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Azo Dye Doped Polymer Films for Nonlinear Optical Applications

L. Guru Prasad*
Department of Science & Humanities, M. Kumarasamy College of Engineering, Karur, India

Abstract Azo dye doped polymer films were prepared on glass substrates using spin-coating technique. FTIR, UV-Vis spectra and PL measurements were recorded to characterize the structure of the metanil yellow doped PVA films. Surface morphology and thickness of the films were studied using AFM and FESEM. The magnitude of both real and imaginary parts of third-order nonlinear susceptibility χ^3 of metanil yellow were determined by the Z-scan technique. The nonlinear refractive index n_2 and the nonlinear absorption coefficient β of the azo dye doped polymer films were calculated respectively. The real part of the third-order susceptibility χ^3 is much larger than its imaginary part indicating that the third-order optical response of the metanil yellow doped PVA films is dominated by the optical nonlinear refractive behavior.

Keywords: Azo dye; PVA; Nonlinear optical materials.

INTRODUCTION

Nonlinear optical (NLO) films are currently studied for photonic applications because of their nonlinearity and fast response time[1, 2]. A wide variety of organic polymers with delocalized conjugated electron systems have been investigated for third-order nonlinear optics[3, 4]. Recent studies of these materials have shown their large coefficients of third-order optical nonlinearity. Using this organic polymer one can prepare the doped films with customizable properties. New generation optically controlled devices can be generated using these doped polymer films. In particular, azo based organic films have shown higher optical nonlinearity, good photo-thermal stability, dissolvability and easy preparation virtue, so they can be used as a kind of storage medium. The character of azo dye in its molecular structure is double-bond (N=N) between the two phenyls[5, 6]. These systems possess advantage for high optical nonlinearity due to photoinduced *trans-cis* isomerization, molecular reorientation and nonlinear absorption. The interest in the study of metanil yellow comes from the fact that, as it has a charge transfer group and is a very interesting model compound for NLO studies. Metanil yellow compound consists of both the electronegative (sulfonyl and azo) groups and electropositive (amine and alkali metal) groups. Hence it is planned to coat the potentially active azo dye (MY) doped polymeric films for nonlinear optical applications.

EXPERIMENTAL

Glass substrate was dipped in chromic acid for one day and washed with distilled water. It was etched with diluted hydrochloric acid and then again washed with distilled water. Finally the substrate was dried in air to remove the surface contaminants and to make the surface more conductive for uniform film deposition.

The spin coater consists of a variable rotating vacuum chuck powered by a motor. The slide was held firmly in position by atmospheric pressure. Metanil yellow (MY) dye (Fig. 1) and poly(vinyl alcohol) (PVA) with the

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* Corresponding author: L. Guru Prasad, E-mail: guruphysics@gmail.com

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ratio 1:20 were dissolved in 30 mL of distilled water. This solution was stirred well to obtain a clear solution. The resultant solution was finally filtered and heated well for 1 h maintained at 60 °C. The prepared solution was ultrasonified for 30 min. In a clean environment the prepared solution was allowed to fall with the help of a clean syringe onto the center of a stationary glass substrate[7]. The speed of rotation was set to 3000 r/min and the time of rotation for 30 s. The dropped solution spreads out across the glass substrate under the influence of centrifugal force. As it moves, the solvent evaporates from the solution leaving a smooth continuous film[7]. Hence the MY doped PVA film has been prepared using spin coat technique.

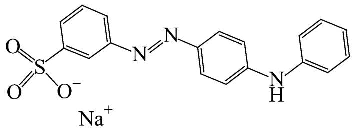

Fig. 1 Chemical structure of metanil yellow

RESULTS AND DISCUSSION

Vibrational Analysis

The vibrational analysis of the coated film was done using FTIR. FTIR spectra were recorded in a range of 400–4000 cm^{-1} using a Spectrum RXI instrument. The recorded spectrum is shown in Fig. 2 and the vibrational assignments for the observed bands are tabulated in Table 1.

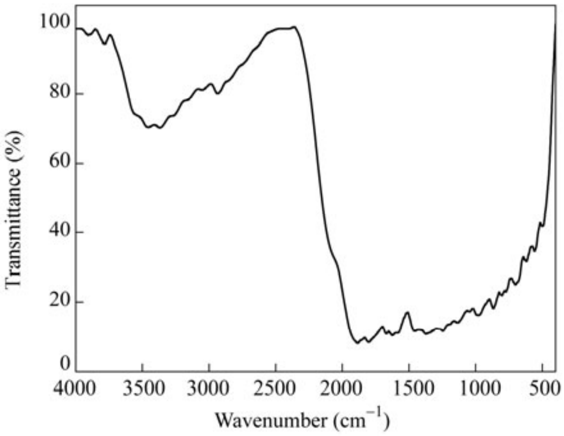

Fig. 2 FTIR spectrum of an MY doped PVA film

Table 1. Observed IR bands of MY doped PVA film and their assignments

Observed wavenumber (cm^{-1})	Assignments
3456vw	OH stretching, CH stretching
2933vw	CH stretching
1465vs	CN asymmetric symmetric, C—C stretching
1380vs	N=N stretching, C—C stretching
973vs	CH out plane bending, CO stretching
863vs	C—N=N in-plane bending, SO_3 asymmetric bending
702vs	SO_3 symmetric bending, C—C out-of-plane bending, CH out-plane bending
618s	C—N=N—C— in-plane bending, CS bending
553s	SO_3 bending

Due to the aromatic stretching, multiple weak bands exhibit in the region of 3100–3000 cm^{-1}. The bands observed at 2933 cm^{-1} is assigned to CH stretching. The strongest absorption peaks of aromatic compounds normally occur in the region 900–650 cm^{-1} and are due to the CH vibrations. The CH out of plane vibration is recognized in the recorded IR spectrum at 973, 863 and 702 cm^{-1}. In MY, the aromatic rings are asymmetrically distributed benzene derivatives. The band observed at 1465 cm^{-1} is consigned to C—C stretching modes. Many ring modes are affected by the substitution in the aromatic ring. Secondary amine shows a single sharp weak band near the region of 3300–3000 cm^{-1}. In the present investigation, the vibration of OH band in the PVA gets overlap with the NH vibration and gives a weak broad band in the region of 3600–3100 cm^{-1}. IR spectra of PVA contain a strong band at 3400 cm^{-1} due to the OH stretching. In the present investigation due to interaction of MY with PVA, this band gets weaker and traced at 3456 cm^{-1}. In addition to that normally PVA shows a strong band due to CO stretching vibrations at 1100 cm^{-1}. Here this band gets shifted to low wave number side and traced at 973 cm^{-1}. These bands confirm that there may be a weak interaction between the dye and the polymer[8].

Due to the symmetry nature of the N=N group, it is hard to observe its vibration in the infrared spectrum. However the two equivalent CN groups in the azo chromophoric group build change in bond length in the N=N bond which results in a change in dipole moment. Due to this, the symmetric N=N stretching can be observed at 1430–1396 cm^{-1} in the infrared spectrum[8]. In the present investigation, due to the existence of amino group this N=N band is shifted to the lower wavenumber side and observed at 1380 cm^{-1}[10–12]. Asymmetric stretching vibration of sulfonyl group is normally observed in the region of 1300–1400 cm^{-1}. Symmetric stretching of SO_3 band gives a very strong peak at 702 cm^{-1} in the recorded FTIR spectrum. Due to the overlapping of N=N group a very strong band is observed at 1385 cm^{-1} and is assigned to SO_3 asymmetric vibrations. The band observed at 553 cm^{-1} is assigned to SO_3 bending[13].

Optical Studies

UV-Vis spectrum studies

The UV-Vis spectrum of the prepared film was recorded on a Perkin Elmer Lamda 25 spectrophotometer in the region of 190 nm to 1100 nm. Base line was measured by keeping the two bare glass slides in the double beam spectrometer. Then one slide was removed and the sample slide was kept. The position of the slide was adjusted such that the beam must hit. In the UV-Vis spectrum (Fig. 3), an absorption peak observed at 292 nm is attributed to n to π^* transition which arises from the aromatic ring. Another absorption band observed at 430 nm is due to azo group[14]. This absorption band confirms the colored nature of the prepared film.

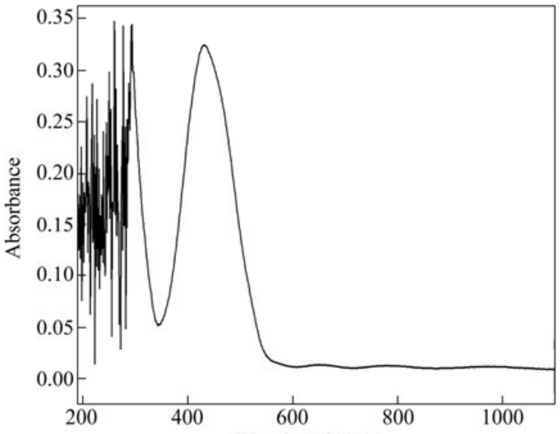

Fig. 3 UV-Vis spectrum of MY doped PVA film

Photoluminescence studies

In order to study the optical behavior of the title compound, it was subjected to photoluminescence (PL) measurements. PL spectroscopy is a contact, nondestructive method of probing the electronic structure of materials[15]. When compared to the optical absorption studies, PL spectroscopy is more preferred to detect the lower concentration defects[16]. PL measurements were made at room temperature using a Horiba Jobinyvon Fluorolog-3 Spectrofluorometer. It is observed from Fig. 4 that the coated film has a broad emission peak at 548 nm. The band gap energy is calculated as 2.2640 eV. This emission peak at 548 nm corresponds to the trans-isomer of the azo-dye[17].

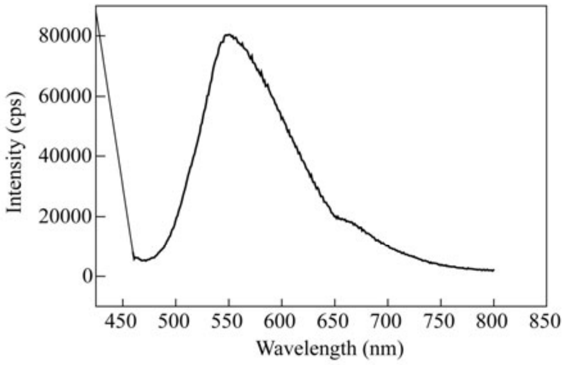

Fig. 4 PL spectrum of MY doped PVA film

Polarizability and hyperpolarizability:

Computational Details:

The nonlinear properties of an isolated molecule in an electric field $E_i(\omega)$ can be represented by the Taylor expansion of the total dipole moment μ_i induced by the field.

Taken at zero field,

$$\text{Dipole moment} = \mu_i = -\left[\frac{\partial^2 E}{\partial F_i \partial F_j}\right]_0$$

Components of polarizability tensor:

$$\alpha_{ij} = -\left[\frac{\partial E}{\partial F_i}\right]_0$$

Components of hyperpolarizibility tensor:

$$\beta_{ijk} = -\left[\frac{\partial^3 E}{\partial F_i \partial F_j \partial F_k}\right]_0$$

For calculating the first, second and third polarizability, the geometry of the MY is treated as a isolated molecule (gas). The optimization has been carried out in the PM7 level using MOPAC software[18].

The calculated values of dynamics polarizibility with function of energies ($\acute{\omega}$) are tabulated in Tables 2a, 2b and 2c. This high value of γ and the non-zero value of μ are responsible for the third order nonlinear optical properties as third harmonic generation (THG); therefore these values suggested the possibility of technological applications.

Table 2a. First order polarizability

	ώ = 0 ev	ώ = 0.25 ev	ώ = 0.50 ev
α_{xx} (ESU × 10^{-30})	3.556822776	3.566634106	3.596900006
α_{yy} (ESU × 10^{-30})	3.441108583	3.450856558	3.469749416
α_{zz} (ESU × 10^{-30})	2.478770732	2.48043120	2.485463661
α_{total} (ESU × 10^{-30})	3.158900697	3.165973955	3.184037694

Table 2b. Second order polarizability

	ώ = 0 ev	ώ = 0.25 ev	ώ = 0.50 ev
β_{xxx} (ESU × 10^{-30})	6.36540678	6.70850483	7.915802858
β_{xyy} (ESU × 10^{-30})	9.026692605	9.380721875	1.062160933
β_{xzz} (ESU × 10^{-30})	−3.250339303	3.351264988	−3.696434742
β_{yyy} (ESU × 10^{-30})	−8.810785267	−9.039228057	−9.796489915
β_{yxx} (ESU × 10^{-30})	9.176761307	9.399568767	1.012498254
β_{yzz} (ESU × 10^{-30})	1.198362055	1.243054017	1.393946476
β_{zzz} (ESU × 10^{-30})	−9.503764773	−9.526390235	−9.603253224
β_{zxx} (ESU × 10^{-30})	2.258944207	2.314227779	2.498471478
β_{zyy} (ESU × 10^{-30})	2.215840234	2.3021998	2.596291421
β_{total} (ESU × 10^{-30})	12.73934626	13.3510258	15.50209606

Table 2c. Third order polarizability

	ώ = 0 ev	ώ = 0.25 ev	ώ = 0.50 ev
γ_{xxxx} (ESU × 10^{-36})	153192.00041	171338.05648	251857.31927
γ_{yyyy} (ESU × 10^{-36})	196928.47592	210924.45797	265836.97363
γ_{zzzz} (ESU × 10^{-36})	3538.09089	3739.25493	4477.38151
γ_{xxyy} (ESU × 10^{-36})	137463.93236	151120.67500	210529.47562
γ_{xxzz} (ESU × 10^{-36})	5696.99123	5334.55443	2649.15015
γ_{yyzz} (ESU × 10^{-36})	2385.72640	2323.97770	1817.13432
γ_{total} (ESU × 10^{-36})	298167.0132	394758.768	534425.8551

Z-scan studies

A diode pumped Nd: YAG laser of wavelength 532 nm (Coherent Ccompass TM 215-M-50) was used as the excitation source for the Z-scan technique. The laser of Gaussian beam profile was focused by a convex lens of focal length $f = 3.5$ cm to produce a beam waist ω_0 of 20.56 μm. The peak intensity of the incident beam was $I_0 = 2.97$ kw·cm^{-2} and the difference length Z_R was found to be 2.5 mm. A 1 mm wide film is translated across the focal region along the axial direction that is the direction of the propagation of laser beam. The transmission of the beam through an aperture placed in the far field is measured using photo detector fed to the digital power meter. For a closed aperture Z-scan, the aperture is placed in front of the detector. In closed aperture Z-scan the measurement is sensitive to both nonlinear refraction and nonlinear absorption.

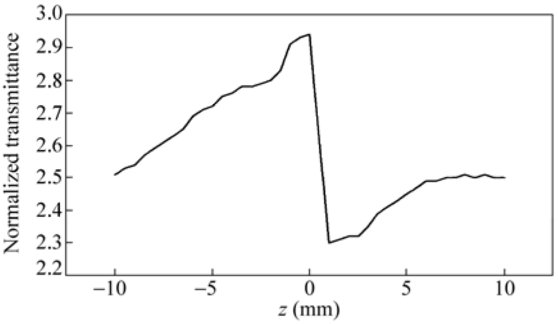

Fig. 5 Closed aperture Z-scan curve of MY doped PVA film on glass substrate

The third-order nonlinear refractive index n_2, the nonlinear absorption coefficient β and the real and imaginary part of the third-order nonlinear optical susceptibility [χ^3], of the azo dye doped polymer film for the intensity I_0 = 2.97 kw·cm^{-2} were evaluated by the measurements of Z-scan. Figure 5 shows the closed Z-scan curve for the dye doped polymer film.

The nonlinear absorption coefficient β is obtained from the following formula.

$$\beta = 2\sqrt{2}\, \Delta T / I_0\, L_{\mathrm{eff}}$$

where, ΔT is the normalized transmittance of the sample at position Z.

The aperture linear transmittance is given by

$$S = 1-\exp(-2r_a^2/\omega_a^2)$$

where r_a = the aperture radius, ω_a = the radius of laser spot before the aperture.

The on-axis phase shift $\Delta\phi_0$ at the focus is related to the third order nonlinear refractive index (n_2) by

$$\Delta\phi_0 = k\, n_2 L_{\mathrm{eff}} I_0$$

where, I_0 = The intensity of the laser beam at the focus Z = 0, k = The wave number ($k = 2\pi/\lambda$), λ = The wavelength of the light used, $L_{\mathrm{eff}} = (1-e^{-\alpha L})/\alpha$ = The effective thickness of the sample, L = The thickness of the sample and α = The linear absorption coefficient.

The peak followed by a valley-normalized transmittance curve obtained from the closed aperture Z-scan data, indicates that the sign of the refraction nonlinearity is negative, *i.e.* self defocusing. The self defocusing effect is due to the local variation of the refractive index with temperature. The measurable quantity $\Delta T_{\mathrm{P-V}}$ can be defined as the difference between the normalized peak and valley transmittance $T_{\mathrm{P\text{-}V}}$, the variation of this quantity[19] as a function of $|\Delta\phi_0|$ is given by,

$$\Delta T_{\mathrm{p-v}} = 0.406(1-S)^{0.25}|\Delta\phi_0|$$

Experimentally determined nonlinear refractive index n_2 and nonlinear absorption coefficient β can be used in finding the real and imaginary parts of the third-order nonlinear optical susceptibility [χ^3] according to the following relations[20]:

$$\mathrm{Re}(\chi^3)\ (\mathrm{esu}) = (10^{-4}\epsilon_0 C^2 n_0^2/\pi)\, n_2\ (\mathrm{cm^2/w})$$

$$\mathrm{Im}(\chi^3)\ (\mathrm{esu}) = (10^{-2}\epsilon_0 C^2 n_0^2 \lambda/4\pi^2)\, \beta\ (\mathrm{cm/w})$$

where, ϵ_0 = The vacuum permittivity and C = The light velocity in vacuum

The absolute value of the third-order nonlinear optical susceptibility is given by the relation,

$$|\chi^3| = [(\mathrm{Re}(\chi^3))^2 + (\mathrm{Im}(\chi^3))^2]^{1/2}$$

The nonlinear parameters calculated are listed in the Table 3. From the calculated values the result is concluded as, the real part of the third-order nonlinear susceptibility χ^3 is much larger than the imaginary part, indicating that the third-order optical nonlinear response[21] in the dye doped polymer film is dominated by the optical nonlinear refractive behavior.

Table 3. Nonlinear optical parameters of MY doped PVA film

The aperture linear transmittance	$S = 0.5422$
On-axis phase shift	$\Delta\phi_0 = 3.4441$
Third order nonlinear refractive index	$n_2 = 9.8 \times 10^{-8}$ cm^2/w
Nonlinear absorption coefficient	$\beta = 10.944 \times 10^{-3}$ cm/w
Real part of the third-order nonlinear optical susceptibility	Re (χ^3) = 4.2031×10^{-6} esu
Imaginary part of the third-order nonlinear optical susceptibility	Im (χ^3) = 1.9873×10^{-6} esu
Absolute value of the third-order nonlinear optical susceptibility	$|\chi^3| = 4.6492 \times 10^{-6}$ esu

Surface Characterization of the Azo Dye Doped Polymer Film

AFM analysis and FESEM analysis

The surface topography of the MY doped PVA film was examined using AFM Nanonics imaging MV1000. The AFM 3D-image is revealed with thickness of the film in the Z-direction. Figure 6(a) is the 3D topography image showing that the film contains dome shaped domains with lateral sizes ranging from 0 µm to 6 µm and heights ranging from 95 nm to 100 nm. The particles are more elongated and oriented, while a more random distribution of length and orientation is observed when the polymer is coated on glass substrate.

Thickness of the film is the most significant parameter, which plays an important role in the properties of the film. To determine the thickness of the prepared film FESEM micrograph was taken on the cross-sectional view using QUANTA FEG.

The micrograph of the sections of the film is reported in Fig. 6(b), where the upper side of the micrograph represents the MY doped polymer film, while the lower side corresponds to the bare glass. The average thickness evaluated from the interface region was 60 µm.

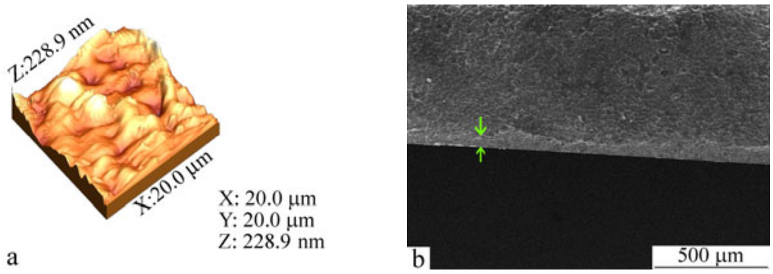

Fig. 6 (a) 3D topography image of MY doped PVA film and (b) FESEM micrograph of MY doped PVA film

CONCLUSIONS

Films of azo dye doped PVA have been deposited on glass substrates by spin coating method at constant spinning speed. The vibration analysis confirms the presence of azo groups and sulphonyl groups in the backbone of PVA. The colored nature of the prepared films was confirmed in UV-Vis spectrum analysis and the nature of the electronic transitions was studied. The photoluminescence studies conclude the presence of trans-isomer character of the azo dye. The third-order optical coefficients were derived using Z-scan measurements and it was concluded that the third-order optical nonlinear response in the MY doped polymer film is dominated by the optical nonlinear refractive behavior. In the surface analysis, the AFM technique proves that the film contains large number of dome shaped domains and the thickness of the coated film was found by FESEM technique to be 60 µm. These results are quite encouraging for possible applications in nonlinear optical devices.

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