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Third order nonlinear optical properties and two photon absorption in newly synthesized phenyl sydnone doped polymer

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Abstract

We have investigated third order nonlinear optical properties of three newly synthesized 3-phenyl sydnones, doped into PMMA and determined both real and imaginary part of $\chi^{(3)}$. The measurements were performed using nanosecond laser pulses at 532 nm wavelength by employing Z-Scan technique. The nonlinear refractive index is found to be of the order of 10^{-14} cm^2/W. The magnitude of third order susceptibility is of the order of 10^{-13} esu. Their two photon absorption coefficient and absorption cross section have also been determined. The optical power limiting behavior of sydnone moieties doped PMMA was also investigated. The results suggest that among the three organic phenyl sydnone moieties, 2-benzylhydrazono-5-(3-*p*-tolylsydnone-4-yl)1,3,4,-thiadiazine doped PMMA is a promising class of nonlinear optical material due to its simple molecular structure with *p*-tolyl group. It also shows a very good optical limiting behaviour with a limiting threshold of 0.21 mJ/pulse. The nonlinear parameters obtained are comparable with the values obtained in stilbazolium like dye such as *trans*-4-[2-(pyrrl)vinyl]-1-methylpyridium iodide. Hence this material may be tailored suitably for applications such as optical power limiters, switches and modulators.

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Keywords: Third order nonlinear optical susceptibility; Phenyl sydnones; Z-Scan; Nonlinear refraction; Two photon absorption; Optical power limiting

1. Introduction

Nonlinear optical properties have been the subject of numerous investigations by both theoreticians and experimentalists during recent years [1] due to potential applications in optical signal processing and computing. The detailed investigation of linear and nonlinear optical coefficients enables us to fabricate materials, appropriately designed at the molecular level for a specific device. Effective materials generally contain donor and acceptor groups positioned at either end of a suitable conjugation path. The increased effective conjugation and hence the large π delocalization length, has been recognized as a factor leading to large third order nonlinearities. Two photon absorption (TPA) is a third-order nonlinear process and for good TPA efficiency, materials must have large absorption cross section which are directly related to the imaginary part of the second hyperpolarizability [Im $\gamma(-\omega,\omega,\omega,-\omega)$] [2].

Amongst the nonlinear materials, organic polymers are particularly attractive because of properties such as low density, mechanical flexibility and high nonlinear response [3–5].

Polymethyl(methacrylate) is a hard, rigid and transparent polymer with a glass transition temperature of 125 °C. Its average molecular weight is 6×10^4. It is tougher than polystyrene. PMMA is a polar material and has large dielectric constant. PMMA matrix is most preferred for designing components because of its better resistance to hydrolysis and good outdoor weather resistance. It is a thermoplastic and can be molten and molded into any thing we want. Its physical durability is far superior to that of other thermoplastics.

Additions of dopants to the polymer matrix modify the properties pertaining to optical, electronic and electrical conductivity behavior of polymer [6]. It gives flexibility in designing the

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required size and shape of the material for devices even with a small quantity of the dopant.

Sydnone chalcones are a novel class of heterocyclic compounds having diverse pharmacological properties. They constitute a well defined class of mesoionic compounds consisting of 1, 2, 3-oxadiazole ring system. It possesses a sextet of electrons in association with the five atoms comprising the ring as shown in Fig. 1. The ring bears a fractional positive charge balanced by a negative charge on the exocyclic atom (O^-). The symbol in the ring represents the electronic distribution. Sydnones have fairly substantial dipole moments which would assist their orientation under poling conditions, but their third order nonlinear optical properties are unknown. The present studies have been directed at the experimental investigation of the third order nonlinear optical properties three 3-phenylsydnones containing a donor group in the phenyl rings, viz., 2-benzylhydrazono-5-(3-*p*-tolylsydnone-4-yl)1,3,4,-thiadiazine (sydnone A); 1-morpholinomethyl-3-(benzoylaminomethyl)-4-(3′-*p*-tolyl sydnonylidene)amino-1,2,4-triazole-5-thione (sydnone B) and 3-benzoylaminomethyl-6-(3′-phenyl sydnone-4-yl)-8-(2′6′-dichlorophenyl)-1,3,4-triazolo[3,4-*b*]-1,3,4-thiadiazepines (sydnone C) doped into PMMA matrix and their optical power limiting behavior.

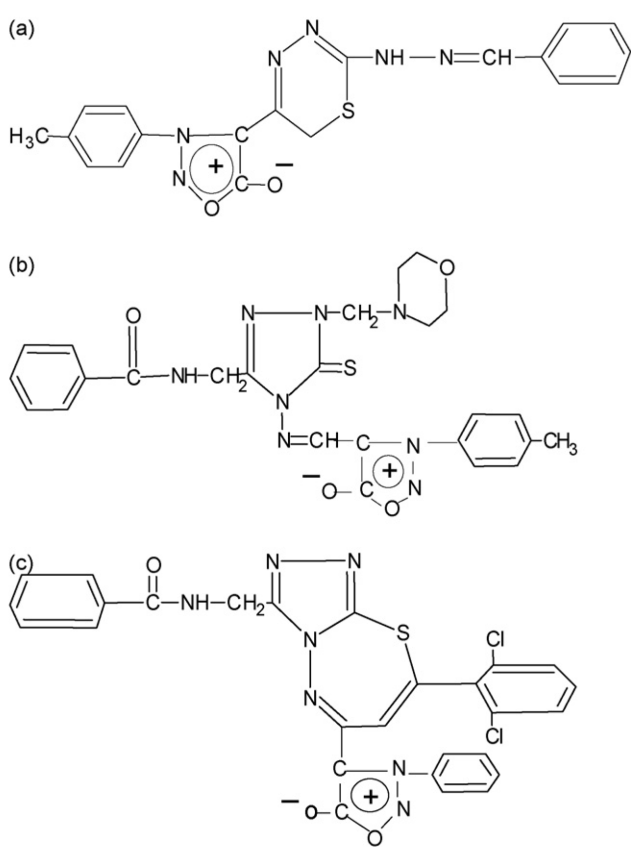

Fig. 1. Structure of sydnone compounds. (a) 2-Benzylhydrazono-5-(3-*p*-tolylsydnone-4-yl)1,3,4,-thiadiazine, (b) 1-morpholinomethyl-3-(benzoylaminomethyl)-4-(3′-*p*-tolyl sydnonylidene)amino-1,2,4-triazole-5-thione and (c) 3-benzoylaminomethyl-6-(3′-phenyl sydnone-4-yl)-8-(2′6′-dichlorophenyl)-1,3,4-triazolo[3,4-*b*]-1,3,4-thiadiazepines.

2. Experiment

The transmission coefficient of the samples prepared was measured by Z-Scan technique using Q-switched laser pulses at a wavelength of 532 nm. This technique is an increasingly popular method for the measurement of the nonlinear absorption coefficient (β) and the nonlinear refractive index (n_2) of the samples and has the advantage that it immediately indicates the sign and type of nonlinearity (refraction or absorption) [7–9].

The sydnone compounds were prepared using procedures described elsewhere [10]. About 0.954 wt% of each sydnone chalcone was incorporated in PMMA. By using research grade DMF as a solvent, the solution of concentration 4.5×10^{-4} mol/L was prepared for the experiment. This sample was taken in a quartz cuvette of thickness 1 mm for the measurement purposes.

A frequency doubled Q-switched Nd: YAG laser (Model: GCR 170 Spectra-Physics) producing 7 ns pulses of wavelength 532 nm was used as the light source. The energy used was 500 μJ. The beam was focused on the sample using a 25 cm focal length lens. The beam waist at the focal point was estimated to be 18.9 μm and the corresponding Rayleigh range was 2.11 mm. The sample was moved along the *Z*-axis using a motorized translation stage. An aperture of 5 mm diameter was mounted in front of the detector placed about 15 cm away from the beam focus. The intensity transmitted by the sample was measured as a function of the sample positions along the *Z*-axis, thereby obtained the "closed aperture" data. The measurements were repeated after removing the aperture in order to obtain the "open aperture" data. All the data were collected in single shot mode to eliminate thermal effects. The optical power limiting study was also performed by keeping the samples at the focus.

The same procedure was followed for other sydnone doped samples.

The linear absorption spectrum of the samples was recorded by using a scanning spectrophotometer (UV-160A Shimadzu) in the wavelength region 200–800 nm at room temperature using DMF solvent as reference. Linear refractive index values of the samples used for the experiment have been obtained using Abbe's Refractometer at the experimental wavelength.

3. Results and discussion

The optical absorption spectra, shown in Fig. 2, indicate that there is negligible one photon absorption at a wavelength of 532 nm when the phenyl sydnones are incorporated in PMMA matrix. When the sydnone moiety is doped into PMMA, absorption peaks shift towards shorter wavelength side due to the shift of electrons from the dopant to the matrix. The spikes at around 300–350 nm are artifacts of the spectrophotometer. It occurs on account of change of source (lamp) in the spectrometer during scanning. The measured refractive indices of the samples are given in Table 1.

Using a Gaussian laser beam in the tight focus geometry we measured the transmittance of the prepared samples with and without the finite aperture (5 mm diameter) placed in the far field. As seen from Fig. 3, the closed aperture Z-scan curve of

Table 1
Nonlinear optical parameters of 3-phenyl sydnones doped PMMA

Sample	n_o	n_2 (10^{-14} cm^2/W)	Re$\chi^{(3)}$ (10^{-13} esu)	Im$\chi^{(3)}$ (10^{-13} esu)	β (cm/GW)	σ' (10^{-46} cm^4 s/photon)
Sydnone (A) doped PMMA	1.479	−3.433 ± 0.309	−1.41 ± 0.13	0.358 ± 0.03	2.07 ± 0.19	4.86 ± 0.44
Sydnone (B) doped PMMA	1.481	2.698 ± 0.243	1.10 ± 0.10	0.218 ± 0.02	1.26 ± 0.11	3.82 ± 0.34
Sydnone (C) doped PMMA	1.477	0.531 ± 0.048	0.22 ± 0.02	0.123 ± 0.01	0.70 ± 0.06	2.46 ± 0.22

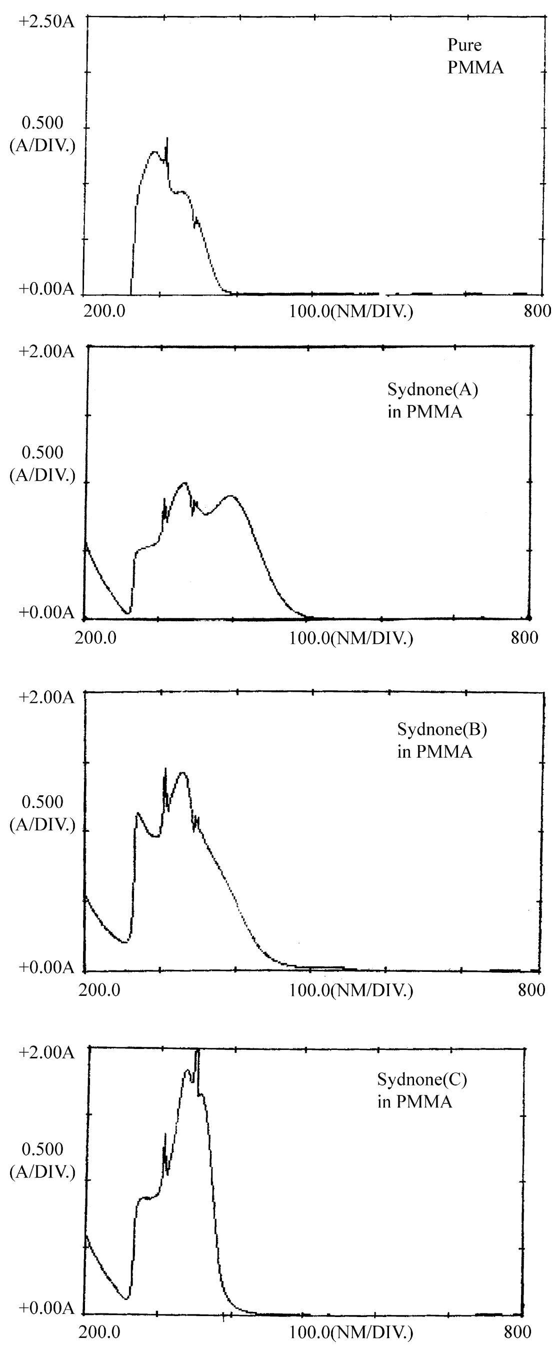

Fig. 2. UV–vis spectrophotographs of pure and doped PMMA.

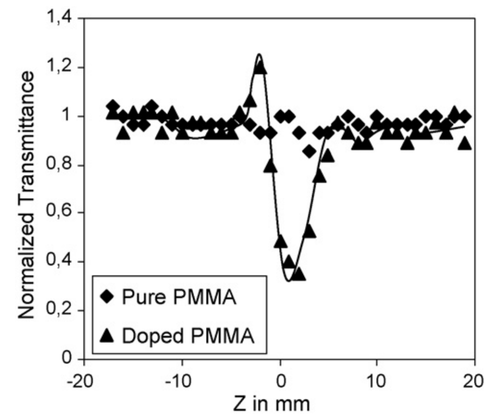

Fig. 3. Closed aperture Z-scan curves of PMMA, sydnone (A) doped PMMA.

sydnone (A) doped PMMA shows the prefocal transmittance peak followed by post focal valley which is the signature of negative nonlinearity.

The measurement of transmittance without aperture ($S = 1$), shown in Fig. 4, enables the separation of nonlinear refraction from the nonlinear absorption by dividing closed aperture data by open one. Fig. 5 shows the normalised pure nonlinear refraction curve which provides the nonlinear refractive index [7,11].

The closed aperture Z-scan measurements performed on sydnone (A) doped PMMA show a peak-valley configuration corresponding to a negative nonlinear refractive index. But Figs. 6 and 7 show that the curve changes to valley-peak configuration for sydnone (B) and (C) doped PMMA which is indicative of positive nonlinear refractive index.

The values of n_2, Re$\chi^{(3)}$ and Im$\chi^{(3)}$ obtained by using $\chi_R^{(3)} = 2n_o^2\varepsilon_o c n_2$ and $\mathrm{Im}\chi^{(3)} = (n_o^2\varepsilon_o c\lambda/2\pi)\beta$ are reported in Table 1 were obtained by repeating Z-scan on each sample and the values were found to be consistent in all the trials. The value of Re$\chi^{(3)}$

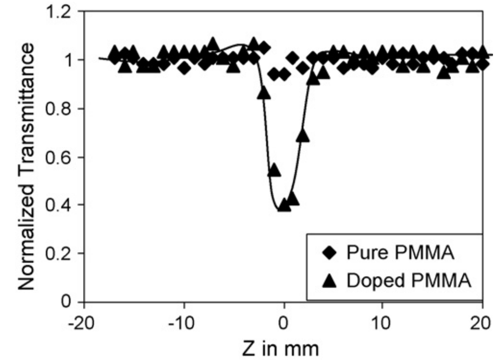

Fig. 4. Open aperture Z-scan curves of PMMA and sydnone (A) doped PMMA.

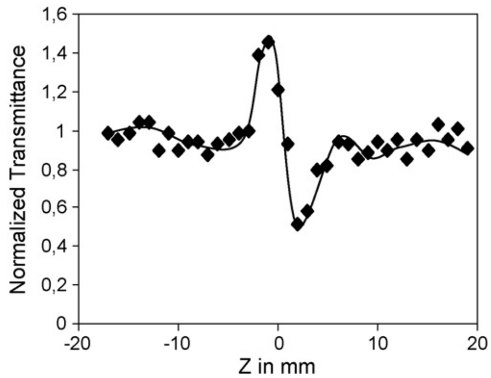

Fig. 5. Normalized pure nonlinear refraction curve for sydnone (A) doped PMMA.

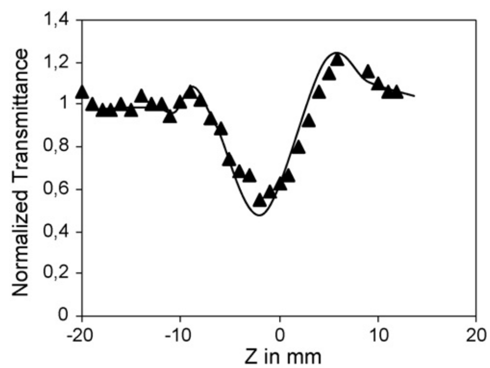

Fig. 6. Closed aperture Z-scan curves for sydnone (B) doped PMMA.

for sydnone (A) doped PMMA calculated from the Z-scan data is 1.41×10^{-13} esu, which is large compared to that of the other two samples, mainly due to enhanced π-electron density [13].

The methyl group in the phenyl ring (*p*-tolyl group) attached to sydnone does not possess an unshared pair of electrons. Yet it is a *p*-director and ring activator. Apart from the electron pumping effect, the methyl 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 to sydnone is enhanced. As a result, there is a greater donation of π-electrons from the donor to the sydnone 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 [14].

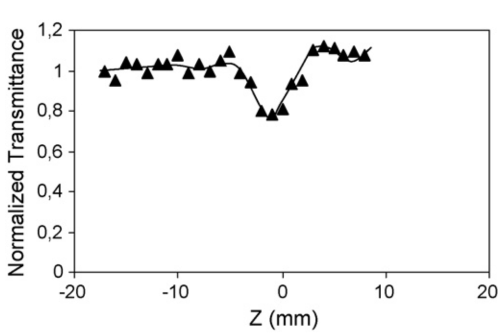

Fig. 7. Closed aperture Z-scan curves for sydnone (C) doped PMMA.

The introduction of a donor into the 3-position (*p*-tolyl group) of the sydnone ring will effectively stabilize the positive charge and the attractor into the 4-position (thiadiazine in sydnone A) of the sydnone ring will effectively stabilize the negative charge at that position.

In the case of sydnone (B) doped PMMA, the value of Re$\chi^{(3)}$ is 1.10×10^{-13} esu due to the presence of methyl group in the phenyl ring. But Re$\chi^{(3)}$ is decreased to 2.2×10^{-14} esu, when the *p*-methyl group is withdrawn from the phenyl ring in sydnone (C). In both sydnone (B) and (C), the presence the five membered triazole ring instead of six membered thiadiazine ring is responsible for the self focusing effect [3,4]. Sydnone (C) is more rigid compared to sydnone (B) because of the presence of the bulky triazolothiadiazepine ring at the fourth position of the sydnone ring. Hence the coplanarity of the system is affected and the conjugation is reduced. The withdrawal of methyl group in the phenyl ring is also one of the reasons for the reduction of π-electron density which leads to decrease in nonlinear response [14]. Therefore, the nonlinear response is electronic in origin and the thermal effect is not a dominant effect for the third order nonlinearity of the samples [15].

Measurements on the pure solvent (DMF) in the cell were also performed under the same measuring condition to verify that the valley and peak in the Z-scan curves originated from the sydnone molecules and not from the solvent or the quartz cell. All the experiments were done at room temperature.

Large optical nonlinearities in materials are commonly associated with resonant transitions which may be of single or multiphoton nature. But for 532 nm outside resonant absorption, the nonlinear absorption behavior is regarded as two photon absorption (TPA) [13,16]. We obtain the observed nonlinear two photon absorption coefficient values (β) by fitting our measured transmittance values to the to the expression [17],

$$T_z = 1 - \frac{\beta I_0 L_{\text{eff}}}{2(1 + (Z^2/Z_0^2))}$$

where $L_{\text{eff}} = (1 - e^{\alpha L})/\alpha$. Here L is the sample length; I_0 is the irradiance within the sample.

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

The value of TPA cross-section [12] for the sydnone (A) in PMMA is 4.86×10^{-46} cm^4 s/photon whereas for sydnone (B) and (C) in PMMA matrix, it is 3.82×10^{-46} and 2.46×10^{-46} cm^4 s/photon, respectively. These values are much larger than the TPA cross section of Rhodamine 6G listed in literature as 10^{-48} to 10^{-50} cm^4 s/photon. This can be attributed to the variation in the delocalized electron density among these compounds [12,13,16].

Fig. 8 shows the optical power limiting behavior of sydnone moieties doped PMMA. Sydnone (A) doped PMMA shows good optical limiting compared to other two sydnones doped PMMA at 532 nm. It exhibits strong TPA at that wavelength. For an input energy less than 0.21 mJ/pulse the output energy increases linearly. However, in excess of this energy, the output energy is nearly a constant value of 0.11 mJ. But in sydnone (B) doped PMMA, for an input energy less than 0.60 mJ/pulse, the output energy increases linearly with the incident energy.

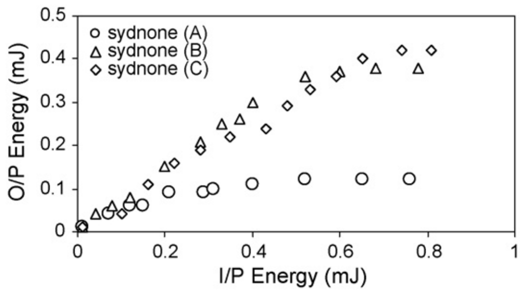

Fig. 8. Optical power limiting behavior of 3-phenyl sydnones doped PMMA.

Beyond this energy, the output energy is nearly a constant value of 0.38 mJ. In the case of sydnone (C) in PMMA matrix, for an input energy less than 0.65 mJ/pulse, the output energy increases linearly. Beyond this energy, the output energy is nearly a constant value of 0.42 mJ. Sydnone (A) doped PMMA shows limiting action at low energy compared to other two samples. The limiting threshold is decreased from 0.65 mJ/pulse to 0.21 mJ/pulse. This due to the variation in delocalized electron density in the compound. Since the third order nonlinear response arises due to delocalisation of the electrons, the power limiting is ascribed to the two photon absorption mechanism [13,18].

The experimentally determined nonlinear parameters are shown in Table 1 and are comparable to that of stilbazolium like dye such as *trans*-4-[2-(pyrrl)vinyl]-1-methylpyridium iodide (PVPI) which is a well known optical limiting material [15].

4. Conclusions

The third order nonlinear optical parameters of three newly synthesized organic 3-phenyl sydnone moieties in PMMA have been investigated by Z-Scan technique. Sydnone (A) in PMMA matrix shows negative nonlinearity whereas sydnones (B) and (C) doped in PMMA show positive nonlinearities. Sydnone (A) in PMMA is seen to be having higher third order nonlinear optical properties compared to other samples. This is ascribed to the presence of *p*-tolyl group and higher length of conjugation. The presence of five membered triazole ring leads the compound acquiring positive nonlinearities. The absence of *p*-methyl group in the phenyl ring and the rigidity of the molecule results in reduced nonlinearity. These compounds in PMMA matrix exhibit strong two photon absorption at 532 nm and the TPA cross section is two orders of magnitude larger than Rhodamine 6G.

Sydnone (A) in PMMA matrix shows good optical limiting behavior with the limiting threshold of 0.21 mJ/pulse, which is mainly ascribed to two photon absorption.

The results also demonstrate that the third order nonlinear parameters of 3-phenyl sydnones doped PMMA compare favorably with those for stilbazolium like dye. Hence these materials may also be used in photonic device applications with the added advantage of flexibility in fabrication.

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