J. Indian Inst. Sci., Sept.–Oct. 1996, 76, 603–614.

Optical phase conjugation in azo-dye-doped polymer films using pulsed and CW lasers

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Received on January 27, 1995, Revised on December 27, 1995.

Abstract

Generation of phase conjugate waves in azo-dye-doped polymer films using high-power pulsed and low-power CW lasers in both four- and two-wave mixing geometries is reported here. The underlying nonlinear mechanisms in each case are identified by studying the influence of various material, geometric and laser parameters on the generation of phase conjugate wave. Experiments have been carried out using pulsed Nd:YAG and CW argon lasers to study the effect of several parameters on phase conjugate reflectivity. The most dominant mechanisms are found to be thermal nonlinearity and saturation of absorption depending on the type of laser–material interaction. The utility of high efficiency and fast response to optical fields shown by the dye-polymer films is also discussed.

Keywords: Optical phase conjugation, dye-doped polymers, saturation of absorption, thermal nonlinearity, wave mixing

1. Introduction

Optical phase conjugation (OPC)[1] is a nonlinear optical phenomenon which involves mixing of optical waves in a nonlinear medium mediated by the third-order nonlinear susceptibility. The technique incorporates nonlinear optical effects to reverse both the direction of propagation and the total phase factor of an arbitrary beam of light. This peculiar mirror-like property has given rise to a vast range of important practical applications like phase distortion correction, pointing and tracking. Majority of the applications involving OPC need nonlinear media with very fast nonlinearities. Fast recovery times, high-phase conjugate (PC) reflectivity and nonphotodegradability are the qualities necessary for real-time image amplification, image processing and image conversion.

The absorbing dye media offer a rich variety of photophysical and photochemical pathways resulting in several nonlinear mechanisms like the saturation of dye absorption, thermalization and photoinduced anisotropy, etc. Organic dyes embedded in polymer matrices which absorb at a wide range of optical frequencies exhibit most of these photoinduced nonlinearities and thus provide a very good medium for efficient generation of a PC wave. Thus dye-doped polymer (DDP) films are ideal candidates for any application of OPC-like image processing or real-time interferometry. The ease of handling of the thin films as opposed to the dye solutions and lesser intensity losses due to scattering at the sample render them very attractive for efficient PC wave generation. The films can be made as thin as desired in such a way that the transit time through the film is much shorter than the relaxation time scales prevalent in the medium.

Dyes belonging to the azo-dye family like aniline yellow, methyl yellow, yellow AB[2,3], etc., embedded in a PMMA matrix have been used as nonlinear media. Thin films were prepared by dissolving measured quantities of the polymer PMMA in chloroform and adding dye solutions to it. This mixture is poured on dry glass plates (2.5 × 5 cm) and allowed to dry slowly. Thin films of 60–70 μm can be prepared easily. The results of investigations[4] on some absorbing organic dyes embedded in polymer thin films using pulsed Nd:YAG and CW argon ion lasers are presented here. The studies deal with the formation of PC signals in four- and two-wave mixing (FWM and TWM) configurations.

2. Nonlinear mechanisms and models

The interaction of strong optical fields with dye molecules held rigidly in polymer matrices can be manifold depending on the energy level structure of the dye, the operating wavelength, laser characteristics and the dye–polymer host interactions. A model, provided by Caro and Gower[5], capable of describing the generation of a PC wave in absorbing media in a degenerate FWM geometry, is briefly discussed here. In this configuration three beams of identical wavelength are incident on a nonlinear medium. Of these, the pump and read beams are intense and counterpropagating while a weak probe beam is incident at a small angle with the pump beam. A fourth wave, PC to the probe, is generated in the direction opposite to the probe wave. The central equation of this degenerate FWM analysis which can be used to explain a variety of mechanisms prevalent in absorbing media that govern the PC reflectivity (defined as the ratio of the intensities of the PC wave and the probe wave) is given by

$$R_{PC} = \left| \frac{2Q_c \sin(HL/2)}{H\cos(HL/2) + \alpha \sin(HL/2)} \right|^2 \text{ where } H = \sqrt{4\left|Q_C^2\right| - \alpha^2}. \tag{1}$$

The coupling parameter, Q_C, assuming that the pump and read beams are of equal intensity, *i.e.*, $I_1 = I_2 = I$, is given by

$$\left|Q_C\right| = \frac{2\omega I \chi^{(3)}(-\omega,\omega,\omega,-\omega) e^{(-\alpha L'/2)}}{4c^2 n^2 \varepsilon_0}. \tag{2}$$

Here $\chi^{(3)}(-\omega,\omega,\omega,-\omega)$ is the third-order nonlinear susceptibility involved in the degenerate FWM process at frequency ω, α, the absorption of the medium and L', the modified interaction length. This parameter varies for different mechanisms and is useful for calculating the third-order susceptibility $\chi^{(3)}$ in each case. Here only two nonlinear optical mechanisms are briefly discussed.

2.1. *Saturation of absorption*

An intense beam of light incident on an absorbing medium can excite the dye molecules and cause redistribution of the population among the energy levels. This leads to a decrease in the ground state absorption. Beyond a certain intensity of the incident radiation, called the saturation intensity, the transmission ceases to increase. A simple 3-level scheme[6] models the photoinduced transitions reasonably well. The schematic representation of the photophysical pathway is $S_0 \rightarrow S_1 \rightarrow T_1$ where S and T represent the singlet and triplet states and 0 and 1, the ground and first excited states, respectively. The line-centre saturation intensity can be obtained as $I_S = \frac{\hbar\omega}{\sigma Q_T T}$, where σ is the absorption cross section, Q_T, the triplet yield and T, the triplet lifetime.

The typical triplet lifetimes measured are of the order of a few milliseconds. Thus, saturable absorption is responsible for the generation of large optical nonlinearities even at low CW laser intensities and also offers a fast response to optical fields. In FWM geometry in dye-doped films, due to fast response to the incidence of the three waves, grating formation and PC wave generation occur with a time constant less than the triplet lifetime of the dye used.

It is assumed that all the four wave vectors are in the same plane perpendicular to the surface of the dye films and their polarizations are perpendicular to that plane. The film is sufficiently thin so that the light transit time in the film is small compared to the dye relaxation times. Considering that the pump and read beams are not depleted the PC reflectivity due to this process can be obtained as

$$R_{PC} = \left|\frac{\kappa}{\alpha + w\cot(wL)}\right|^2 \quad \text{where} \quad w = \left(|\kappa|^2 - \alpha^2\right)^{1/2}. \tag{3}$$

In the equation above, α is the saturable absorption coefficient and κ, the energy coupling coefficient both of which are dependent on the nonlinear susceptibility of the dye and the saturation intensity. The imaginary part of the susceptibility $\chi^{(3)}$ can be calculated using

$$\chi^{(3)} = \frac{4i\alpha c^2 n^2 \varepsilon_0}{3\omega I_S}.$$

2.2. *Thermal mechanism*

In addition[7], the absorption of radiation due to heating of the material in a light channel may also lead to a pronounced change in the refractive index n which has been referred to as the thermal nonlinearity. For media with sufficiently large absorption coefficients the continuously rising change in refractive index due to thermal nonlinearity Δn_T can exceed fairly rapidly the steady-state value of the increments to the refractive index due to electrostriction and Kerr effect. Thus, thermal nonlinearity is found to make the largest contribution to the total variation in refractive index in such media for sufficiently long pulses of the incident radiation. This local thermalization channel can cause local temperature to increase in the medium which in turn leads to a local expansion thereby causing a local reduction of the refractive index.

If an intensity modulation is incident on media with sufficiently good absorption, thermal nonlinearity leads to a modulation of the refractive index which then acts as a grating. If this modulation is switched off, the modulation of refractive index of the medium will decay by thermal diffusion. Such a grating is generally referred to as thermal grating. This thermal grating mechanism can be described using the heat-diffusion model. Using this model which describes the steady-state behaviour an effective susceptibility can be obtained as[5]

$$\chi_{eff}^{(3)} = \frac{dn}{dT}\frac{4n^2 c\varepsilon_0 \alpha\tau f}{3\rho C_p} \tag{4}$$

where $\frac{dn}{dT}$ is the change in refractive index of the medium with temperature, f, the fraction of absorbed radiation converted to heat, τ, the duration of electric fields, and ρ and C_p are the density and specific heat at constant pressure, respectively. The PC reflectivity, in the low-reflectivity regime, is given[5] by

$$R_{PC} = |fD\tau I|^2 e^{(-\alpha L')}\left[1 - e^{(-\alpha L/2)}\right]^2 \tag{5}$$

where D is the solvent-dependent parameter, and L', the modified interaction length. A full hydrodynamic model[8] which also has the relevant time scales incorporated into the analysis is necessary to study the dynamics of thermal nonlinearities.

3. OPC in dye-doped films using a pulsed laser

This part deals with the investigation of azo-dyes in polymer thin films as the nonlinear medium with a nanosecond pulse laser. The possibility of the formation of thermal phase gratings is suggested. The dependence of PC reflectivity on the host and solute parameters is also investigated to confirm that the thermal grating mechanism dominates other mechanisms. Thermal nonlinearity build up in DDP films can be significantly high due to higher viscosity of the host medium. This control over the thermal grating growth and decay times along with the possibility of the formation of a permanent photochemical grating or a population grating can be utilized in information storage, photolithography and interferometry.

3.1. *Experimental*

The FWM experimental layout is shown in Fig. 1. The sample is mounted on a kinematic mount for fine adjustment to ensure normal incidence of the pump beam. The frequency-doubled output of Nd:YAG laser at 532 nm is used as the source. The pulse width is 8 ns and the repetition frequency is 10 Hz. The dependence of PC reflectivity on parameters like overall intensity, concentration and pump-probe intensity ratio is investigated.

The first study was to estimate the $\chi^{(3)}$ of the DDP films by investigating the dependence of PC reflectivity on the pump intensity. Typical plots of the variation of PC reflectivity with the pump-read intensity product for some dye films are shown in Fig. 2. The plots also show the theoretical fit using the thermal grating model. It is clear from the

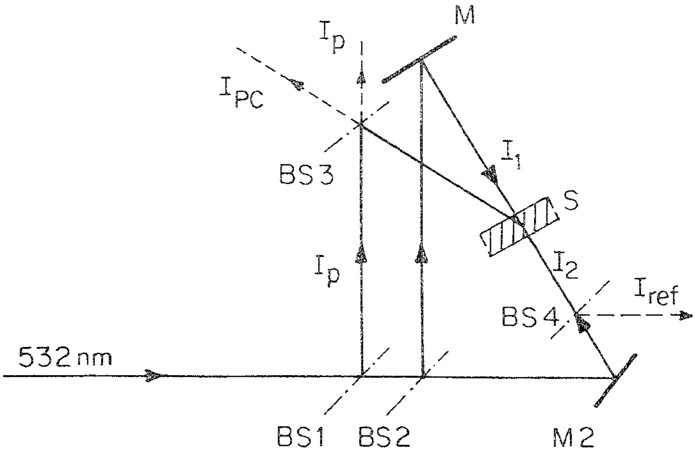

FIG. 1 Experimental layout for OPC-DFWM; M : Mirror, BS . Beam splitter, S · Sample

experimental data that thermal grating mechanism is dominant. The saturation of absorption is dominated by the thermal grating build up due to low thermal diffusion rate or large heat diffusion times owing to high viscosity of the medium.

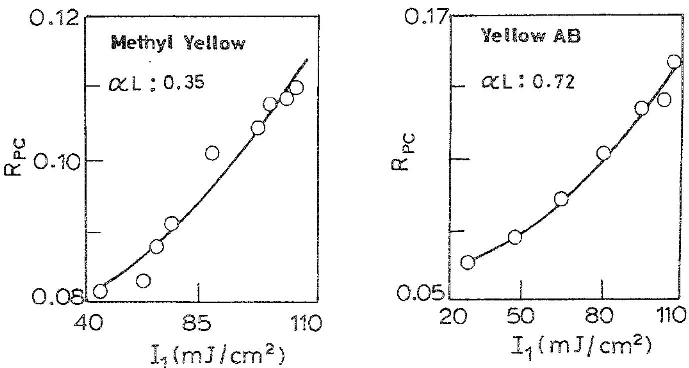

FIG. 2. Dependence of PC reflectivity (R_{PC}) on pump-energy density (mJ/cm^2) for azo-dye/PMMA films using pulsed laser. Theoretical estimates are shown by solid lines.

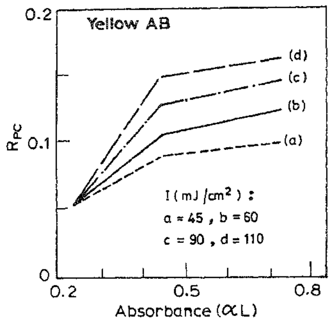

FIG. 3. Effect of the absorbance of azo-dye/PMMA films on PC reflectivity at different pump-energy densities with a pulsed laser.

The variation of PC reflectivity with sample concentration at several intensities for the dye, yellow AB, is shown in Fig. 3. The experiment was carried out by preparing films of different absorbances and similar thickness. The absorbance at the incident wavelength is measured and the concentration effect was studied at different pump intensities. The PC reflectivity was observed to increase with the absorption coefficient up to an optimum value and the reflectivity was uniformly higher at higher incident intensities for a dye film of given concentration. This is in agreement with the predictions of all the theoretical models.

3.2. *Discussion*

The azo-dye films are found to be very good nonlinear media with high nonlinear third-order susceptibility and the values predicted by the thermal grating model are in close agreement with the experimental observations. The damage threshold of the DDP films was found to be quite high and the recyclability can be gauged from the fact that the same samples were used for repeated studies and no permanent damage occurred.

4. OPC with CW laser in azo-dye films

The investigations with a pulsed laser source reported in the earlier section throw up a number of possible applications in which these azo-dyes can be utilized. Owing to their large absorption cross section over the entire visible frequencies, large refractive index modulations can be induced in these media through optical interactions. Importantly, some of the applications like real-time interferometry, image processing, detection of moving objects, etc., require a medium that can generate PC waves with high efficiencies using a CW laser source. This part deals with the study of low-power PC wave generation in DDP films using CW lasers in both FWM and TWM configurations. The dependence of PC reflectivity on the incident intensity, angle of interaction, pump-probe intensity ratio, etc., is also briefly discussed here, along with the factors influencing the growth and decay of the gratings.

4.1. *Four-wave mixing*

Here the results of various experiments carried out to identify the nonlinear mechanism primarily responsible for the nonlinear optical behaviour of these dye films in their interaction with a CW laser source are presented. The theory of FWM in absorbing media discussed earlier can be used here with minor modifications.

4.1.1. *Experiment and results*

The geometry is the same as shown in Fig. 1. The 488 nm wavelength of a CW argon ion laser is used as the excitation source. The dependence of the PC reflectivity on the pump and read intensity is investigated first. Figure 4 shows the change in PC intensity with variation in the incident pump intensity for some DDP films. The absorbance values are also pointed at relevant places. Also shown in the figures are the theoretical fits calculated using the saturation of absorption model for each of the dye samples. The plots show good fits to the experimental data suggesting that the saturation of absorption is the most dominant mechanism.

The growth and decay of the FWM signals are also investigated by modulation of the intensity of the beams. The growth of the signal is an indication of the response of the medium to the optical fields. This is governed by the probability of the $S_0 \rightarrow S_1$ transition and the $S_1 \rightarrow T_1$ transition. The grating decay time is governed by the triplet relaxation time. The larger the triplet lifetime smaller is the saturation intensity and larger the nonlinear susceptibility.

The experiment was carried out to study the growth and decay of the saturation gratings in these dye systems using a mechanical shutter and a storage oscilloscope. The mechanical shutter is used to either block or release any one of the grating writing

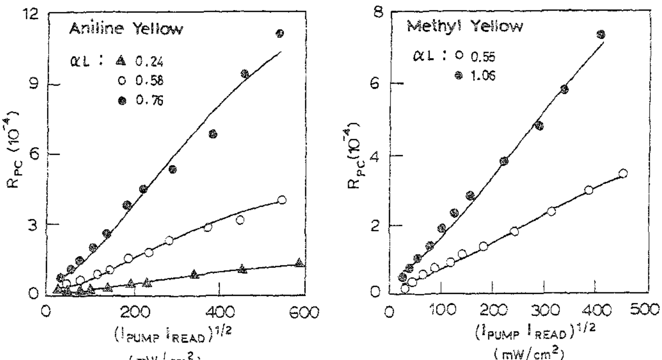

FIG. 4. Dependence of PC reflectivity on pump-read intensity (mW/cm²) for azo-dye/PMMA films using CW laser. Theoretical estimates are shown by solid lines.

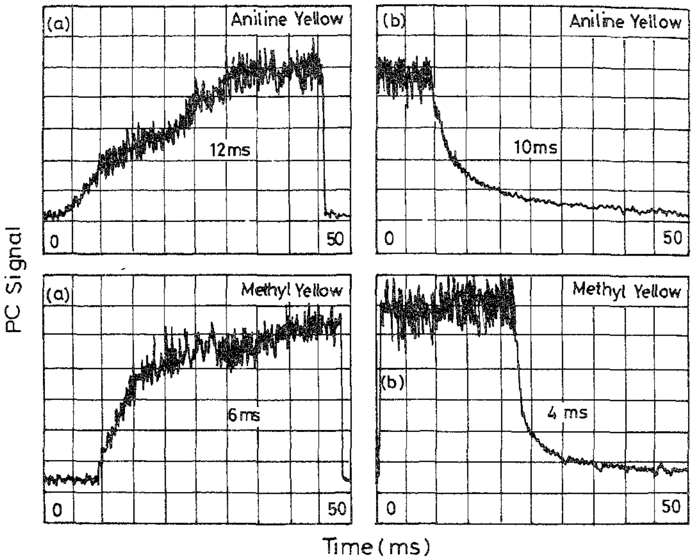

FIG 5. Typical oscilloscope patterns showing the growth and decay of FWM-PC signal using a CW laser at low pump intensities. (a) Growth, and (b) Decay of the grating when pump beam is blocked.

beams, usually the probe beam, and the resulting time-varying signal is captured on the storage oscilloscope for further analysis. Figure 5 shows a series of oscilloscope traces of the growth and decay patterns for some of the dyes. The values are calculated using the Liao and Bloom approach[9] where the risetime is the time taken to reach 40% of the steady-state value.

4.2. *Two-wave Mixing*

This part deals with the generation of higher diffraction orders in a TWM geometry using these DDP films. This is of great interest in holographic applications. This phenomenon can be described as follows. Consider the interference pattern formed by two laser beams in a nonlinear medium which can induce an index variation in the medium. When two waves propagate through this induced grating, they undergo Bragg scattering, *i.e.*, one beam scatters into the other and *vice versa*. Such scattering is akin to the read-out process in holography. This whole process is called self-diffraction. In the FWM process, a backward-propagating read beam generates the diffracted signal while in TWM the forward-propagating beams themselves are diffracted from the grating, Thus the process is also referred to as a forward FWM process. One important feature of the images produced using −1 order diffracted beams is that the images are phase conjugates of the object waves[10]. In general, the amplitude diffracted into first order ($m = \pm 1$) from a grating is to a first approximation proportional to the modulation of complex refractive index $(\Delta\tilde{n})$ or susceptibility $(\Delta\tilde{\chi})$ which in turn is governed by the respective material excitation.

4.2.1. *Regime of diffraction*

Saturable absorbers[11] are known to exhibit this self-diffraction. Here we report the observation of higher-order diffracted beams and the generation of PC signal using TWM in dye-doped thin-film saturable absorbers. One of the most important factors for any analysis is the thickness of the interaction region. This thickness of the grating decides the number of higher-order diffraction waves that can be observed experimentally. Traditionally if more than one order of diffraction appears the grating is said to be in the Raman–Nath regime or the thin grating regime and if only one order appears it is considered as the Bragg regime. One governing parameter is the Q_R parameter[11] defined as $Q_R = \dfrac{2\pi\lambda d}{n_o \Lambda^2}$ where d is the thickness of interaction region and Λ, the grating spacing. If $Q_R \leq 1$ then it is referred to as the Raman–Nath regime and if ≥ 10 then it is called the Bragg regime.

4.2.2. *Experimental details*

The dependence of the first-order diffraction efficiency on the overall incident intensity, the angle of interaction and the intensity ratio between the two beams have been studied. The experimental layout used for the study of self-diffraction is similar to the FWM geometry except that the read beam is absent and the detector measuring the PC signal is moved into the path of the −1 order diffracted pump beam.

4.2.3. *Results*

The diffraction pattern was first verified for the angular separation. It was found that the angular separation between the higher orders was identical and satisfied the Raman–Nath regime diffraction condition stated above. The dependence of the −1 order diffraction efficiency (defined as the ratio of the intensity of the first-order diffracted pump beam to that of the incident pump beam) on the angle of interaction was investigated. The intensity of the pump and the probe is kept fixed. Results of an aniline yellow/PMMA film of about 120 μ thick are presented in Fig. 6.

It can be seen that the diffraction efficiency η' (normalized) decreases with increase in the interaction angle θ. Qualitatively, since the beams have a finite width the effective interaction volume reduces when the angle of interaction is increased, thereby decreasing η. Also with increase in the interaction angle the grating spacing decreases, the spa-

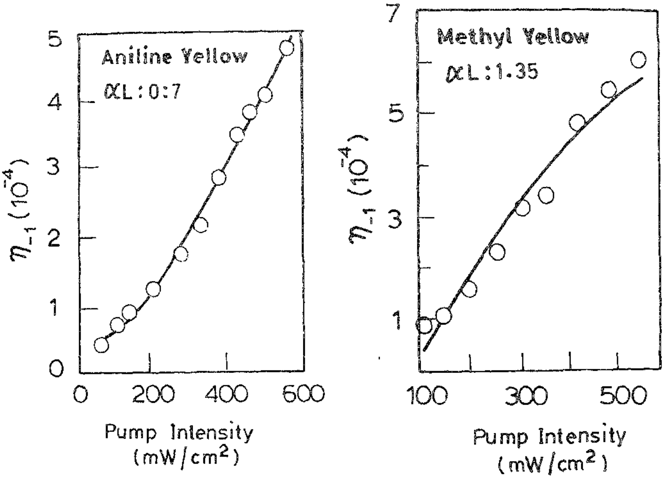

FIG. 6. Dependence of −1 order diffraction efficiency on pump intensity (mW/cm²) for azo-dye/PMMA films using CW laser. Theoretical estimates are shown by solid lines.

tial frequency increases and the dye medium fails to resolve the intensity modulation. The other important factor is a gradual change in the regime of diffraction. The Q_R parameter increases with increase in the interaction angle. Thus the Raman–Nath regime condition breaks down and the Bragg regime becomes dominant. Since Bragg diffraction supports the growth of a single diffraction order the higher-order diffraction efficiency reduces.

Figure 7 shows the dependence of the intensity of −1 order diffracted beam I_D on the total incident intensity I. A methyl yellow/PMMA film ($\alpha L \approx 0.7$) is used. This experiment is done for a fixed small angle of interaction and a fixed pump-probe ratio. The order of the nonlinearity is confirmed by fitting the intensity data to a third-degree polynomial. The diffraction efficiency is found to vary quadratically with the pump intensity. The experimental results are plotted along with the corresponding theoretical predictions using the saturation of absorption model. The theoretical fits are seen to agree very well with experimental values.

Figure 8 shows the variation of the diffraction efficiency with the pump-probe ratio β. The pump intensity is kept fixed and the probe intensity is varied by a neutral density filter. The diffraction efficiency is observed to saturate at a certain value. This gives us an estimate of the optimum contrast that should exist between the pump and the probe while writing the hologram.

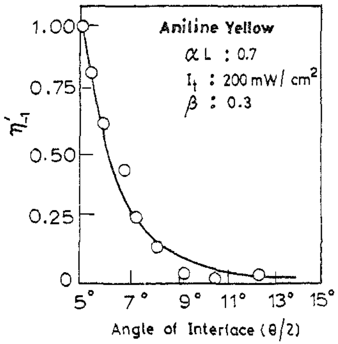

FIG. 7. Influence of the angle of interaction on the −1 order diffraction efficiency using a CW laser. Solid line shows the theoretical fit

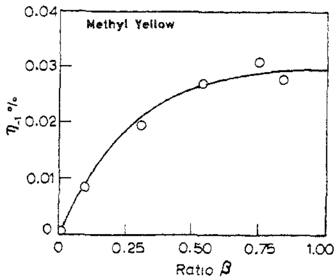

FIG. 8. Influence of probe-pump intensity ratio (β) on −1 order diffraction efficiency, $I_1 = 250$ mW/cm^2, $\alpha L = 1.35$. Solid line shows the theoretical fit.

4.3. *Discussion*

It is observed that the saturation of absorption in a dye described by a three-energy-level structure models the nonlinear behaviour of these azo-dye-doped thin films under CW laser excitation satisfactorily. Most of the dyes have shown high recyclability and no permanent photochemical changes. The dyes offer fast modulation capabilities due to fast growth and decay times. In some applications of TWM, involving real-time readout of the hologram where it might be necessary for some form of separation between the probe or object beam and the diffracted beams, the −1 order PC signal can be put to effective use.

Acknowledgement

The authors thank the Defence Research and Development Organisation (DRDO), India, for financial support. The constant support and inspiration provided by late Prof. P. S. Narayanan is gratefully acknowledged.

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