



## 3,3'-Benzene-1,4-diylbis[1-(substituted)phenylprop-2-en-1-one] derivatives: A new class of materials for third-order nonlinear optical applications

P. Poornesh<sup>a,b,\*</sup>, K. Ravi<sup>c</sup>, G. Umesh<sup>b</sup>, P.K. Hegde<sup>c</sup>, M.G. Manjunatha<sup>c</sup>, K.B. Manjunatha<sup>b</sup>, A.V. Adhikari<sup>c</sup>

<sup>a</sup> Department of Physics, Manipal Institute of Technology, Manipal University, Manipal, Udupi, Karnataka 576104, India

<sup>b</sup> Department of Physics, National Institute of Technology Karnataka-Surathkal, Mangalore, Karnataka 575025, India

<sup>c</sup> Department of Chemistry, National Institute of Technology Karnataka-Surathkal, Mangalore, Karnataka 575025, India

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### ABSTRACT

We have investigated the third-order nonlinear optical parameters of Bischalcones embedded in DMF solution and in solid PMMA matrix, by Z-scan technique using nanosecond laser pulse trains at 532 nm. Z-scan results reveal that the Bischalcones exhibits negative nonlinear refractive index as high as  $10^{-11}$  esu. The molecular two-photon absorption cross-section  $\sigma_2$  of Bischalcones were of the order  $10^{-46}$  cm<sup>4</sup> s/photon, which is nearly two orders of magnitude larger than that of Rhodamine 6G which is  $10^{-48}$  –  $10^{-50}$  cm<sup>4</sup> s/photon. We found that, the two-photon absorption (TPA) is the dominating nonlinear process leading to nonlinear absorption in both the cases in solution and as well as in solid medium. Based on TPA process, the Bischalcones exhibit good optical power limiting of nanosecond laser pulses at the input wavelength. The nonlinear optical parameters found to increase on enhancing the strength of the electron donor groups indicating the dependence and importance of electron donor/acceptor units on third-order nonlinear optical susceptibility  $\chi^{(3)}$ .

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### 1. Introduction

Nonlinear optics has received considerable attention due to their variety of applications in optoelectronic and photonic devices. Especially, nonlinear optical materials exhibiting strong two-photon absorption (TPA) are in great demand, due to their applications in three-dimensional fluorescence imaging and multi-photon microscopy, eye and sensor protection, frequency-upconversion lasing, optical signal reshaping and stabilizing fast fluctuations of laser power [1–5]. A wide variety of materials have been investigated for third-order nonlinear optics, among which organic materials are attractive because of their optical and electronic properties which can be tuned and tailored by structural modification. The large and ultra fast nonlinear optical response has made organics particularly attractive candidates for high-bandwidth applications. There is quest to design and develop the novel nonlinear materials with large molecular two-photon absorption cross-sections to meet the present demand.

Chalcones belongs to the class of low molecular charge transfer (CT) compounds that show large nonlinear optical properties without longer wavelength absorption as found in the case of  $\pi$ -conjugated polymer systems. Generally in charge transfer

compounds, large nonlinear electronic polarization arises due to the large dipole moment change from ground state to an excited state by optical radiation [6]. They have been explored intensively for second-order nonlinear optical applications because of their ability to crystallize in noncentrosymmetric structure and excellent blue light transmittance [7,8]. Unlike in the case of second-order nonlinear optics where symmetry restriction plays an important role, the third-order nonlinear optics does not possess any such symmetry restriction [9], which has widened the application of using chalcones as a possible material for third-order nonlinear optics. As far as our knowledge is concerned, there are no or few reports until John Kiran et al. [10] have explored dibenzylideneacetone and its derivatives for third-order nonlinear optical properties. The nonlinear susceptibility in these molecules was found to be of the order of  $10^{-13}$  esu. Recent research investigations have shown that chalcones are emerging as promising candidates for third-order nonlinear optics because of their noticeable third-order nonlinearity and good optical power limiting property [10–14]. Moreover chalcone molecules offer greater flexibility in adopting suitable design strategies [15,16], such as donor–acceptor–donor (D–A–D), donor– $\pi$ –donor (D– $\pi$ –D), donor– $\pi$ –acceptor (D– $\pi$ –A), donor–acceptor–acceptor–donor (D–A–A–D), and acceptor–donor–acceptor (A– $\pi$ –A), there by enhancing the nonlinear optical coefficients.

Realization of organic materials in practical device applications has been hampered due to several reasons, inadequate transparency, poor optical quality, lack of robustness and low laser damage

\* Corresponding author. Address: Department of Physics, Manipal Institute of Technology, Manipal University, Manipal, Udupi, Karnataka 576104, India. Tel.: +91 820 2925621; fax: +91 820 2571071.

E-mail addresses: [poorneshp@gmail.com](mailto:poorneshp@gmail.com), [poornesh.p@manipal.edu](mailto:poornesh.p@manipal.edu) (P. Poornesh).

threshold. Chalcones being an organic molecule has its limitations to be used in practical photonics device applications because of the possibility of getting degraded or bleached when exposed to intense optical signals. In order to overcome this drawback, they can be introduced into a suitable polymer matrix. This enhances the chemical and physical stability of the organic materials, while retaining the nonlinear optical properties and linear optical transmittance [17,18]. Polymer matrices offer advantages such as ease of processing which allows the fabrication of devices at low cost and have better compatibility with the organic molecules. Poly(methylmethacrylate) PMMA is a hard, rigid and transparent polymer with a glass transition temperature of 125 °C. It is tougher than polystyrene. PMMA is a polar material and has larger dielectric constant than other thermoplastics [18–20]. We have, therefore, selected PMMA as a solid matrix in to which the Bischalcone molecules are incorporated.

Following the strategy reported by Albota et al. [15] where they have shown that large two-photon cross-sections can be achieved by having symmetric charge transfer from the end of a conjugated system to the middle or vice versa. We adopted similar strategy in designing the Bischalcone molecules. In this paper, we present our investigations on third-order nonlinear optical properties of three Bischalcone molecules namely, 3,3'-benzene-1,4-diylbis(1-phenylprop-2-en-1-one) (Bis1), 3,3'-benzene-1,4-diylbis[1-(4-aminophenyl)prop-2-en-1-one] (Bis2) and 3,3'-benzene-1,4-diylbis[1-(3,4-dimethoxyphenyl)prop-2-en-1-one] (Bis3) doped in solid PMMA matrix investigated using nanosecond Z-scan technique. We also demonstrate the strong optical power limiting property of nanosecond laser pulses at 532 nm based on the two-photon absorption (TPA) process.

## 2. Experiments

The Bischalcone derivatives were synthesized by the following procedure, 0.1 mol terphthaldehyde was dissolved in 20 mL of absolute alcohol and 0.2 mol of corresponding acetyl compound was added into the solution. To this 20 mL of 5% alcoholic NaOH was added. The reaction mixture was stirred for overnight at room temperature. The precipitated product was filtered and re-crystallised using appropriate solvent. Before doping, the compounds were purified by re-crystallization from ethanol. The synthetic schemes of Bischalcones are given in the Fig. 1. The structures of the Bischalcones studied here are given in Fig. 2. The Bischalcones doped PMMA films were prepared by solution casting method. The doped polymer films were of ~0.36 mm thick. The linear absorption spectra of the Bischalcones were obtained at room temperature by using the UV-vis fiber optic spectrometer (Model SD2000 from Ocean optics Inc.). The spectra, shown in the Fig. 3 indicates negligible absorption at 532 nm wavelength. Hence, our measurements would correspond to non-resonant nonlinearity only.

The single beam Z-scan technique [21–23] was used to measure the third-order nonlinear optical susceptibility of Bischalcones in both solution and solid medium. This technique allows simultaneous measurement of nonlinear refraction (NLR) and nonlinear absorption (NLA). Basically, the technique relies on the fact that the Gaussian beam is tightly focused by a lens on the sample and by translating the sample through the focus, the change in the far-field intensity pattern is monitored. Experiments were performed using a Q-switched frequency doubled Nd:YAG laser (Spectra-Physics USA, Model-GCR170) with a temporal pulse width of 7 ns (FWHM) at 532 nm and a repetition rate of 10 Hz. The Gaussian beam was focused by a lens of 25 cm focal length. The laser beam waist at the focused spot was estimated to be 18.9 μm and the corresponding Rayleigh length is 2.11 mm. The sample thickness of 0.36 mm is less than the Rayleigh length

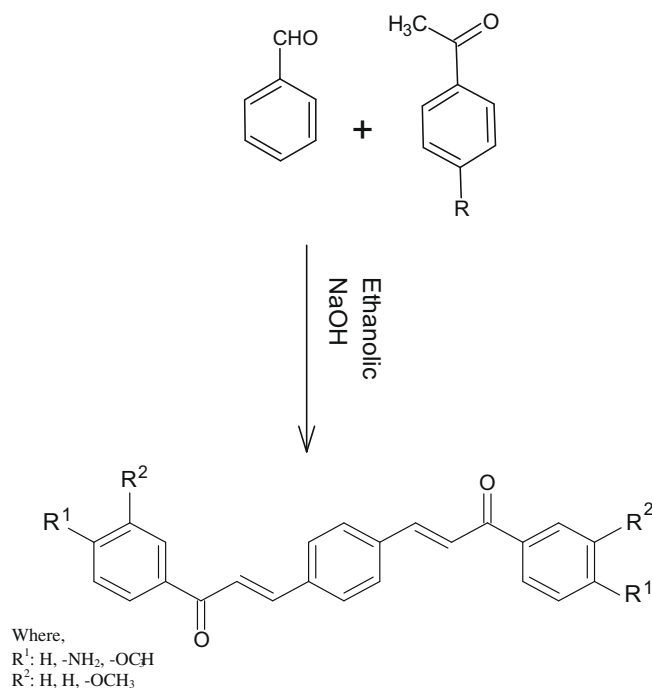


Fig. 1. Synthetic scheme of Bischalcones.

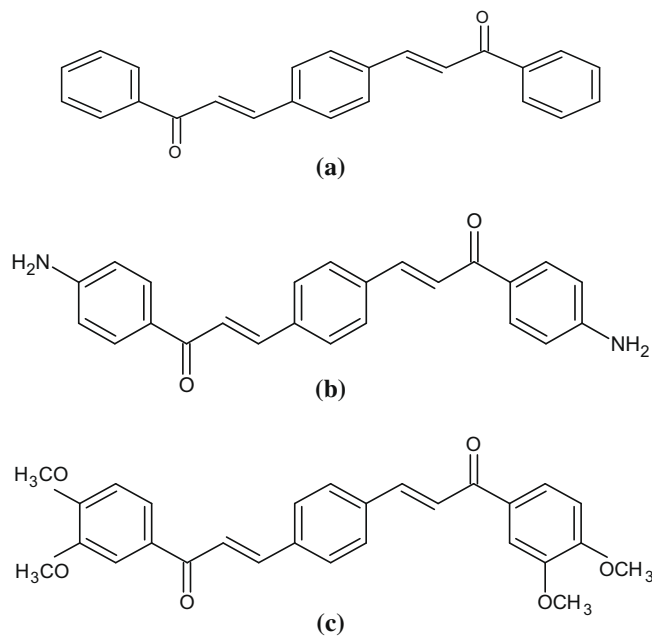


Fig. 2. Structure of Bischalcones: (a) 3,3'-benzene-1,4-diylbis(1-phenylprop-2-en-1-one) (Bis1) (b) 3,3'-benzene-1,4-diylbis[1-(4-aminophenyl)prop-2-en-1-one] (Bis2) and (c) 3,3'-benzene-1,4-diylbis[1-(3,4-dimethoxyphenyl)prop-2-en-1-one] (Bis3).

and, hence, the thin sample approximation is valid [21]. The Z-scan experiments were performed for input pulse energy of 100 μJ, which corresponds to an on-axis-peak irradiance of 2.39 GW/cm<sup>2</sup>. The optical limiting study was performed by keeping the polymer samples at the focus of the lens and by varying the input laser energy and monitoring the output laser energy using two pyroelectric detectors with Laser Probe Rj-7620 Energy Meter.

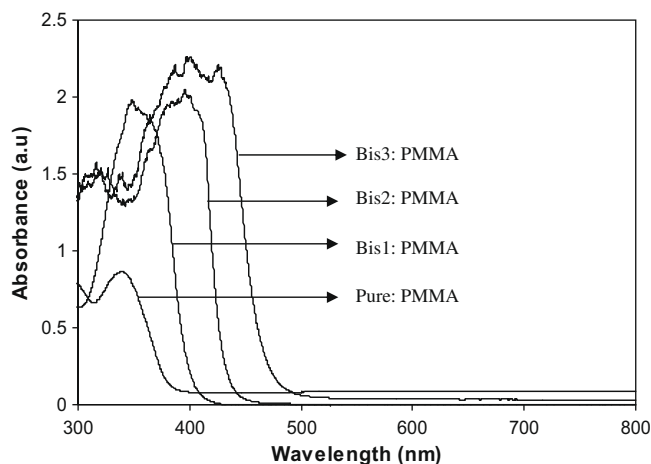


Fig. 3. UV-vis absorption spectrum of Bis1, Bis2, Bis3 and pure PMMA films.

### 3. Z-scan results and discussions

In the presence, high intensity laser beam, the total nonlinear absorption and nonlinear refraction not only depends linear indices (linear absorption coefficient  $\alpha$  and linear refractive index  $n$ ) but also becomes functions of nonlinear indices (nonlinear absorption coefficient  $\beta$  and nonlinear refractive index  $n_2$ ) expressed as,

$$\alpha(I) = \alpha + \beta I \tag{1}$$

$$n(I) = n + n_2 I \tag{2}$$

#### 3.1. Nonlinear absorption

If the input laser beam has a Gaussian transverse intensity distribution, then TPA-induced transmissivity change is described by [24–26],

$$T(z) = \ln \frac{[1 + q_0(z)]}{q_0(z)} \quad \text{for } |q_0(z)| < 1, \tag{3}$$

where,  $q_0(z) = \frac{\beta I_0 (1 - e^{-\alpha L})}{(1 + z^2/Z_0^2)\alpha}$   $\alpha$  is the linear absorption coefficient,  $L$  is the thickness of the sample,  $I_0$  is the on-axis-peak irradiance at the focus, and  $Z_0$  is the Rayleigh length.

The nonlinear absorption coefficient  $\beta$ , of Bischalcones in solution and in solid medium were determined by performing the open aperture Z-scan (i.e. without aperture). Figs. 4 and 5 shows the open aperture Z-scan traces for the Bis-chalcones Bis1, Bis2 and Bis3 in solution and in solid PMMA matrix (0.25 wt.%), which is found to be symmetric with respect to the focus indicating intensity-dependent absorption. If the nonlinear transmissivity change is due to the pure TPA process, then the nonlinear absorption coefficient  $\beta$  should be independent of the input intensity  $I_0$ . However, if there are addition nonlinear absorption process such as excited state absorption or three photon absorption, the apparently measured values of nonlinear absorption coefficient  $\beta$  will not remain constant [25,27,28]. One can see from the Fig. 6 and 7 the measured  $\beta$  values for the Bis-chalcones Bis1, Bis2 and Bis3 in solution and as well as in solid PMMA matrix are independent of the input intensity  $I_0$ . It is also supported by UV absorption spectra where the samples show negligible single photon absorption at 532 nm wavelength and the intensity-dependent transmissivity experiment [25,30], shown in the Figs. 8 and 9. Therefore, the major contribution to the observed nonlinear absorption in the Bischalcones is probably due to the TPA process. Bandgap energies of the films calculated from the UV-vis spectra shows that the Bis1 has bandgap of 3.55 eV (resonance peak at 350 nm), Bis2 has bandgap of 3.09 eV (resonance peak at 402 nm), and Bis3 has bandgap of

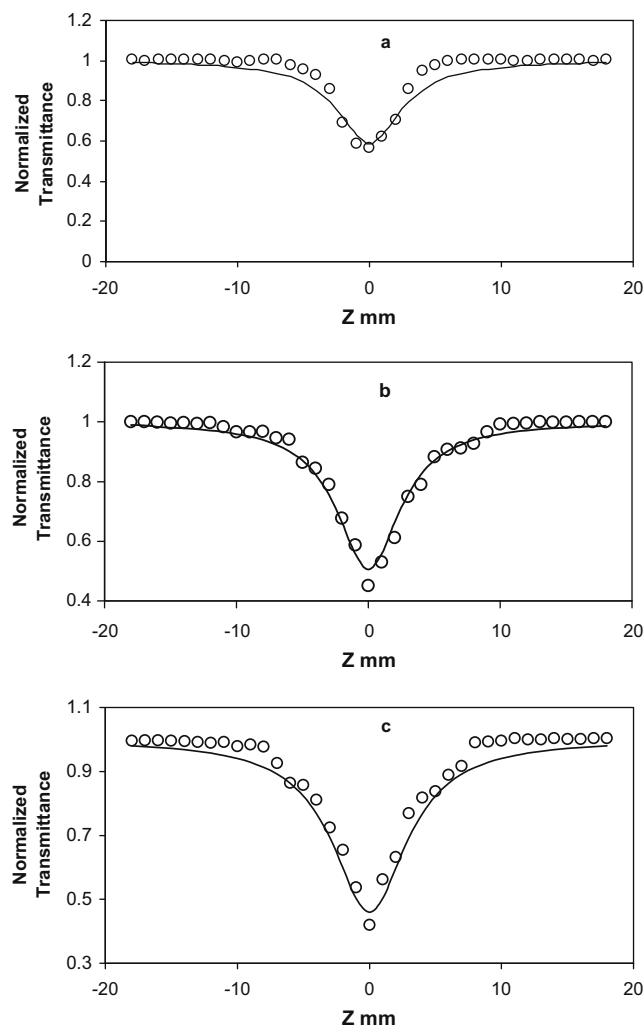


Fig. 4. Open aperture Z-scan traces of Bischalcones: (a) Bis1 (b) Bis2 (c) Bis3 in DMF solution. Solid line is a theoretical fit to the experimental data.

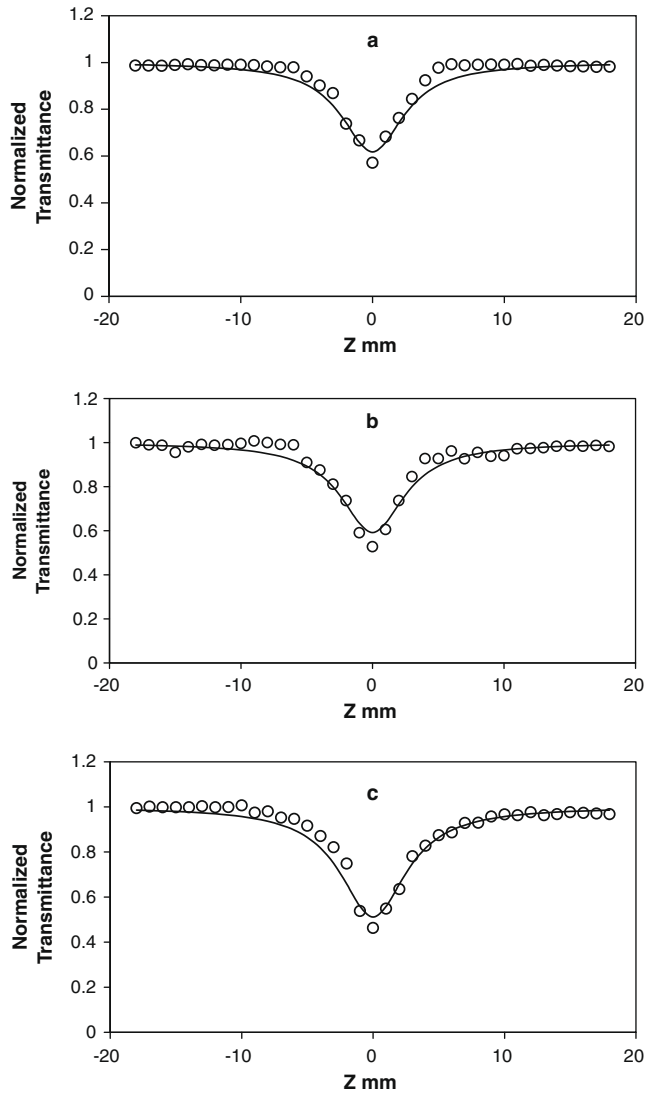
2.96 eV (resonance peak at 420 nm). At the experiment wavelength of 532 nm, the bandgap is found to be 2.34 eV. For the TPA mechanism to contribute to the nonlinear mechanism, the resonance peak should fall at 4.68 eV which is not true in our case. The possible reason could be, the redshift in the absorption maxima of the Bis3 and Bis2 in UV-vis spectrum on substitution, of electron donor groups indicating the increase in conjugation length. The improvement in nonlinear properties confirms the increase conjugation length. It is known that nonlinear absorption coefficient  $\beta$ , depends on the number of absorptive centers in a unit volume. Assuming that this number is  $N_0$ , in units of  $\text{cm}^{-3}$ , we have [25,29,30],

$$\beta = \alpha_2 N_0 = \sigma_2 N_A d \times 10^{-3} \tag{4}$$

Here,  $N_0$  is the molecular density of the sample (in units of  $1/\text{cm}^3$ ),  $\sigma_2$  is the molecular TPA coefficient (or cross-section) (in units of  $\text{cm}^4/\text{GW}$ ),  $d$  is the concentration of the chalcone in PMMA (in units of M/L), and  $N_A$  is the Avogadro number. For known  $\beta$  and  $d$ , the value of  $\sigma_2$  can be obtained. In the literature [25,30], molecular TPA cross-section (is in units of  $\text{cm}^4 \text{ s}/\text{photon}$ ) is also defined as,

$$\sigma'_2 = \sigma_2 h\nu \tag{5}$$

where  $\sigma'_2$  is in units of  $\text{cm}^4 \text{ s}$  and  $h\nu$  is the energy (in joules) of an incident photon.



**Fig. 5.** Open aperture Z-scan traces of Bischalcones: (a) Bis1 (b) Bis2 (c) Bis3 doped PMMA films (0.5%). Solid line is a theoretical fit to the experimental data.

Now the nonlinear absorption coefficient  $\beta$ , is related to the imaginary part of third-order nonlinear optical susceptibility through the equation [21],

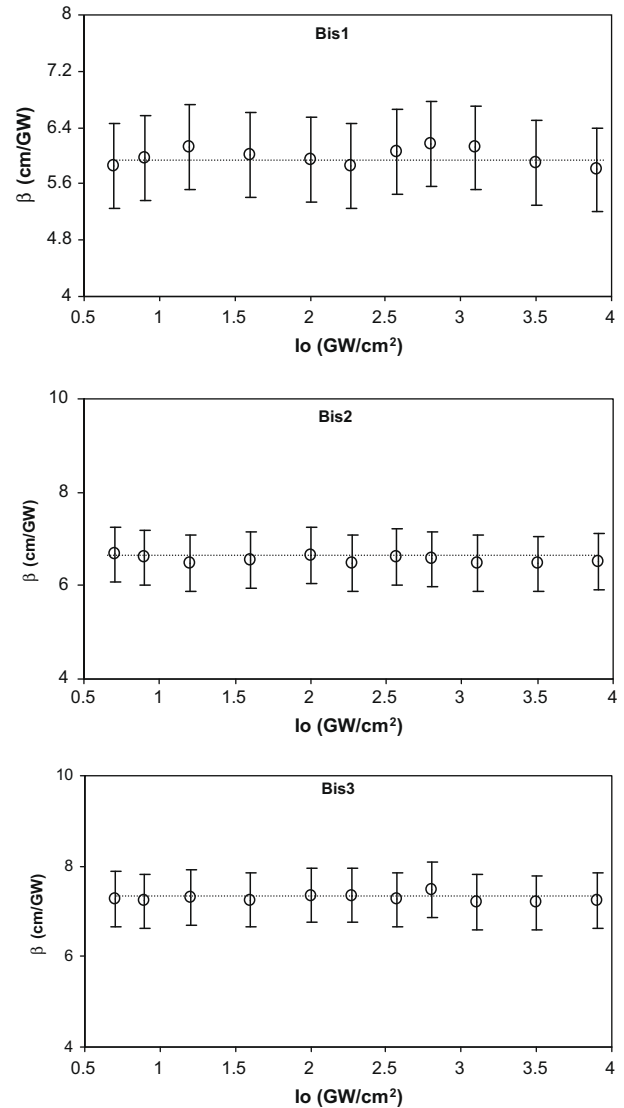
$$\text{Im}\chi^{(3)} = n_0^2 c \epsilon_0 \lambda \beta / 2\pi, \quad (6)$$

where  $n_0$  is the linear refractive index,  $\epsilon_0$  is the permittivity of free space and  $c$  is velocity of light in vacuum.

The measured values of molecular two-photon absorption cross-section of Bischalcones in PMMA are given in Table 1. The values  $\sigma_2$  of Bischalcones are nearly two orders of magnitude larger than the  $\sigma_2$  values of Rhodamine 6G which is  $10^{-48}$ – $10^{-50}$   $\text{cm}^4$  s/photon [31], and azoaromatic compounds which are of the order  $(1-6) \times 10^{-50}$   $\text{cm}^4$  s/photon [32] and are also comparable with the recently obtained values in asymmetric Zn(II) porphyrin complexes substituted in the meso or  $\beta$  pyrrolic position by  $-\text{C}=\text{C}-\text{C}_6\text{H}_4\text{X}$  moieties ( $\text{X} = \text{NMe}_2$  and  $\text{NO}_2$ ) [4].

### 3.2. Nonlinear refraction

To determine the sign and magnitude of nonlinear refraction closed-aperture Z-scan was performed by placing an aperture in front of the detector. Bischalcones doped polymer samples found



**Fig. 6.** Measured values of nonlinear absorption coefficient ( $\beta$ ) for Bis-chalcone Bis1, Bis2 and Bis3 in DMF solution.

to exhibit peak–valley characteristic, indicating negative nonlinear refraction or self defocusing effect. The nonlinear refractive index  $\gamma$  ( $\text{m}^2/\text{W}$ ) is given by the formula [21].

$$\gamma = \frac{\Delta\phi_0 \lambda}{2\pi L_{\text{eff}} I_0} (\text{m}^2/\text{W}), \quad (7)$$

where  $L_{\text{eff}} = \frac{(1-e^{-\alpha L})}{\alpha}$  and  $\Delta\phi_0$  is the on-axis phase change given by the equation,

$$\Delta\phi_0 = \frac{\Delta T_{\text{p-v}}}{0.406(1-S)^{0.25}} \quad \text{for } |\Delta\phi_0| \leq \pi \quad (8)$$

where  $\Delta T_{\text{p-v}}$  is the peak to valley transmittance difference and  $S$  is the linear aperture transmittance. Then nonlinear refractive index  $n_2$  (in esu) is related to  $\gamma$  ( $\text{m}^2/\text{W}$ ),

$$n_2(\text{esu}) = (cn_0/40\pi)\gamma(\text{m}^2/\text{W}) \quad (9)$$

Usually, the closed aperture Z-scan data also includes the contribution from nonlinear absorption, in order to extract the pure nonlinear refraction part, we followed the division method given by Sheik-Baha et al [21]. Figs. 10 and 11 show the pure nonlinear refraction curve obtained by division method. It is observed that the peak–valley of closed-aperture Z-scan satisfies the condition

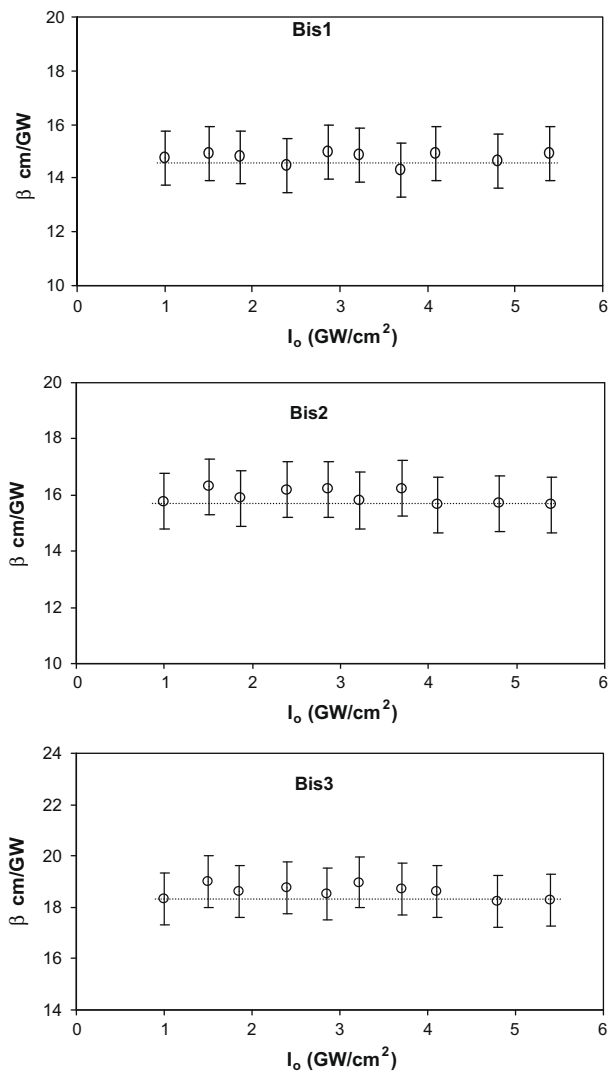


Fig. 7. Measured values of nonlinear absorption coefficient ( $\beta$ ) for Bis-chalcone Bis1, Bis2 and Bis3 doped PMMA film at various input intensity.

of  $\Delta Z \sim 1.7\Delta Z_0$ , thus confirming the third-order nonlinearity is due to electronic process [15]. The normalized transmittance for pure nonlinear refraction is given by [21]

$$T(Z) = 1 - \frac{4x\Delta\phi_0}{[(x^2 + 9)(x^2 + 1)]} \quad (10)$$

The nonlinear refractive index  $n_2$  (esu) is related to the real part of third-order nonlinear optical susceptibility through the equation [21]

$$\text{Re}\chi^{(3)} = 2n_0^2 c \epsilon_0 n_2 (\text{esu}) \quad (11)$$

where  $n_0$  is the linear refractive index,  $\epsilon_0$  is the permittivity of free space and  $c$  is velocity of light in vacuum.

Damage of the films was checked by using an optical microscope soon after performing the Z-scan measurements. We found there was no damage of the films at the region where Z-scan data was obtained at the input intensity used. While performing the Z-scan from  $-Z$  to  $+Z$ , it was again repeated by translating the sample from  $+Z$  to  $-Z$  and calculated the values, we did not found significant differences. The third-order nonlinear optical parameters of the Bischalcones in solid PMMA matrix given in Tables 1 and 2 found to be consistent in all the trials. To determine the any contributions from the solid PMMA matrix to the observed nonlinearity,

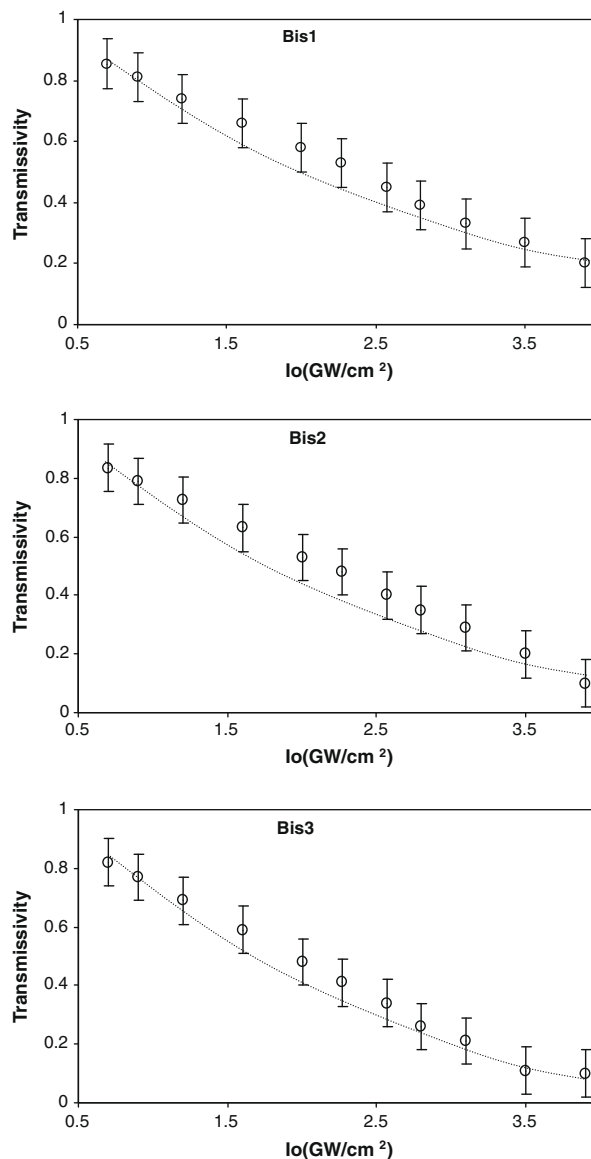
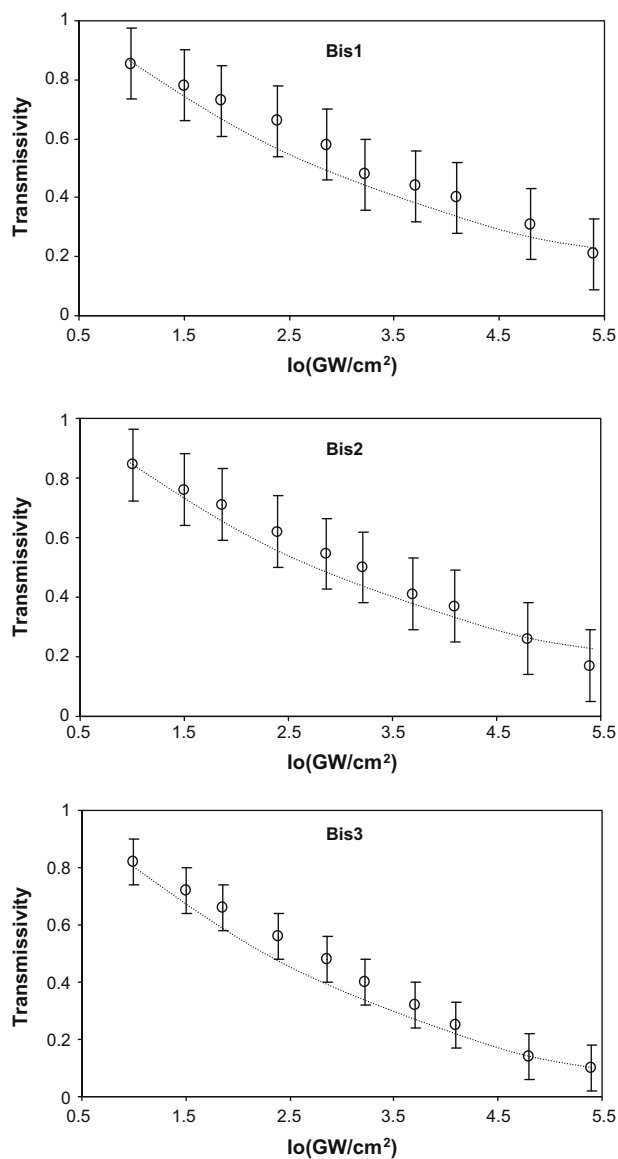


Fig. 8. Measured values of nonlinear absorption coefficient ( $\beta$ ) for Bis-chalcone Bis1, Bis2 and Bis3 in DMF solution.

we conducted Z-scan experiment on pure PMMA film (i.e. with 0 wt.% dopant concentration) and found negligible contribution both for nonlinear refraction and nonlinear absorption at the input energy used. Therefore any contribution from pure PMMA film to the observed nonlinearity is negligible at the input intensity used. It is evident that the total nonlinearity has significant contributions from both real and imaginary parts of third-order nonlinear optical susceptibility  $\chi^{(3)}$ . We expect the large nonlinearity in Bischalcone arises due to the electronic response to the applied optical field.

The Bischalcones investigated here are designed based on the scheme (D–A–A–D) donor–acceptor–acceptor–donor. Unlike the chalcones investigated earlier which had only two phenyl rings and one carbonyl group had connected through the electron transmitting bridge [10–14]. Here, we have three phenyl rings and two carbonyl group connected through conjugated  $\pi$ -bond system. Hence, there is an increase in the conjugation as a result the density of  $\pi$ -electrons is also increased, so one can expect enhancements in the nonlinear optical response of these molecules. The two carbonyl groups act as an electron accepting units. The amino and methoxy groups act as electron donating units. We found that



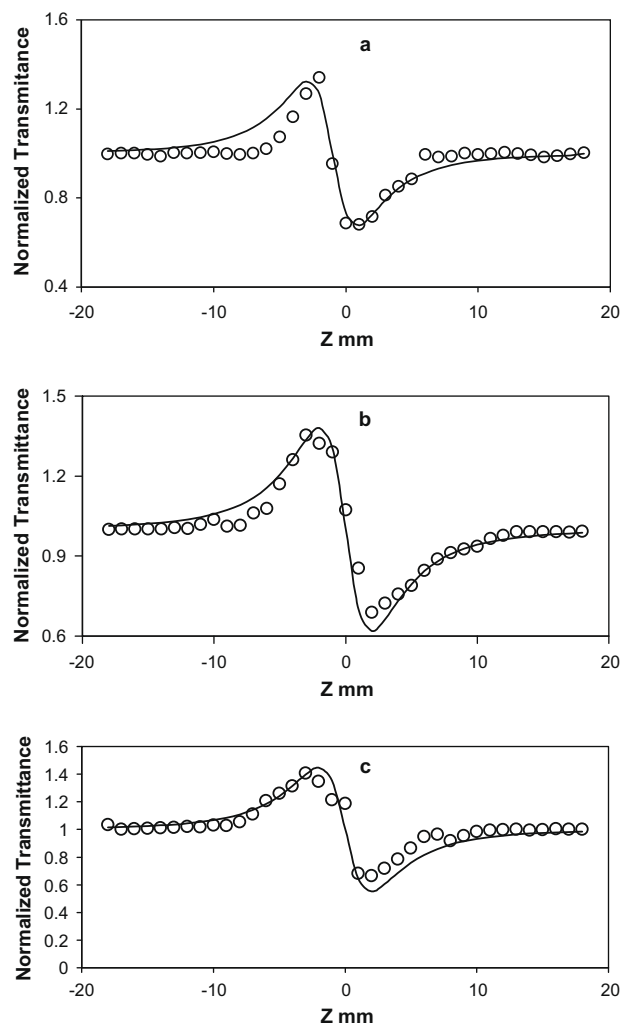
**Fig. 9.** Transmissivity as a function of input intensity levels for Bis-chalcone Bis3 doped PMMA film.

nonlinear optical response tends to increase on enhancing the electron donating ability of the donor units. Here charge transfer takes place from the ends of the molecule to the center. Hence, the large third-order nonlinear optical response arises due to the strong delocalization of  $\pi$ -electrons in Bischalcones. The current investigations show that there exists a relationship between the molecular structure and the nonlinear optical properties in the Bischalcones. The values of nonlinear absorption coefficient  $\beta_{\text{eff}}$ , nonlinear refractive index  $n_2$ , and the real and the imaginary parts of third-order nonlinear optical susceptibility  $\chi^{(3)}$ , of the Bischalcones in solid PMMA matrix are given in Table 2. The real and imaginary parts of third-order nonlinear optical susceptibility

**Table 1**

Third-order nonlinear optical parameters of Bischalcones in DMF solution at concentration of  $3 \times 10^{-2}$  mol/L.

Sample in DMF	$n_2 (\times 10^{-11}$ esu)	$\beta$ (cm/GW)	$\text{Re } \chi^{(3)} (\times 10^{-13}$ esu)	$\text{Im } \chi^{(3)} (\times 10^{-14}$ esu)	$\sigma (\times 10^{-19}$ cm <sup>4</sup> /GW)	$\sigma' (\times 10^{-47}$ cm <sup>4</sup> s/photon)
Bis1	-1.964	5.917	-2.005	8.861	3.274	12.185
Bis2	-2.226	6.508	-2.344	9.752	3.376	12.565
Bis3	-2.638	7.337	-2.794	11.08	3.802	14.151



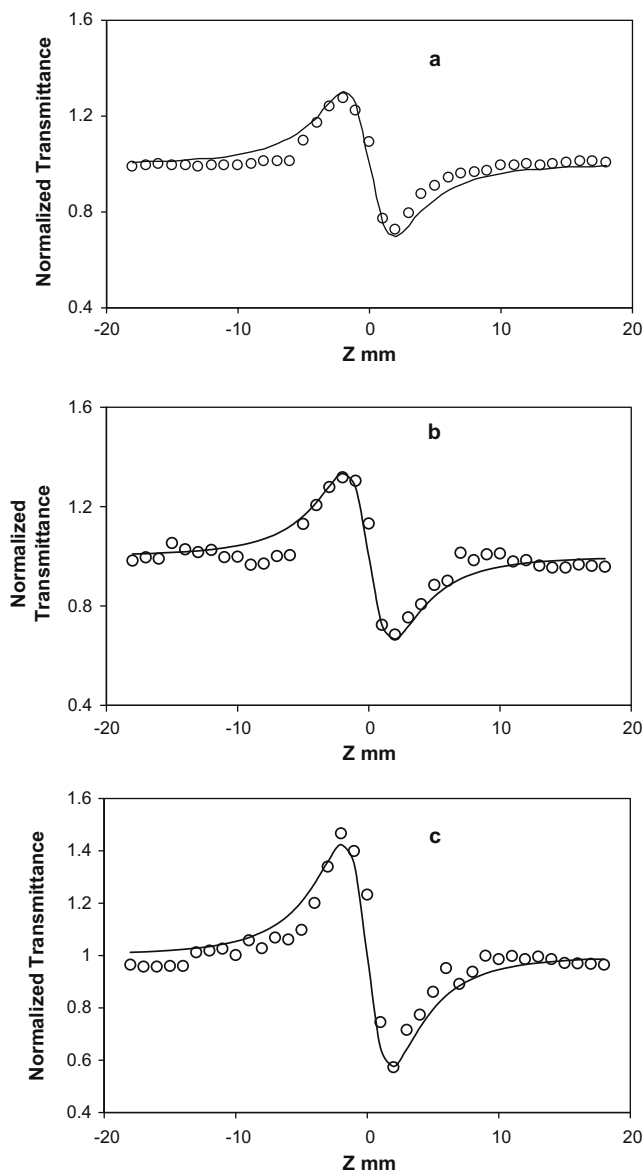
**Fig. 10.** Pure nonlinear refraction Z-scan traces of Bischalcones: (a) Bis1 (b) Bis2 (c) Bis3 in DMF solution. Solid line is a theoretical fit to the experimental data.

$\chi^{(3)}$ , are one order larger when compared to the values obtain by John Kiran et al. [10,11], Shettigar et al. [12,13] and Ravidra et al. [14] and also found be comparable with values obtained by Sun et al. [33,34] for stilbazolium derivatives, a well-known class of optical materials for photonics and biophotonics applications.

#### 4. Optical power limiting studies

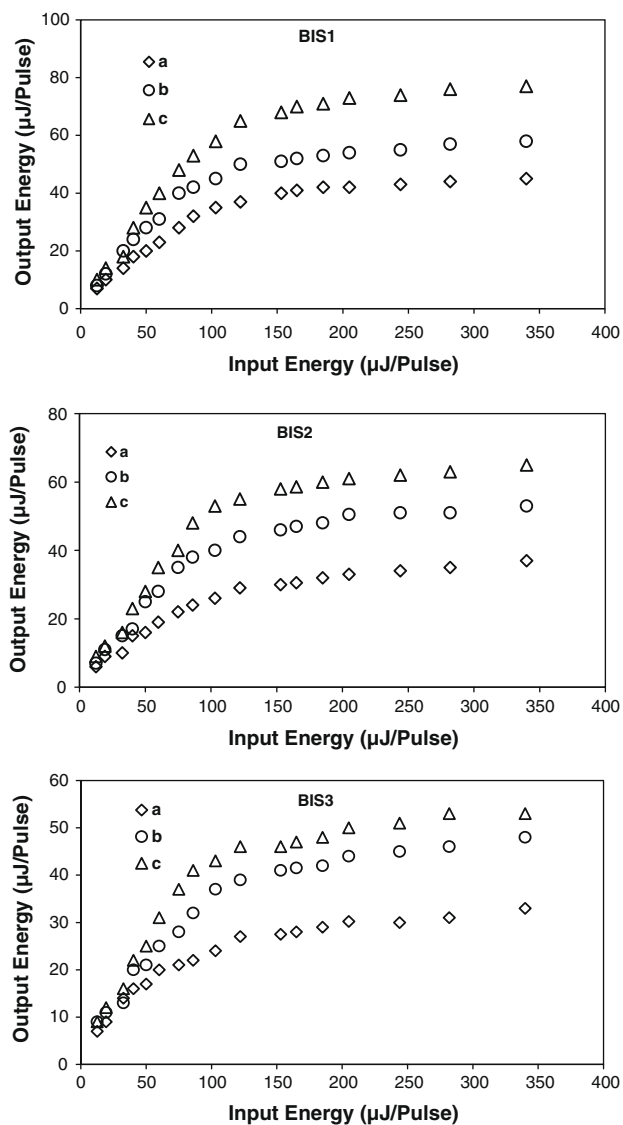
Optical power limiting is an area of growing interest due to applications such as eye and sensor protection against intense light [2,35]. The nonlinear optical process leading to optical power limiting includes two-photon absorption, free carrier absorption, reverse saturable absorption and nonlinear scattering. Advantages of using the materials exhibiting pure TPA process is that, they have very high initial transmission for weak optical signals, very fast response to a change in the intensity of the input optical sig-





**Fig. 11.** Pure nonlinear refraction Z-scan traces of Bischalcones (a) Bis1 (b) Bis2 (c) Bis3 doped PMMA films (0.5%). Solid line is a theoretical fit to the experimental data.

nals, retention of the optical quality of the input beam after passing through the nonlinear medium [25]. The Bischalcones investigated here found to possess TPA mechanism as a major contribution to nonlinear absorption. Therefore, we expect these molecules to exhibit good optical power limiting properties based on TPA. Optical



**Fig. 12.** Optical power limiting behavior of Bis-chalcones Bis1, Bis2 and Bis3 in DMF solutions.

power limiting experiments were performed by placing the sample at the focus of the laser beam and by measuring the transmitted energy for different input laser energies. Fig. 12 shows the optical power limiting behavior of Bis-chalcone Bis1, Bis2 and Bis3 in DMF solutions. The Bis-chalcone Bis1 exhibits optical limiting threshold of ~150, ~120 and ~100 μJ, with the output energy clamped at ~75, ~58 and ~44 μJ, respectively, at concentrations of  $1 \times 10^{-2}$ ,

**Table 2**  
Third-order nonlinear optical parameters at various concentrations of Bischalcones in PMMA matrix.

Sample in PMMA	Dopant concentration (wt.%)	$\beta$ (cm/GW)	$\sigma$ ( $\times 10^{-19}$ cm <sup>4</sup> /GW)	$\sigma'$ ( $\times 10^{-46}$ cm <sup>4</sup> s/photon)	$n_2$ ( $\times 10^{-11}$ esu)	Re $\chi^{(3)}$ ( $\times 10^{-12}$ esu)	Im $\chi^{(3)}$ ( $\times 10^{-12}$ esu)
Bis1	0.5	14.6	14.180	5.524	-5.1	-0.6	0.2
	1.0	19.72	8.480	3.163	-6.2	-0.7	0.3
	1.5	24.2	7.652	2.854	-9.1	-1.0	0.4
Bis2	0.5	15.5	16.410	6.120	-5.8	-0.6	0.2
	1.0	21.6	10.150	3.786	-7.7	-0.9	0.3
	1.5	25.6	8.826	3.283	-9.4	-1.1	0.4
Bis3	0.5	18.4	24.110	8.993	-7.3	-0.8	0.3
	1.0	23.0	13.200	4.998	-8.6	-1.0	0.4
	1.5	27.2	11.690	4.368	-9.6	-1.1	0.5

$1.5 \times 10^{-2}$  and  $3.0 \times 10^{-2}$  mol/L. The Bis-chalcone Bis2 exhibits optical limiting threshold of  $\sim 130$ ,  $\sim 115$  and  $\sim 103 \mu\text{J}$ , with the output energy clamped at  $\sim 63$ ,  $\sim 50$  and  $\sim 35 \mu\text{J}$ , respectively, at concentrations of  $1 \times 10^{-2}$ ,  $1.5 \times 10^{-2}$  and  $3.0 \times 10^{-2}$  mol/L. The Bis-chalcone Bis3 exhibits optical limiting threshold of  $\sim 100$ ,  $\sim 80$  and  $\sim 85 \mu\text{J}$ , with the output energy clamped at  $\sim 50$ ,  $\sim 45$  and  $\sim 30 \mu\text{J}$ , respectively, at concentrations of  $1 \times 10^{-2}$ ,  $1.5 \times 10^{-2}$  and  $3.0 \times 10^{-2}$  mol/L. Fig. 13 shows the optical power limiting behavior of Bis-chalcones Bis1, Bis2 and Bis3 in PMMA matrix at various doping concentrations. The Bis-chalcone Bis1 exhibits the optical limiting threshold of  $\sim 110$ ,  $\sim 92$  and  $\sim 80 \mu\text{J}$  with the output energy clamped at,  $\sim 115$ ,  $\sim 70$  and  $\sim 37 \mu\text{J}$  at dopant concentrations 0.5%, 1.0% and 1.5% respectively. The Bis-chalcone Bis2 exhibits the optical limiting threshold of  $\sim 92$ ,  $\sim 80$  and  $\sim 70 \mu\text{J}$  with the output energy clamped at,  $\sim 60$ ,  $\sim 44$ , and  $\sim 33 \mu\text{J}$  at dopant concentrations 0.5%, 1.0% and 1.5% respectively. The Bis-chalcone Bis3 exhibits the optical limiting threshold of  $\sim 82$ ,  $\sim 70$  and  $\sim 64 \mu\text{J}$  with the output energy clamped at,  $\sim 50$ ,  $\sim 40$  and  $\sim 28 \mu\text{J}$  at dopant concentrations 0.5%, 1.0% and 1.5% respectively. We found that the film was damaged when the input energy was increased beyond  $400 \mu\text{J}/\text{Pulse}$ . So we repeated the optical limiting experiment again by increasing the input energy up to  $350 \mu\text{J}/\text{Pulse}$  and also we noted the energy while decreasing the input energy, the reverse path was found to be same as the initial

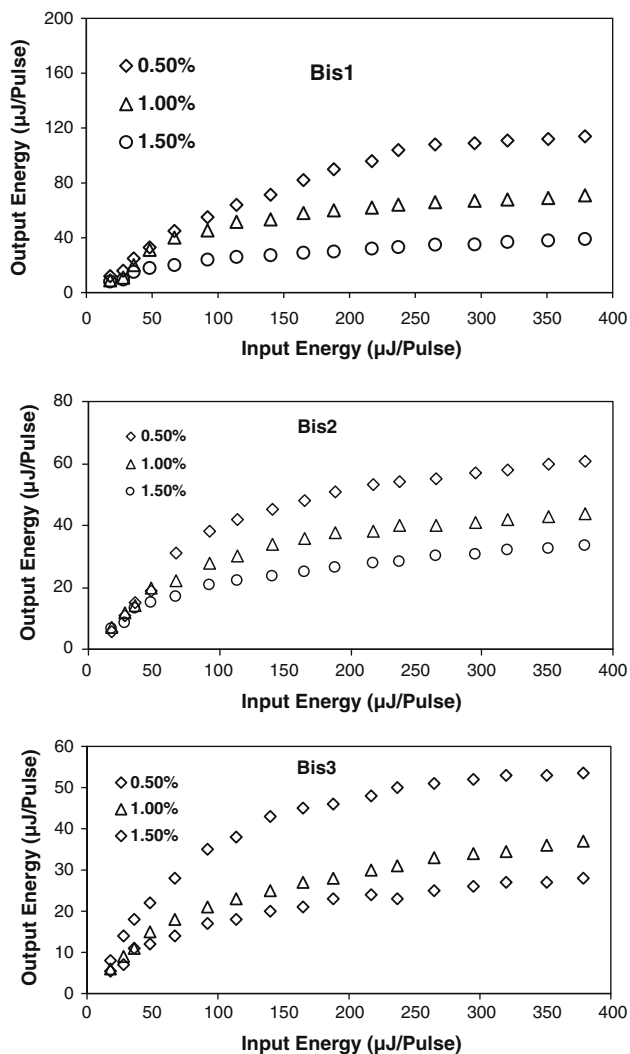


Fig. 13. Optical power limiting behavior of Bis-chalcones Bis1, Bis2 and Bis3 in PMMA at various dopant concentrations.

which confirmed that the film was not damaged up to  $350 \mu\text{J}/\text{Pulse}$ . The threshold damage for the films is around  $400 \mu\text{J}/\text{Pulse}$  which corresponds to on-axis peak irradiance of  $9.56 \text{ GW}/\text{cm}^2$ . All the three Bischalcones investigated here found to exhibit good optical power limiting of nanosecond laser pulses at  $532 \text{ nm}$  wavelengths. The bischalcone Bis3, showed good optical power limiting response compared to other two molecules due to the strong electron donating nature of the two methoxy groups attached at both the ends of the molecule. Thus, the Bischalcones doped in solid PMMA matrix seems to be promising candidates for making optical power limiting devices.

## 5. Conclusions

In summary, third-order nonlinear optical parameters of three Bischalcone molecules in DMF solution and in PMMA matrix were studied using Z-scan technique. Z-scan measurements indicate that the Bischalcones exhibits negative nonlinear refractive index. The real and imaginary parts of third-order nonlinear optical susceptibility were found to be as large as  $10^{-12} \text{ esu}$ . We also measured the molecular two-photon absorption cross-section of these molecules. The molecular two-photon absorption cross-section was of the order  $10^{-46} \text{ cm}^4/\text{s/photon}$  which is nearly two orders of magnitude large compared to that of Rhodamine dyes. Two-photon absorption was found to be the major contribution to the observed nonlinear absorption. The Bischalcones studied here exhibits good optical power limiting of nanosecond laser pulses at  $532 \text{ nm}$  wavelength in both solution and as well as in solid state form. Hence, the Bischalcone derivatives investigated here emerge as promising class of materials for future photonic and optoelectronic applications.

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