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Comparative Study on Azo dye-doped Polymer Films for Optical Phase Conjugation

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Abstract: In this paper, *we have studied the linear optical properties and nonlinear optical Phase Conjugation properties of two azo dye-doped polymer films by considering organic dyes disperse orange (DO-25) and disperse yellow (DY-7) doped in a polymer matrix Polymethyl methacrylate methacrylic acid (PMMA-MA). The nonlinear optical phase conjugation properties are studied using Degenerate Four Wave Mixing set-up using 532 nm wavelength CW laser beam. The effect of dye concentration, intensity of backward, forward pump, and inter beam angle between probe and forward pump beam on phase conjugation reflectivity are also studied and compared.*

Keywords: Azo Dye-doped Polymer films, Degenerate Four Wave Mixing, Nonlinear Optical Properties, Optical Phase Conjugation.

1. Introduction

It is well known that some of organic materials/dyes exhibit exceptional nonlinear optical properties [1]. In addition to it, they have several advantages compared to inorganic nonlinear materials due to easy to prepare solution or solid form and low dielectric constant which eliminate the need for poling while maintaining the refractive index [2]. However, these organic materials have some of the drawbacks inherent in the processing of comparable inorganic materials like of intense light induced degradation or bleaching and aggregation at higher dye concentration. In order to overcome these drawbacks and for effective use of highly nonlinear dyes, we can dope the dye molecules in a polymer matrix [3]. This idea of dye-doped polymer material matrix may increase the concentration of absorptive or fluorescence centers as well as the opto-chemical and opto-physical stability [4-5]. The third-order NLO properties of materials have many potential practical exciting applications, and motivated material scientists to continually explore new materials with high third-order NLO properties. The demands of materials for all-optical information process and high-speed all-optical switches include large nonlinear refraction index, small linear and nonlinear absorption coefficient, fast response and low propagation loss [6]. Nonlinear optical phase conjugation (OPC) of signals by degenerate four-wave mixing (DFWM) is an important technique with applications in many fields of science and technology including image transmission, optical image processing, optical information storage, optical filtering, and laser resonators [7]. When two counter propagating and intense beams of light interact with a nonlinear medium, together with a less intense third one, a fourth beam is generated from the nonlinear medium, which will be the phase conjugation of the third beam. This technique is called four-wave mixing. The special feature of a pair of phase-conjugate beams is that the aberration influence imposed on the forward (signal) beam passed through an inhomogeneous or disturbing medium can be automatically removed from the backward (phase-conjugated) beam passed through the same disturbing medium [8]. The DFWM techniques are also used in areas like nonlinear spectroscopy, real time holography, and phase conjugation. Phase conjugation by DFWM has been demonstrated in many organic or inorganic materials using pulsed or continuous-wave (cw) lasers [9].

The organic molecules exhibit large polarizabilities because exited π-bond electrons are delocalized and hence easily polarizable. Nonlinear absorption like two photon absorption and saturable absorption plays a very important role when dyes are used for the production of phase conjugation light, because χ^3 is inversely proportional to the saturation intensity. These systems exhibit large third-order susceptibilities. OPC has been reported in Glasses and other solid matrices doped organic dyes emerged as promising materials for OPC because of their large third-order nonlinear susceptibilities $\chi^{(3)}$. In these materials, the phase-conjugate wave can be generated at low light intensities provided by the continuous-wave lasers [10,11]. Moreover, these materials can be easily prepared in the laboratories. The important fundamental physical processes like nonlinear refraction, thermal grating, saturation and reverse saturable absorption, two photon induced fluorescence, photorefraction, and stimulated brillouin scattering etc. may lead to the formation of a laser-induced grating in the medium are associated with the generation of phase conjugated wave [12].

In this paper we have compared the linear optical properties and nonlinear optical Phase Conjugation properties of two azo dye-doped polymer films by considering organic dyes disperse orange and disperse yellow doped in a polymer matrix Polymethyl methacrylate methacrylic acid (PMMA-MA). The nonlinear optical phase conjugation properties is studied using Four Wave Mixing set-up using 532 nm wavelength CW laser beam. The linear absorption, single photon fluorescence, two photon induced fluorescence behavior are studied. PC reflectivity as function of recording time at different concentrations of dyes, PC reflectivity as function of angle between the probe beam and forward pump beam, dependence of PC reflectivity as a function of backward pump intensity, PC reflectivity as function of probe beam intensity, PC reflectivity as function of forward pump power and transmittance as a function of time are studied.

2. Design of Nonlinear Molecule

One of design strategy is proposed recently by Albota et.al, [13] dealing with molecules based on benzene ring as π-center which is attached symmetrically by either electron-donor (D) or electron-acceptor (A) through various lengths of conjugated connectors; D-π-D or A-π-A. They concluded that σ is increased by increasing the length of conjugation; change with the D/A strength and the extent of symmetric intramolecular charge-transfer (CT) from the D ends to the π-center or vice versa, meaning that symmetric charge redistribution effectively occurs upon excitation of such symmetric molecules.

A similar approach was made in designing molecules by Reinhardt [14] and his coworkers. dealing with benzene ring as π-center which is symmetrically coupled with two electron acceptor (A-π-A) or asymmetrically with D and A (D-π-A), respectively. There is no clear effect of structural symmetry on σ values, although increasing conjugation length of π-center brings about a significant improvement of the value. In fact, an asymmetric structure, D-π-A. This seems to suggest that there must be more crucial molecular factors other than structural symmetry involved. In this study we have considered two azo dye molecules.

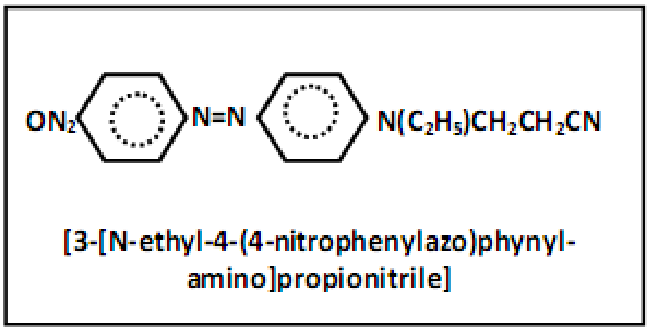

Figure 1: Molecular structure of Disperse Orange -25

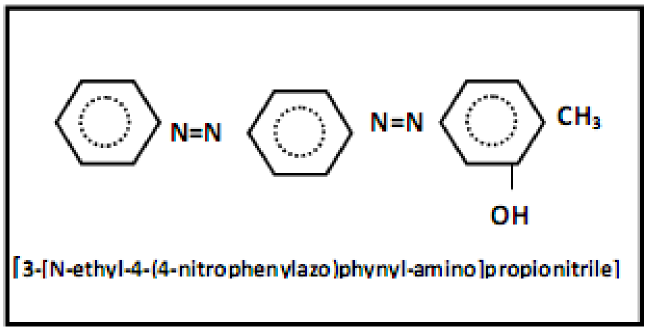

Figure 2: Molecular structure of Disperse Yellow -7

Commercially available [3-[N-ethyl-4-(4-nitrophenylazo) phynyl-amino]propionitrile (Disperse Orange-25) as shown in Fig. 1 and 4-[4-(Phenylazo)phenylazo]-o-cresol (Disperse Yellow-7) as shown in Fig. 2 (Aldrich Chemical Co.) are purified by recrystallization twice with spectrograde ethanol and by vacuum sublimation. The purity is determined spectroscopically. Purified chloroform is used as the solvent. To prepare the film, Polymethyl methacrylate – metacrylic acid was used as polymer matrix. The thin films of DO-25 and DY-7 doped in PMMA-MA is prepared using hot press technique. Thin films of variable thickness are obtained between two glass slides.

3. Linear Optical Properties of DASPB

The linear absorption spectra of DO-25 and DY-7 doped in PMMA-MA are measured on a VARIAN Cary UV-vis-IR recording Spectrophotometer. Fig. 3 and Fig. 4 show the linear absorption spectrum of these samples respectively. The spectral curve has shown that there is a strong absorption band with peak absorption located at 468 nm in case of DY-7 and at 468 nm with a bandwidth of 100 nm, a medium absorption peaked at 270 nm with a bandwidth of 60 nm in case of DO-25 and no linear absorption is observed in entire spectral range of 580 to 1200 nm.

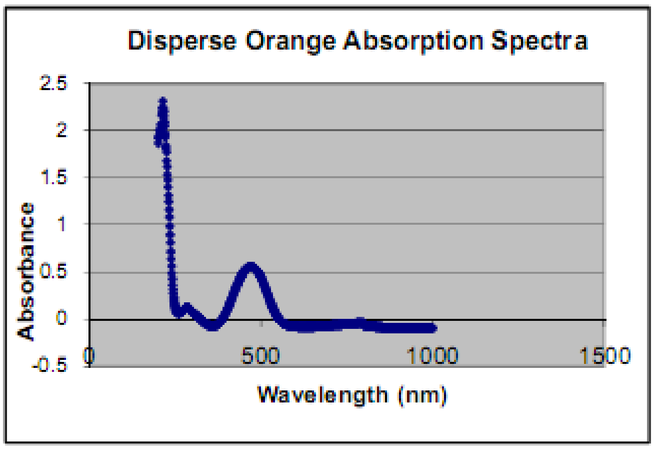

Figure 3: Linear absorption spectrum of DO-25 in PMMA-MA polymer matrix.

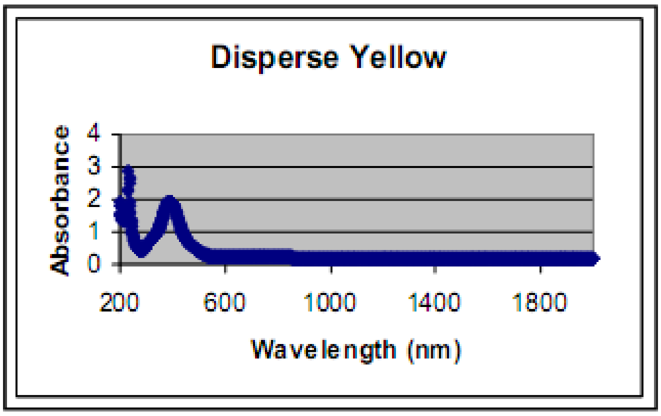

Figure 4: Linear absorption spectrum of DY-7 in PMMA-MA polymer matrix

4. Experimental Configuration for DFWM

The schematic diagram of the experimental set-up for studying phase conjugation signal is shown in Fig. 5. A CW Nd:YAG laser beam of variable input power at 532 nm was divided into three beams, two counter-propagating pump beams E_1 and E_2 namely forward-pump and backward-pump beams respectively and a probe beam E_3 to form the DFWM configuration. The spot size of each of these three unfocussed beams at the nonlinear medium was 1.0 mm in diameter. The constant power ratio of the probe beam (E_3), forward-pump beam (E_1) and backward-pump beam (E_2) used in this work was ≈ 1 : 10 : 10. The angle between the probe beam and the forward-pump beam was initially 8^o. The sample was exposed simultaneously to all these three beams. The optical path lengths of all the three beams were made equal, so that they were coherent at the sample. The phase-conjugate wave retraces the path in the opposite direction to that of the probe beam E_3 and was detected with the help of a photo detector and power meter. The experimental set-up was mounted on a vibration isolation table to avoid the destruction of the laser-induced gratings formed in the DO-25/DY-7 dye-doped polymer matrix due to mechanical disturbances. The effect of Phase Conjugation signal strength (PC reflectivity) as a function of recording time for different concentrations of dyes doped in PMMA-MA polymer matrix, PC reflectivity as a function of angle between the probe beam and the forward-pump beam, dependence of PC reflectivity on backward pump Intensity by keeping the power of the forward pump and probe beams constant, dependence of PC reflectivity on forward pump power by keeping the power of the backward pump beam and probe beam constant, the conjugate beam reflectivity as a function of the input probe beam intensity, and Transmittance of the sample as a function of time were studied [15 - 17].

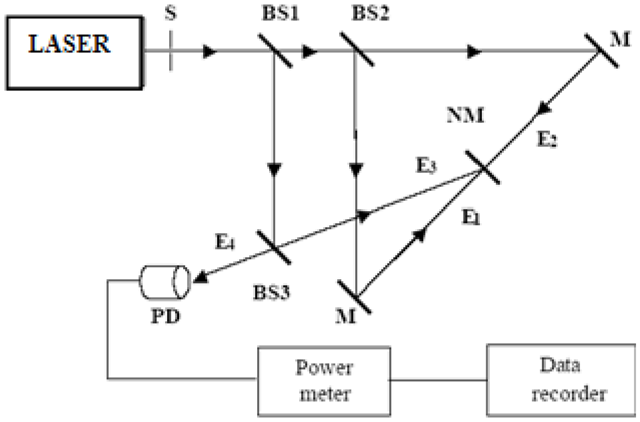

Figure 5: Experimental set-up for observation of PC wave, S, Shutter; BS1–BS3, Beam splitters; M, Mirror; NM, Nonlinear medium; PD, Photo-detector

5. Results & Discussions

The PC signal measurements are taken by varying the parameters which influence the PC signal reflectivity during the DFWM process. Fig. 6 shows the PC signal strength versus the time for different dye concentration of the DO-25 doped polymer films and Fig. 7 shows the PC signal strength versus the time for two dye concentration of the DY-7 doped polymer film. It is found that the PC intensity rises linearly to a maximum and then starts decreasing. The phase grating formed is transient. To get maximum reflectivity, it is necessary that there be a perfect overlap of the probe and the pump beams in the nonlinear medium. Fig. 8 shows the PC reflectivity as a function of recording angle between the forward pump and probe beam of DO-25 and DY-7 samples. It seems from the figure that, as the angle between the probe beam and the forward pump beam increases, the PC reflectivity first increases and then decreases. This may be because as the angle increases, the probe beam becomes elliptical and only a fraction of its area falls within the interaction region. Because of two-wave coupling, the maximum PC reflectivity is achieved when the angle is 7 degrees in case of both DO-25 and DY-7 samples.

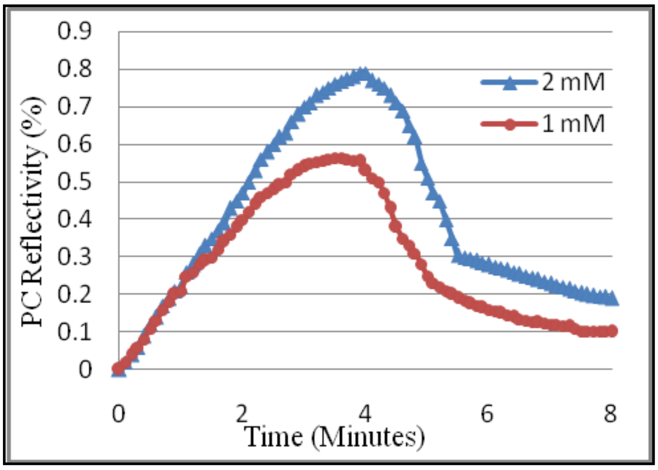

Figure 6: PC signal versus recording time for different concentration for DO-25.

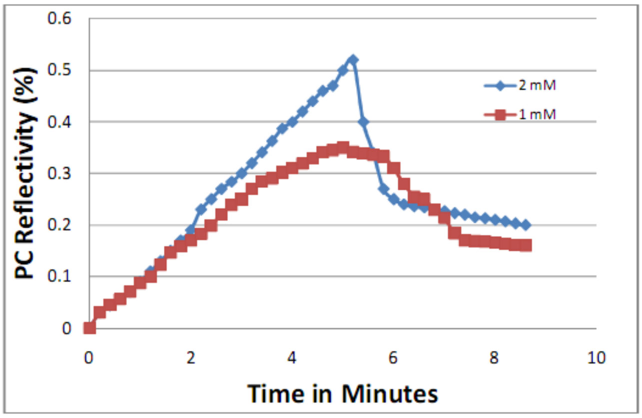

Figure 7: PC signal versus recording time for different concentration for DY-7.

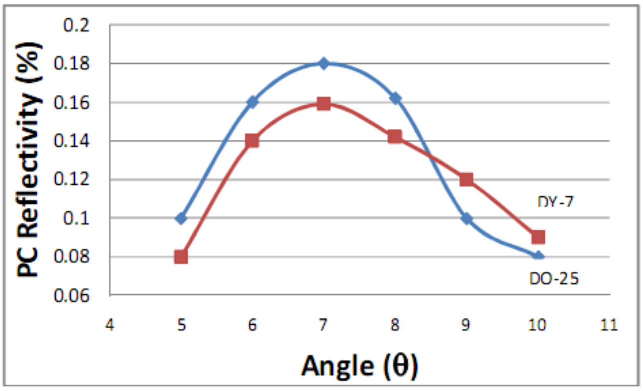

Figure 8: PC Reflectivity as function of angle between the probe and forward pump beams.

A maximum reflectivity value of 0.28 % is observed in case of DO-25 and of 0.16 % is observed in case of DY-7 for pump beam intensity at 2.5 W/cm^2, and further increase in pump beam intensity resulted to decrease in PC reflectivity. The effect of the backward pump beam power on the PC reflectivity of both the samples by keeping the power of the forward pump and probe beams constant and varying the backward pump beam is shown in Fig. 9.

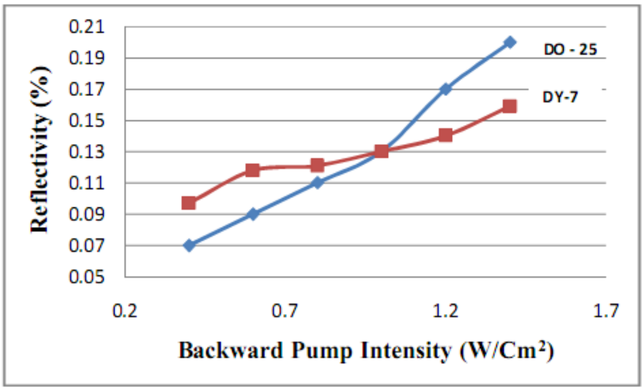

Figure 9: Dependence of PC reflectivity on backward pump Intensity

Fig. 12 shows the influence of the input probe beam intensity on the conjugate beam reflectivity. A maximum reflectivity value of 0.22% is observed in case of DO-25 and of 0.17% is observed in case of DY-7 for probe beam intensity at 0.11 W/cm^2 respectively, and further increase in probe beam intensity resulted to decrease in PC reflectivity. Similar observations have been reported in other kinds of material doped with organic dyes [16 18]. Fig. 13 shows the variation of reflectivity for different power of forward pump beam for both the samples. The PC reflectivity increases linearly with the power of forward pump beam. There are two main processes which must be considered in the discussion of origin of OPC in dye doped PMMA-PA films: (1) the formation of thermal grating and (2) third order nonlinear optical processes. The DO-25 and DY-7 films illuminated with 532 nm radiation of variable intensity and the transmittance of the sample is measured simultaneously by using photodetector. If the effect observed in our experiments is of purely thermal nature, bleaching of the sample film will be observed. The results obtained for the sample are shown in Fig. 10 and Fig. 11 respectively. It is clearly demonstrated that the transmission of sample increases with time. The experiment described above indicates that the third order nonlinear processes like reverse saturable absorption mainly responsible for OPC in the sample under study.

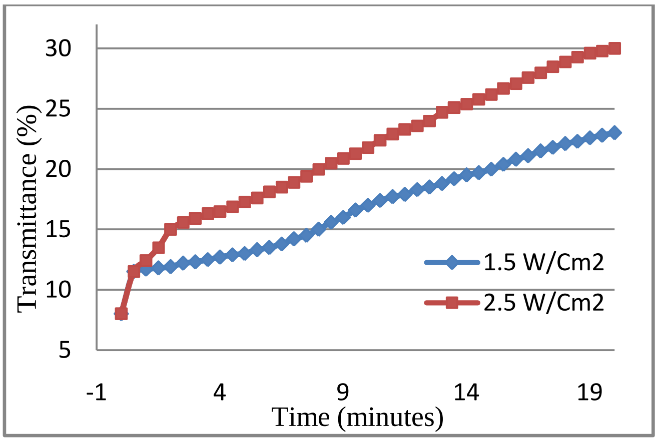

Figure 10: Transmission as a function of time for DO-25.

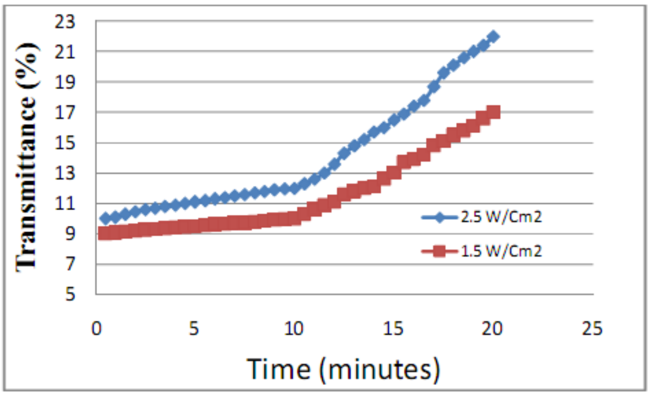

Figure 11: Transmission as a function of time for DY-7.

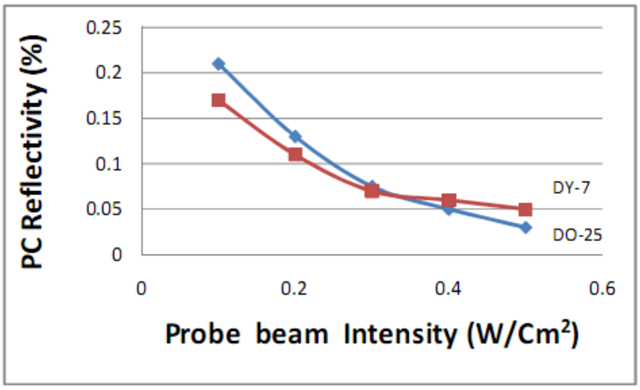

Figure 12: Conjugate reflectivity as a function of probe beam intensity.

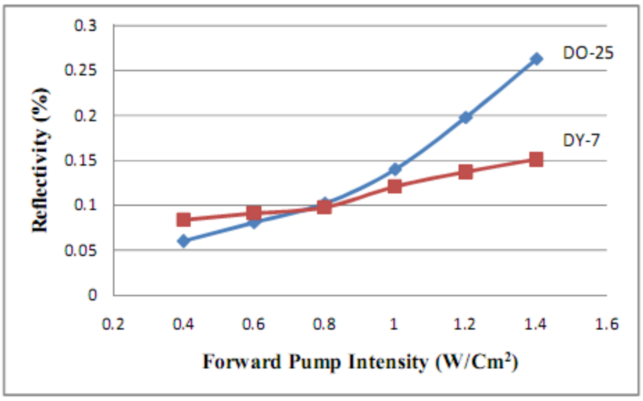

Figure 13: Dependence of PC reflectivity on forward pump power.

Dyes doped in polymer matrix have the capability of generating a phase-conjugate wave by not only DO-25/DY-7 but also holographic process [19-20]. To distinguish the phase-conjugate wave generated by DFWM from that by the holographic process, the transient behavior of the PC signal was studied. For this, the DO-25/DY-7 dyes doped in PMMA – MA polymer matrix were first illuminated with three waves E_1, E_2 and E_3 for a specified duration, and afterwards, E_1 and E_3 were successively turned off, so that only E_2 was incident on the dye film. Fig. 10 and Fig. 11 show the measured phase-conjugate signal as a function of time. The initial rise to a peak within a few minutes is due to DFWM and holographic processes; the sudden drop in the intensity of the PC signal after shutting off both the write beams E_1 and E_3 indicates the contribution from the fast DFWM process. Due to the holographic process the PC signal is present even after E_1 and E_3 are shut off, and it decays rather slowly. If the phase-conjugate wave was generated only by DFWM, the lack of only one of the three beams E_1, E_2 and E_3 would have stopped generation of the phase-conjugate wave. Therefore, it is inferred that the rapidly decaying component corresponds to the phase-conjugate wave which is generated by the DFWM. On the other hand, if spatially modulated information formed by E_1 and E_3 can be recorded in the DO-25 and DY-7 dyes in PMMA – MA polymer film, the phase-conjugate wave can still be generated when E_2 tries to read this stored information, during the lifetime of the holographic grating. Table 1 contains the results of comparison of PC reflectivity at different pump beam, probe beam and angle between them.

Table 1: Comparison of PC reflectivity of of samples :

S.No.	Measuring Parameter	DO-25	DY-7
1	Maximum PC reflectivity at pump beam intensity of 1.5 W/cm^2	0.28%	0.16%
2	Maximum PC reflectivity angle between forward pump and probe beam	7°	7°
3	Maximum PC reflectivity at probe beam intensity 0.11 W/cm^2	0.22%	0.17%

6. Conclusion

We have observed low-intensity optical phase-conjugation in DO-25 dye in PMMA – MA polymer matrix and DY-7 dye in PMMA – MA polymer matrix using a degenerate four-wave mixing set-up, employing 532 nm light radiation from a CW Nd;YAG laser. The phase-conjugate signal is found to have contributions from the DFWM and the holographic processes. The maximum phase-conjugate beam reflectivity observed in these dye films is about 0.22% in DO-25 doped PMMA-MA matrix and 0.17% in case of DY-7 doped PMMA-MA polymer matrix. The maximum PC reflectivity is achieved when the angle between probe and forward pump beam is 7 degrees. The effects of dye concentration, intensity of backward, forward pump and inter beam angle between probe and forward pump beam on phase conjugation reflectivity are also studied. PC signal strength first increases and then decreases. PC reflectivity is increased by increasing the intensity of the backward and forward pump beam. The polarization and intensity profile are verified to be preserved in the conjugate signal. The predominant phase conjugation signal is attributed to the facts that reverse saturable absorption and large third order susceptibility of the dye molecules. Since the DO-25 and DY-7 dyes in PMMA – MA polymer film are used at 534 nm and this may be suitable for low-power semiconductor lasers in the red wavelength region, DO-25/DY-7 dyes in PMMA – MA polymer film may be a promising material for real-time double-exposure phase-conjugate interferometry.

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