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Studies on third-order nonlinear optical properties of chalcone derivatives in polymer host

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Abstract

In this paper we present the experimental study of the third-order nonlinear optical properties of two chalcone derivatives, viz., 1-(4-methoxyphenyl)-3-(4-butyloxyphenyl)-prop-2-en-1-one and 1-(4-methoxyphenyl)-3-(4-propyloxyphenyl)-prop-2-en-1-one in PMMA host, with the prospective of reaching a compromise between good processability and high nonlinear optical properties. The nonlinear optical properties have been investigated by Z-scan technique using 7 ns laser pulses at 532 nm. The nonlinear refractive index, nonlinear absorption coefficient, magnitude of third-order susceptibility and the coupling factor have been determined. The values obtained are of the order of 10^{-14} cm^2/W, 1 cm/GW, 10^{-13} esu and 0.2, respectively. The molecular second hyperpolarizability for the chalcone derivatives in polymer is of the order of 10^{-31} esu. Different guest/host concentrations have also been studied. The results suggest that the nonlinear properties of the chalcones have been improved when they are used as dopants in polymer matrix. The nonlinear parameters obtained are comparable with the reported values of II–VI compound semiconductors. Hence, these chalcons are a promising class of nonlinear optical dopant materials for optical device applications.
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1. Introduction

Nonlinear optical (NLO) materials with large intensity dependent refractive index and absorption coefficient are very useful for optical device applications. These parameters determine whether an intense laser beam will undergo self focusing or self defocusing as it propagates in the material medium [1]. An NLO effect in the organic molecules originates from a strong donor–acceptor intermolecular interaction due to delocalized π-electrons. Chalcone derivatives have such a configuration, with two planar rings connected through a conjugated double bond [2], and hence, show significant nonlinearity.

The chalcone samples cannot be used directly since they could get degraded or bleached when exposed to strong laser light. In order to overcome these drawbacks and for effective use of these materials in devices they can be doped into a polymer matrix. This is expected to increase the opto-chemical and opto-physical stability and provide sufficient concentration of absorptive or fluorescent centers [3].

Here we report an experimental investigation of the third-order nonlinear optical parameters of 1-(4-methoxyphenyl)-3-(4-butyloxyphenyl)-prop-2-en-1-one (BN1) and 1-(4-methoxyphenyl)-3-(4-propyloxyphenyl)-prop-2-en-1-one (BN2) in poly(methylmethacrylate) (PMMA) with

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single beam Z-scan technique [4]. The results have been compared with the pure molecules.

2. Experimental

The chalcones have been synthesized by taking 4-methoxy-acetophenones in ethanol (0.01 mol) mixed with 4-butyloxy/propyloxy-benzaldehydes (0.01 mol) in ethanol and the mixture was treated with an aqueous solution of potassium hydroxide (20 ml, 5%). This mixture was stirred well and kept aside for 24 h. The resulting solid mass was collected by filtration. The compounds were dried and recrystallized three to four times with ethanol [5]. The structure of the compounds is given in Fig. 1. About 5 wt% of the synthesized chalcone compounds have been used as dopant in PMMA matrix. Samples were prepared by solution technique using research grade DMF.

The liquid samples of concentration of 0.8×10^{-4} mol/L were taken in a quartz cell of 1 mm thickness for measurement purpose. The Z-scan experiment was performed using 532 nm laser pulses of 7 ns duration. The output beam has a Gaussian intensity profile and was focused, using a lens of 25 cm focal length, to a waist of radius (ω_0) 25 μm (maximum), which corresponds to a Rayleigh range z_0 of 3.7 mm. The input energy used was 0.8 mJ. A partially closed aperture was placed at the entrance of the detector and the detector output was monitored as the sample translated along the beam axis (Z-axis) in the focal region of the focusing lens. To obtain the open aperture Z-scan data, the aperture was removed.

The concentration dependent experiment has also been performed by taking different wt% of the chalcones in PMMA matrix. The optical limiting study was performed by keeping the sample at the focus in 1 mm thick cuvette.

UV–vis spectra shown in Fig. 2 for the samples, obtained using UV-160A (Shimadzu) spectrophotometer in the wavelength region 200–800 nm, show that they have no linear absorption at a wavelength of 532 nm. The PMMA absorption peak is observed at approximately 300 nm. This peak is not seen separately in the absorption spectrum of chalcone:PMMA sample as it is merged with it. Linear refractive index values of the samples used in the experiment were measured using Abbe's refractometer.

3. Results and discussion

In order to determine the sign of third-order susceptibility ($\chi^{(3)}$) and to investigate the relative contributions from its real

and imaginary parts, Z-scan studies were conducted in 0.8×10^{-4} mol/L solutions of chalcones doped PMMA. Fig. 3 shows the experimental Z-scan data for BN1 doped PMMA. The measurement of open aperture Z-scan data enables the separation of nonlinear refractive index from the nonlinear absorption by dividing closed aperture data by open one [4,6]. Similar curves, shown in Fig. 4, have been obtained for BN2 doped PMMA with the same input energy.

3.1. Nonlinear refraction

The real part of $\chi^{(3)}$ is related to the nonlinear refraction coefficients by [4]

$$\chi_R^{(3)} = 2n_0^2 \varepsilon_0 c n_2 \tag{1}$$

$$n_2 = \frac{\Delta\phi\lambda}{2\pi I_0 L_{eff}}. \tag{2}$$

In this equation, $L_{eff} = \frac{1 - e^{\alpha L}}{\alpha}$. Here L is the sample length; I_0 is the irradiance within the sample.

In the limit of linear absorption $\alpha \to 0$ and $L_{eff} = L$.

The real $\chi^{(3)}$ values of the chalcones in PMMA matrix are given in Table 1.

On an atomic or molecular scale, the nonlinear response can be described in terms of the local electric field (E_{loc}) that the atom or the molecule experiences, which for isotropic media is related to the incident electric field, E by the equation,

$$E_{loc} = (n_0^2 + 2)E/3, \tag{3}$$

where n_0 is the linear refractive index of the medium. The nonlinear induced polarization per molecule is then described by the microscopic susceptibilities, i.e. the hyperpolarizabilities. For third-order effects, the corresponding hyperpolarizability γ is related to the susceptibility by the equation [7,8]

$$\gamma = \chi^{(3)}/N_c L, \tag{4}$$

where N_c is the molecular number density in cm^{-3} (no. of moles/cc) and L is the Lorentz field-factor, which may be approximated by $[(n_0^2 + 2)/3]^4$. The value of molecular second hyperpolarizability given in Table 1 is of the order 10^{-31} esu, which is well comparable with the value reported for silicon naphthalocyanine, SiNc ($\gamma = 1.7 \times 10^{-31}$ esu), a widely known optical limiting material [9] and also the most interesting optical limiting organic material *trans*-4-[2-(pyrrl)vinyl]-1-methylpyridium iodide[PVPI] – a stilbazolium like dye ($\gamma = 1.6 \times 10^{-31}$ esu in methanol at 6.8 ns laser pulses at 532 nm) [10].
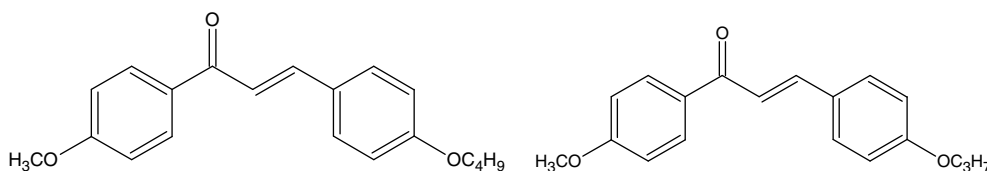
Fig. 1. Structure of the compounds: (a) 1-(4-methoxyphenyl)-3-(4-butyloxyphenyl)-prop-2-en-1-one; (b) 1-(4-methoxyphenyl)-3-(4-propyloxyphenyl)-prop-2-en-1-one.
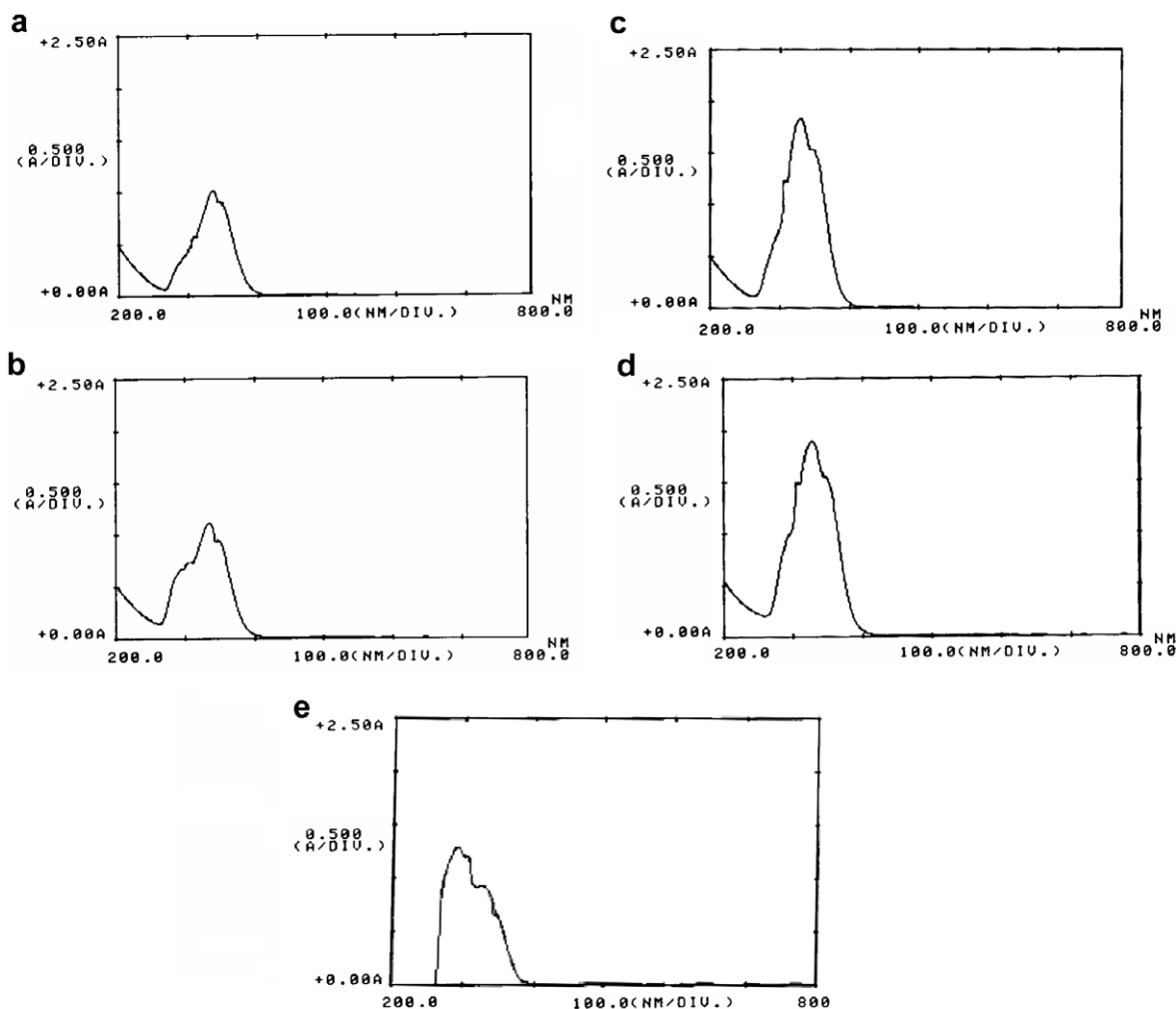
Fig. 2. UV–vis spectra of chalcones: (a) pure BN1; (b) BN1:PMMA; (c) pure BN2; (d) BN2:PMMA; (e) pure PMMA.

In Fig. 5, we report the NLO coefficient of the polymer at different guest concentrations. We can see a good linearity of the $\chi^{(3)}$ value as a function of the guest concentration, in particular if one excludes the contributions from matrix and the solvent [11].

It should be pointed out that the Z-scan method could be very sensitive as a way to locate the focus of the laser beam. Any uncertainty in the location may lead to the change in ΔT_{p-v} and the distortions appear on Z-scan signals. To compensate, the third-order nonlinearities are often associated with large error bars [12].

Under identical conditions, $\chi^{(3)}$ values for pure BN1 and BN2 molecules in DMF solvent are found to be 0.563×10^{-13} esu and 0.23×10^{-13} esu, respectively.

The methoxy group in the phenyl ring attached to propene does not possess an unshared pair of electrons. Yet it is a ring activator. Apart from the electron pumping effect, this group attached to the conjugate system is known to exhibit a special type of resonance called hyperconjugative or no bond resonance. Hence the electron density of the phenyl ring attached, is enhanced. As a result, there is a greater donation of π-electrons to the acceptor.

Thus the introduction of electron donors or ring activators into the phenyl ring results in an increase in the magnitude of the dipole moment which leads to large nonlinear susceptibilities [13].

The results also show that the chalcones exhibit larger third-order NLO properties in PMMA host compared to the pure compounds. This is because, a polymeric chain with only saturated bonds – all σ bonds on the backbone does not give large polarizabilities, because, all the electrons will be completely localized at the carbon atoms. The π-electrons associated with the dopant molecules will form a cloud around the chain and can be distorted by applying an electric field. This ease of polarizability of polymers makes them attractive candidates for nonlinear optics.

The $\chi^{(3)}$ value of BN1 in PMMA matrix is seen to be higher than that of BN2 in PMMA, which is due to higher conjugation of butyloxy phenyl donor group.

3.2. Nonlinear absorption

The intensity-dependent nonlinear transmission of the sample BN1 in PMMA matrix, shown in Fig. 6, dropped
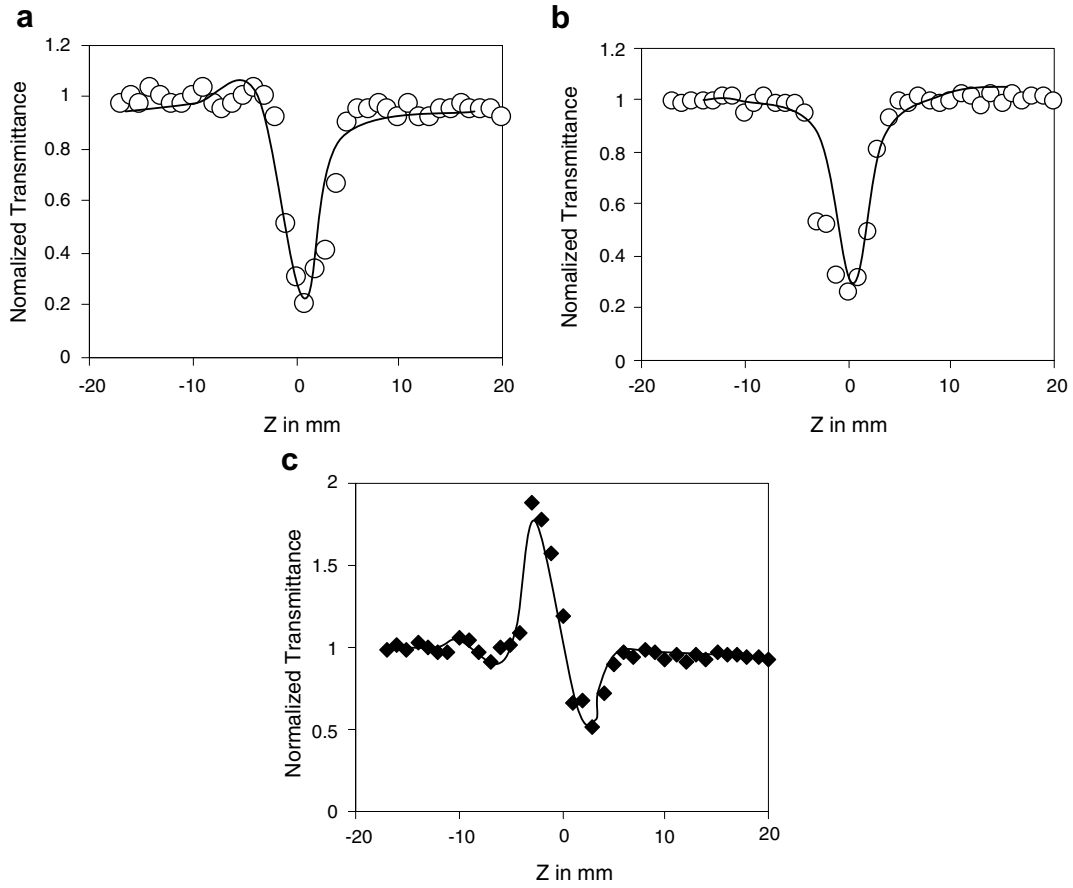
Fig. 3. Z-scan curves of BN1:PMMA: (a) closed aperture; (b) open aperture; (c) pure nonlinear refraction.
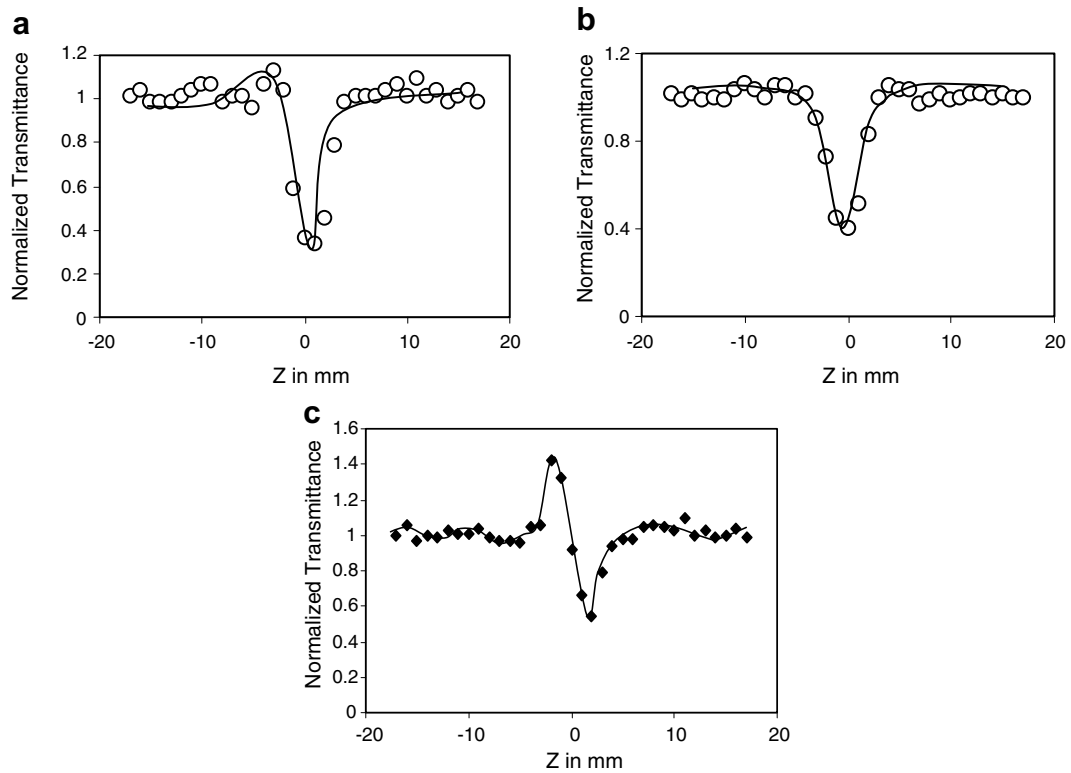

Fig. 4. Z-scan curves of BN2:PMMA: (a) closed; (b) open; (c) pure nonlinear refraction.

Table 1
Third-order nonlinear parameters of chalcones in PMMA host

Sample	$\Delta\Phi_0$	n_2 (10^{-14} cm^2/W)	$\chi_R^{(3)}$ (10^{-13} esu)	γ (10^{-31} esu)
BN1:PMMA	4.796	−2.207	−0.876	1.42
BN2:PMMA	3.074	−1.594	−0.584	0.98

$\chi^{(3)}$ Values for pure BN1 and BN2 in DMF solvent are 0.563×10^{-13} esu and 0.23×10^{-13} esu, respectively.

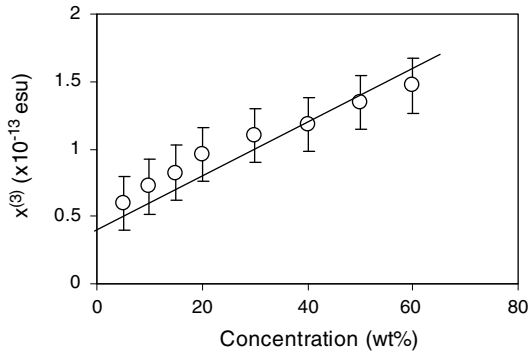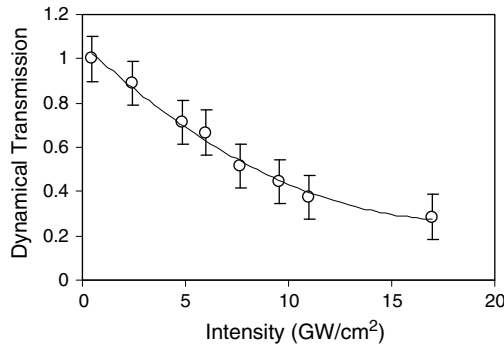Fig. 5. Dependence on the molecular concentration of the NLO coefficient of BN1:PMMA.

Fig. 6. Measured dynamical transmission of BN1:PMMA.

Fig. 7. Measured values of nonlinear absorption coefficients of chalcones in PMMA at various input intensity levels.

from 1.0 to 0.286 as the input intensity increased from 0.48 to 16.98 GW/cm^2. Similar curve has been obtained for BN2 in PMMA matrix.

However the sample has negligible linear absorption at the operating laser wavelength, 532 nm. Hence the drop in the transmission of the sample is ascribed to the nonlinear two photon absorption (TPA). It is confirmed by intensity-dependent nonlinear absorption coefficient (Fig. 7), described by [14,15]

$$dI/dz = -\beta I^2, \tag{5}$$

where β is the nonlinear absorption coefficient.

The solution of Eq. (4) may be written as

$$I(z) = I_0/(1 + \beta z I_0), \tag{6}$$

where I_0 is the initial input intensity. Hence the dynamic transmissivity can be written as

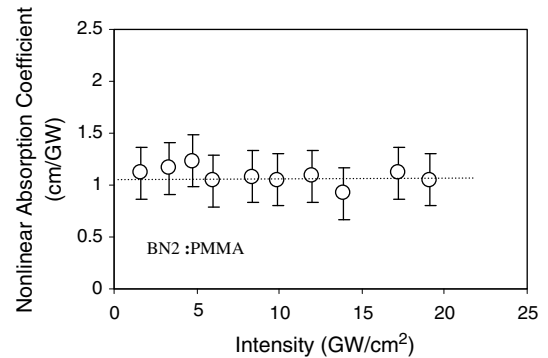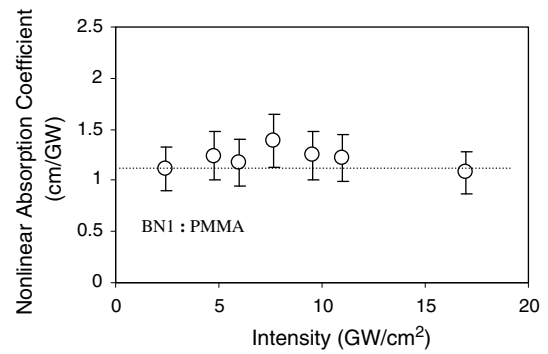$$T(I_0, z) = I(z)/I_0 = 1/(1 + \beta z I_0). \tag{7}$$

The above results are true if the input is a plane wave with a uniform transverse intensity distribution. For a Gaussian transverse intensity distribution, the TPA-induced transmissivity change is described by

$$T(z) = \frac{\ln[1 + q_0(z)]}{q_0(z)}, \tag{8}$$

where $q_0(z) = \frac{\beta I_0 L_{\text{eff}}}{(1 + z^2/z_0^2)}$. When there is no linear absorption, $\alpha \rightarrow 0$, $L_{\text{eff}} = L$, the thickness of the nonlinear medium.

The imaginary part of the susceptibility is related to nonlinear absorption, β by

$$\text{Im}\,\chi^{(3)} = (n_0^2 \varepsilon_0 c\lambda/2\pi)\beta. \tag{9}$$

Introducing the coupling factor ρ, the ratio of imaginary part to real part of third-order nonlinear susceptibility,

$$\rho = \text{Im}\,\chi^{(3)}/\chi_R^{(3)} = \beta/2k\gamma_{\text{esu}}. \tag{10}$$

The observed values of coupling factor given in the Table 2 is seen to be less than 1/3, which indicates that the nonlinearity is electronic in origin.

It is known that, the nonlinear absorption coefficient, β is dependent on the number of absorptive centers in a unit

Table 2
Nonlinear absorption parameters of chalcones in PMMA host

Sample	$\Delta\Psi_0$	β (cm/GW)	$\mathrm{Im}\chi^{(3)}$ (10^{-13} esu)	σ_2 (10^{-19} cm^4/GW)	σ_2' (10^{-46} cm^4 s/Photon)	ρ
BN1:PMMA	1.05	1.136	0.191	2.4	0.90	0.218
BN2:PMMA	0.856	1.045	0.163	2.2	0.82	0.279

volume. Assuming this number is N_0 in units of cm^{-3}, then for a solution system, we have [14,16],

$$\beta = \sigma_2 N_0 = \sigma_2 N_A d \times 10^{-3}. \qquad (11)$$

Here N_0 is the molecular density of the sample (in units of 1/cm^3), σ_2 is the molecular TPA coefficient (or cross-section) of the same compound (in units of cm^4/GW), d is the concentration of TPA compound in the solution (in units of mol/L), and N_A is the Avogadro number. For a known β and d, the value of σ_2 can be easily calculated.

In the literature, another definition of the molecular TPA cross-section is sometimes used,

$$\sigma_2' = \sigma_2 h\upsilon, \qquad (12)$$

where σ_2' is in units of cm^4 s and $h\upsilon$ is the energy (in Joules) of an incident photon.

The results of nonlinear absorption of the chalcones doped PMMA are given in Table 2.

3.3. Optical power limiting studies

Optical power limiting characteristic is ideal for use in optical peak-power (peak-intensity) stabilization. The prin-

ciple of this type of optical stabilization is based on the fact that a larger input intensity change only leads to a smaller output intensity change. This means that a larger input peak-power fluctuation will lead to a smaller output fluctuation by passing through a nonlinear absorptive medium with a larger β value.

For optical power limiting studies, we have used samples with the same concentration as used for Z-scan measurements. The experiment was performed by keeping the sample at the focus. The input laser pulse energy was steadily increased and the output energy was recorded. Fig. 8 shows the optical power limiting behavior of chalcone in PMMA host. The output energy increases linearly for an input energy less than 0.2 mJ/pulse in BN1:PMMA and 0.15 mJ/pulse BN2:PMMA.

The variation in the limiting threshold is due to the variation in conjugation length and the presence of acceptor/donor end groups [17] in the compound. Since the third-order nonlinear response arises due to delocalisation of the electron, the power limiting is ascribed to the two photon absorption mechanism [18,19].

4. Conclusions

The third-order nonlinear parameters of newly synthesized delocalized π-conjugate systems, chalcones in PMMA matrix, have been investigated by Z-scan technique. The molecules show negative nonlinearity. The results show that the chalcones exhibit larger third-order NLO properties in PMMA host as compared to the pure compounds. The change in the nonlinear parameters was observed when butyloxy group was replaced by propyloxy group. Both class of molecules show good optical limiting behavior. The third-order nonlinear parameters of the newly synthesized samples compare favourably with those for semiconductors such as ZnSe, CdS, and ZnTe [12] and the most interesting optical limiting organic material trans-4-[2-(pyrrl)vinyl]-1-methylpyridium iodide[PVPI]. Hence the chalcones in PMMA host may be suitably used for optical device applications including optical peak-power stabilizer.

Fig. 8. Optical power limiting behavior of: (a) BN1:PMMA and (b) BN2:PMMA.

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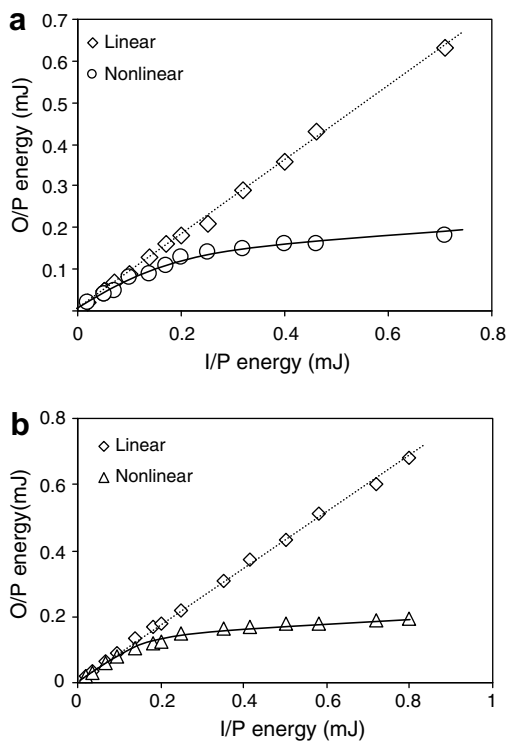[5] D.N. Dhar, The Chemistry of Chalcones and Related Compounds, Wiley, New York, 1981.

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