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Polystyrene-DCM Laser Dye Thin Films Optical Properties at Different Temperatures

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Abstract: Different samples of polymeric thin films of Poly Styrene (PS) mixed with DCM laser dye at fixed concentration were synthesized by casting method under varied annealing temperatures range of (25, 50, 75°C). The effect of varying annealing temperature on the some physical properties of these polymeric films has been studied. The optical electronic energy gaps of the films were evaluated from absorption spectra and studying the temperature varying on these energy gaps.

Key words: Thin films, casting method, DCM, energy gaps, styrene, polymeric

INTRODUCTION

The assembly of polymers and dyes is attractive sources of researches in modern physics. Different applications of dye blended with polymers such as waste water treatment, painting and textiles, medicine, optical sensors and electrochemical applications (Fleischmann *et al*., 2015). Dye-polymers are new materials which present optical properties. Dye-polymers find application in fields of new photonic apart from its employ as an alternative to solid state lasers (Kurian *et al*., 2002).

Organic compositions have been the topic of intense studies because of their broad range applications in different life science fields. Such as tumble solid-state dye laser, energy transfer experimentations, biomedical applications, sensing and probe instruments (Sharma *et al*., 2008). The laser dyes is an un-saturated hydracarbonic organic compound comprehend a reciprocal series of carbon atoms with single and dual bonds (Fukuda and Mito, 2000).

The main reasons to use the solid matrix as a host for dyes are due to its rigidity and compactness, nontoxicity and solvent evaporation (Nedumpara *et al*., 2004). Various materials like glasses, polymers and sol gel materials were spaciously studied and employed as host materials due to their properties and trade viability (Popov, 1998).

Organic polymers used as host to organic dyes because these polymers have homogeneity. Combine dyes in polymeric hosts lessening the degeneration the dye, the stability of the dye rises and the fluorescence intensity increases likewise. This is due to the dimmers decomposition which cuts out the absorption operation that accrues in the same region of fluorescence producing from re-absorption (Amat-Guerri *et al*., 1993).

The polymer Poly Styrene (PS) is transparent elastic material with high refractive index having very good optical proprieties. It is used with organic dyes to enhance the dye laser forming dimers aggregations (Hermes *et al*., 1993). The laser dye used in this research is fluorescence dye, DCM, [2-[2-[4-(dimethylamino) phenyl] ethenyl]- 6-methyl- 4H-pyran-4 -ylidene]-propanedinitrile: $C_{19}H_{17}N_3O$ (Brackmann, 2000). In current study PS $(C_8H_8)_n$ was used as a host to the DCM to synthesis thin film and exploring the optical properties of these films under different annealing temperatures.

MATERIALS AND METHODS

Experimental part: Dissolving 15 mg of DCM in 10 mL of THF to obtain laser dye solution at 5×10^{-3} mol/L concentration and on the other hand the polystyrene polymer thin film was synthesis by dissolving 1.5 g of PS in 30 mL of THF then 5 mL of the final solution of PS dissolved in THF was mixing with 1 mL of dye solution and stirred 10 min to obtain homogenous solution. This mixture casting on glass substrate at 25°C and atmosphere pressure this sample was heated at 50 and 75°C.

Thickness of the thin films was measured using the optical interferometer method employing He-Ne laser 0.632 μm. The absorption spectrum was measured using UV-VIS double beam spectrometer in the wavelength optical a range 190-900 nm, the measurements were achieved at room temperature. Absorption coefficient a calculated using Eq. 1 (Han *et al*., 2008):

$$\alpha = \frac{2.303A}{t} \quad (1)$$

The energy gaps of these films were calculated with the help of the absorption spectra. To determinate the energy gap, $(\alpha h\upsilon)^{1/2}$ are plotted versus (photon energy) using Eq. 2 (Thutupalli *et al*., 1976):

$$\alpha h\upsilon = B\left(h\upsilon - E_g \pm E_{ph}\right)^r \quad (2)$$

Where:

E_g = Energy gap for indirect transitions
E_{ph} = Phonon energy
(r = 2) = The indirect transition
B = Constant
υ = Frequency

The extinction coefficient k is proportional to the absorption coefficient as in Eq. 3 (Baker and Dyer, 1993):

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

The refractive index (n) can be found from the Reflectance (R) via. Eq. 4 (Ashour *et al*., 2006):

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

The real and imaginary complex dielectric constant can be expressed by Eq. 5 and 6, respectively (Al-Ramadin, 2000):

$$\varepsilon_r = n^2 - K^2 \quad (5)$$

$$\varepsilon_i = 2nK \quad (6)$$

The optical conductivity of thin films can be computed using the Eq. 7:

$$\sigma = \frac{\alpha nc}{4\pi} \quad (7)$$

RESULTS AND DISCUSSION

The absorption spectra of the thin films were measured at (25, 50 and 75°C). Figure 1 shows the absorption spectrum of PS film with and without 5×10^{-3} mol/L DCM dye solution at (25, 50 and 75°C). It can be seen from Fig. 1 that the optical spectrum of dye-polymer influenced noticeably by the kind of the host. The shifting toward the red in the absorption spectrum is spotted for the thin film of DCM dye solution blend with PS. This red shift is referring to the fluctuation in the reflective index of the thin film of PS with and without DCM. While the increasing in the annealing temperature causing decreasing in the absorption intensity for all samples this may be attributed that the annealing leads to reducing the crystalline defects and the number of local energy levels located within the optical energy gap. The opposite occurs in reflection spectra as shown in Fig. 2. Figure 3 shows the variation of molar absorption coefficient of the PS-DCM thin films against the photon energy at (25, 50 and 75°C). It is clear from Fig. 3 that the molar absorption coefficient increases with increasing

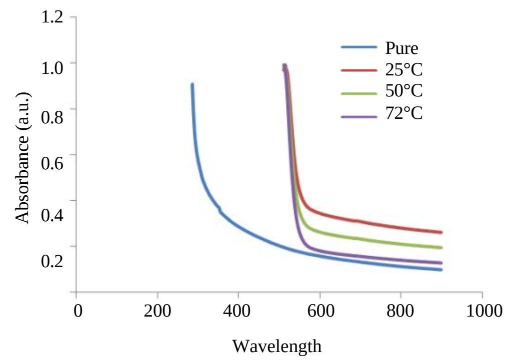

Fig. 1: Absorption spectra of thin film of PS with and without DCM at (25, 50 and 75°C)

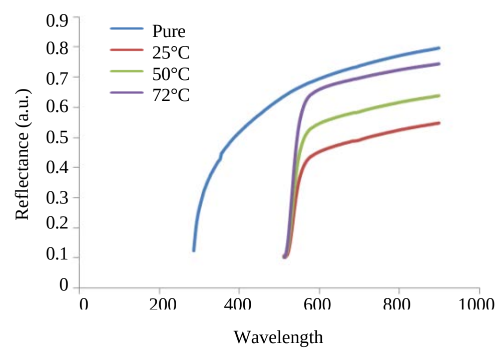

Fig. 2: Reflection spectra of thin film of PS with and without DCM at (25, 50 and 75°C)

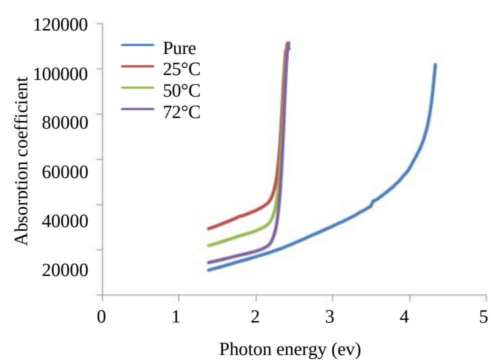

Fig. 3: The molar absorption coefficient of the PS with and without DCM dye at (25, 50 and 75°C)

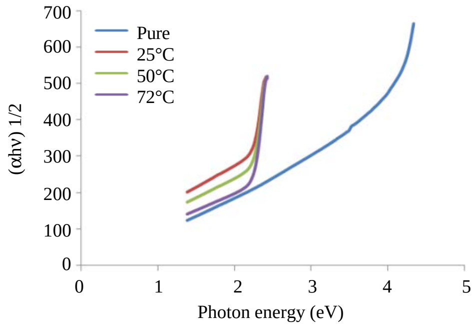

Fig. 4: The relation between $(\alpha h\nu)^{1/2}$ and the photon energy of the PS with and without DCM dye at (25, 50 and 75)

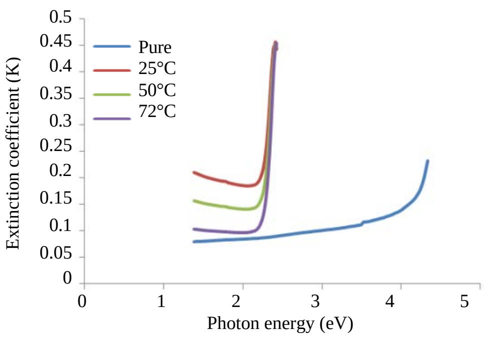

Fig. 5: Extinction coefficient and photon energy of the PS with and without DCM dye at (25, 50 and 75°C)

photon energy for all films. While the increasing in the annealing temperature driving lessening in the molar absorption coefficient. One can observe that these films have indirect electronic transitions which due to the values of molar absorption coefficient that more than 10^4 cm^{-1} (Sanchez-Gonzalez *et al*., 2006) for these films. The relation between $(\alpha h\nu)^{1/2}$ and the photon energy of PS-DCM thin film at 25, 50 and 75°C is shown in Fig. 4 from this figure one can get the indirect electronic transitions of this film.

From Fig. 4, the energy gap for indirect electronic transitions in case of pure PS thin film was 3.25 eV while the energy gaps for PS doped with DCM dye thin film were (1.8, 1.9 and 2) eV at 25, 50 and 75°C, respectively. Figure 5 shows the relation between extinction coefficient (K) and photon energy of the prepared samples at 25, 50 and 75°C. In low intensity of incident photon, increasing in annealing temperature will reducing the probability of electronic transitions between valance and conductance bands. The refractive index is varying with photon energy of PS-DCM films at (25, 50 and 75°C) was shown in Fig. 6.

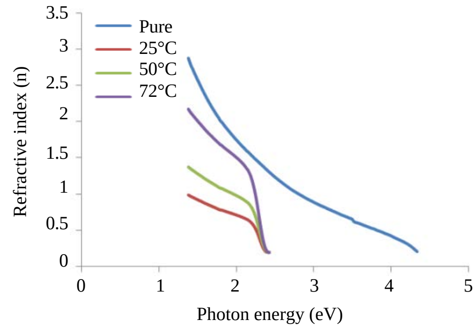

Fig. 6: Refractive index and photon energy of PS with and without DCM dye at (25, 50 and 75°C)

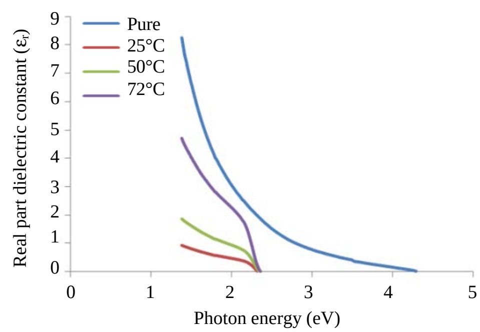

Fig. 7: Real parts of dielectric constants and photon energy of PS with and without DCM dye at (25, 50 and 75°C)

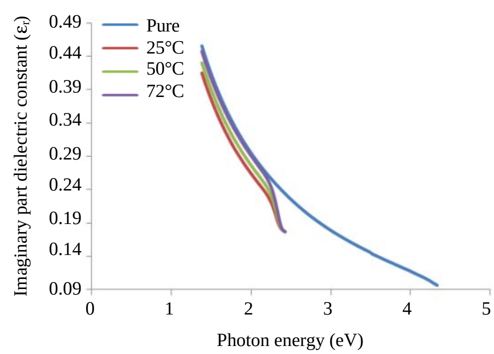

Fig. 8: Imaginary parts of dielectric constants and photon energy of PS with and without DCM dye at (25, 50 and 75°C)

The behavior of the refractive index spectrum is similar to that of reflectance one, since, the refractive index depending directly on the reflectance. Rising in the annealing temperature of the samples leads to enhance in the filling density of these films that because of the increasing of the energy levels within the forbidden

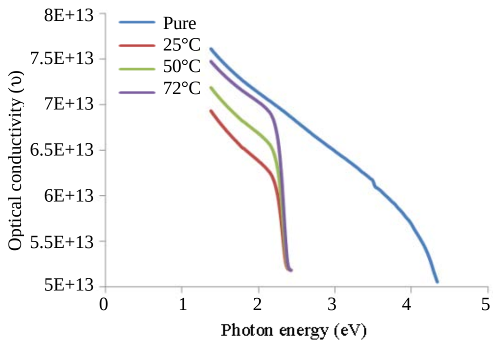

Fig. 9: The optical conductivity and photon energy of PS with and without DCM dye at (25, 50 and 75°C)

energy gap which act as scattering centers to the incident photons. Figure 7 and 8 shows the relation between both real and imaginary parts of dielectric constants with the energy of incident photons. From Fig. 7 and 8, it is clear that the behavior of both real and imaginary parts of dielectric constants spectra are similar to behavior of the refractive index due to the reliance of the dielectric constant on the refractive index more that on the extinction coefficient according to Eq. 5 and 6. It is evident from Fig. 9 that the optical conductivity decreases exponentially with photon energy and with decreasing the annealing temperature for PS-DCM at (25, 50 and 75°C).

CONCLUSION

The optical characterizations of PS and PS doped with DCM dye at (25, 50 and 75°C) prepared using casting method were studied. The optical absorption measurements exhibit a red shift in the spectrum is observed for the thin film of DCM doped with PS relative to thin film of pure PS. Indirect band gap of PS is found to be was 3.25 eV while the energy gaps for PS doped with DCM dye thin film were (1.8, 1.9 and 2 eV) at (25, 50 and 75°C), respectively.

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