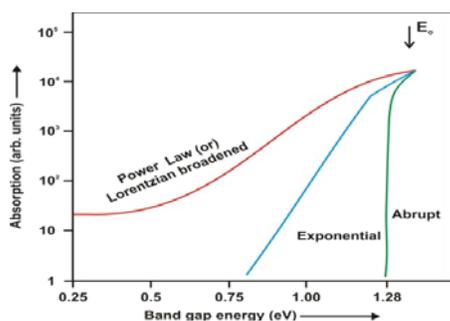


Figure 5. Types of absorption edges in solids a lorentzian broadened (power law) edge.

Normally, the fundamental absorption edges are Lorentzian in most of the solids due to the fact that the atomic absorption lines are broadened by collisions and by radioactive damping [21–25]. In the lowest part of the absorption edge, the absorption coefficient varies exponentially with photon energy which obeys an exponential law [26–30].

$$\alpha = \alpha_o \exp \left[\frac{h\nu}{E_u} \right] \tag{1.7}$$

called Urbach’s rule. Here, E_u is a characteristic energy known as band tail or Urbach energy.

The frequency dependence of the absorption coefficient reasonably fit with the empirical law, $\alpha = A (h\nu - E_g)^P$ when the value of $P = \frac{1}{2}$ for pure PANI and Azopolyester doped with PANI films [31, 32]. The plots of $(\alpha h\nu)^2$ versus $h\nu$ are linear functions, indicating that the existences of direct and allowed transitions in pure PANI and doped Azopolyester which are shown in Figure 6. The energy gap is related to the extent of conjugation between the adjacent rings in the polymer chain [33]. The reduction of optical band gap in the Azopolyester doped with PANI can be attributed to the extent of conjugation in a double bond system. As a result, the energy required to produce a transition from occupied to unoccupied level increases [34–38]. The refractive index also decreases with increase in wavelength and becomes constant at higher wavelengths [39–40]. It is observed from Figure 6 that for undoped Azopolyester, the band gap start decreasing from 1.28 eV to 0.7 eV, when doping percentage of PANI is increased from 10% to 50%. It also reveal that the blend film obeys the allowed direct and indirect transitions respectively.

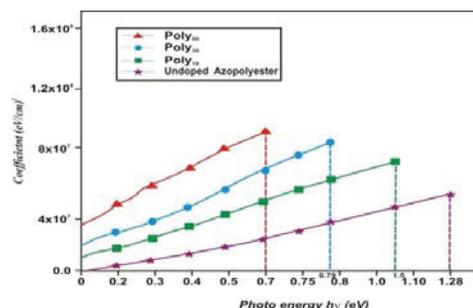


Figure 6. Plots of $(\alpha H\nu)^2$ versus photon energy $h\nu$ shows that direct transition in undoped, doped azopolyester blend films.

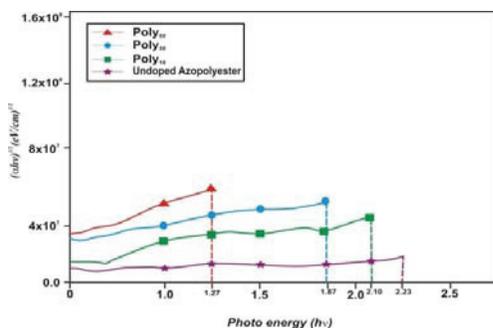


Figure 7. Plots of $(\alpha hv)^{1/2}$ versus photon energy ($h\nu$) shows indirect transition in undoped, doped azopolyester blend films.

Table 1.2 Optical band gap energy (eV) of undoped, doped azopolyester blends

Sample Name	Band gap energy (eV)	
	Direct allowed transition	Indirect allowed transition
Undoped Azopolyester	1.28	2.23
10% doped Azopolyester Poly ₁₀	1.15	2.10
30% doped Azopolyester Poly ₃₀	0.79	1.87
50% doped Azopolyester Poly ₅₀	0.7	1.27

The direct allowed transition, indirect allowed transition, the optical band gaps of the blends are shown in Figures 6 and 7 and the same is given in Table 1.2.

4. Conclusion

It is observed from Figures 6, 7 and Table 1 that with a shift from 1.28 to 0.70 eV and 2.23 to 1.27 eV respectively due to the bathochromic shift occurred in bonds. The optical band gap energy of the blends increases from direct allowed transition to indirect allowed transition. The study of optical absorption / transmittance is a useful method for the investigation of optically induced transitions which provide information on the band structure and energy gap in both crystalline and non-crystalline materials.

It is also observed that the optical band gap energy of the blends decreases in both direct, indirect allowed transition with an increase of PANI weight percentage ratio of 10%, 30% and 50% PANI doped with Azopolyester, because

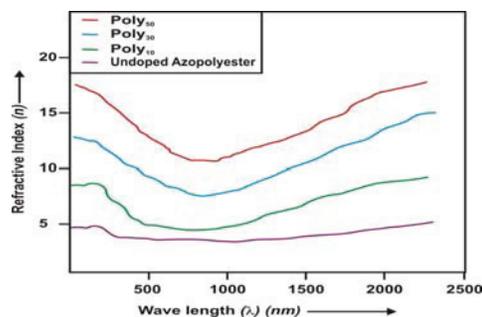


Figure 8. Variation of refractive index of undoped, doped azopolyester blends with wavelength.

of high optical transmittance it is used for fiber optic cable in telecommunication network.

The variation of the refractive index of the undoped, doped Azopolyester blends with wavelength is shown in Figure 8.

The nature of curve shows that electronic transitions take place in the films and a similar trend was reported for the doped Azopolyester films.

The refractive index shows dispersion in the lower wavelength region and it decreases with increase in wavelength and becomes constant at longer wavelength region due to random fluctuations of the internal field. As a result, the energy required to produce a transition from occupied to unoccupied level increases.

5. References

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