

Third-Order Nonlinear Optical Properties and Two-Photon Absorption in Polymers Doped with *p*-Phenyl Sydnone

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ABSTRACT: We report the measurements of the third-order susceptibilities and two-photon absorption in three different polymers doped with *p*-phenyl sydnone moiety viz., 2-benzylhydrazono-5-(3-*p*-tolylsydnone-4-yl)1,3,4-thiadiazine, which is recently synthesized and characterized, with the prospective of reaching a good compromise between processability and high nonlinear optical properties. The measurements were done using nano second Z-scan at 532 nm. The Z-scan spectra reveal a large negative nonlinear refraction coefficient n_2 of the order 10^{-14} cm²/W and a two-photon absorption β , which is determined to be the order of cm/GW. The absorption cross section is 10^{-46} cm⁴

s/photon. The molecular second-order hyperpolarizability in PMMA matrix was calculated to be 1.47×10^{-31} esu, comparable with stilbazolium derivatives, a well-known class of optical materials for photonics and biophotonics applications. The chromophore shows its optical power limiting behavior in all the three polymer matrices. All these results suggest that this moiety has potential for the application of all-optical limiting and switching devices. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3218–3224, 2008

Key words: sydrones; nonlinear doped polymers; optical power limiting; NLO

INTRODUCTION

The third-order NLO materials have attracted considerable attention because of their potential applications including optical limiting and switching, 3D optical memory and two-photon photodynamic therapy. To be practically useful, the nonlinear media must possess three main parameters: nonlinear refractive index (n_2); nonlinear absorption; and ultra fast nonlinear refractive index response and relaxation times. Thus, design and synthesis of new molecules with large macroscopic optical nonlinearities has become an active research field in modern chemistry and material science.

Generally, materials with extended π conjugation are known to exhibit strong optical nonlinearity. The increased effective conjugation and hence the large π delocalization length has been recognized as a factor leading to large third-order nonlinearities.^{1–6}

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 $[\text{Im } \gamma(-\omega, \omega, \omega, -\omega)]$.⁷

Here, we report an experimental investigation of the third-order nonlinear optical properties and two-photon absorption in three polymeric materials viz., poly(methylmethacrylate) (PMMA), poly(vinylalcohol) (PVA), and poly(4-vinylpyridine) (P4VP) doped with newly synthesized 2-benzylhydrazono-5-(3-*p*-tolylsydnone-4-yl)1,3,4-thiadiazine, a *p*-phenyl sydnone moiety, using Z-scan technique at 532 nm with 7-ns laser pulses.

PMMA 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's physical durability is far superior to that of other thermoplastics. 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 desired shape.

p-Phenyl sydnone chromophore is a novel class of heterocyclic compound having diverse pharmacological properties. It constitutes a well-defined class of mesoionic compound consisting of 1,2,3-oxadiazole ring system. It possesses a sextet of electrons associated with the five atoms comprising the ring as

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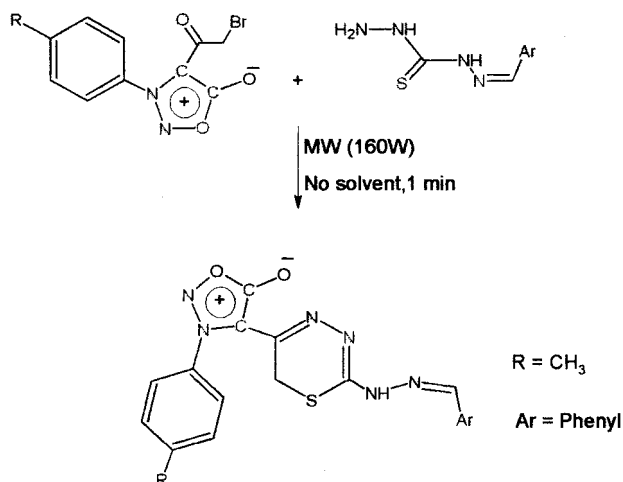


Figure 1 Structure of sydnone compound, 2-benzylhydrazono-5-(3-*p*-tolylsydnone-4-yl)1,3,4-thiadiazine.

shown in Figure 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. Sydnone has fairly substantial dipole moments which would assist their orientation under poling conditions, but their third-order nonlinear optical properties are unknown.^{8,9}

To make optical components, the chromophore samples cannot be used directly because they could get degraded or bleached when exposed to strong laser light. To overcome these drawbacks and for effective use of these materials in devices they can be doped into a polymer matrix. Doping also enhances mechanical and thermal properties, while retaining optical transparency and NLO effects.¹⁰

Additions of dopants to the polymer matrix also modify the energy band gap and other properties pertaining to optical behavior of these materials.¹¹ Besides, it gives flexibility in designing the required size and shape of the material for devices even with a small quantity of the dopant.

To investigate the effect of matrix on third-order nonlinear response, the experiments were also carried out by incorporating the moiety in poly(vinylalcohol) (PVA) and in poly(4-vinylpyridine) (P4VP).

PVA is a semi-crystalline copolymer of great interest because of its relatively simple chemical structure and ease of processing. Preparing transparent PVA gels with high mechanical integrity has been of great interest particularly for bio-optical applications. The average molecular weight of PVA is 12.5×10^4 .

P4VP is a transparent conducting polymer having high molecular weight, 14.8×10^5 . Such conducting polymers are gaining much attention because of their nonlinear optical, electrochemical, and photochemical applications.¹²

EXPERIMENTAL

Sample preparation and optical characterization

The common method of preparation of sydnone is by the cyclodehydration of *N*-nitroso-*N*-substituted amino acids using acetic anhydride.

The moiety, 2-benzylhydrazono-5-(3-*p*-tolylsydnone-4-yl)1,3,4-thiadiazine was prepared by microwave irradiation of the mixture of 3-aryl-4-bromoacetylsydnone and thiocarbohydrazone at 160 W under solvent-free conditions⁹ as in Figure 1. The compound, 3-aryl-4-bromoacetylsydnone is prepared by photochemical bromination of 3-aryl-4-acetylsydnone and thiocarbohydrazone was obtained upon the condensation of thiocarbohydrazone with aryl aldehydes.

To prepare doped polymer samples for measurement, initially a known quantity of chromophore molecules and PMMA are dissolved separately at room temperature, in research grade DMF. The solutions are then mixed and stirred slowly for an hour to get uniform solution. Then, by using the solvent, the solution of concentration 6.7×10^{-4} mol/L was prepared. Polymer doped with sydnone molecules of mass fraction 0.95 wt % was prepared by using the relation,¹³

$$M(\text{wt } \%) = \frac{m_d}{m_p + m_d} \times 100$$

where m_d and m_p are the weight of dopant and polymer, respectively.

For optical characterization of the doped samples, UV-visible, FTIR, and refractive index techniques were employed.

Transmission measurements

The third-order NLO properties of the samples were determined by Z-scan method.^{14,15} 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).

A frequency doubled Q-switched Nd : YAG laser (Model: GCR 170 Spectra-Physics, Inc., Mountainview, CA) producing 7-ns pulses of wavelength 532 nm was used as the light source. The energy used was 0.5 mJ. 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 taken in a quartz cell of 1 mm thick and moved along the Z-axis using a motorized translation stage and the energy transmitted through

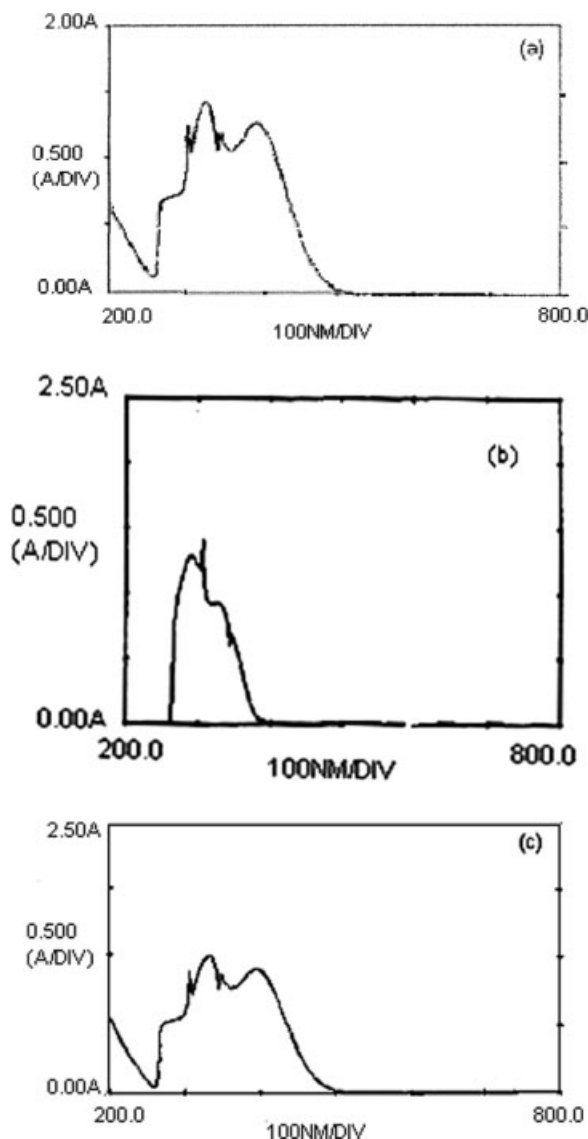


Figure 2 UV-vis spectrophotographs of (a) pure dopant (b) PMMA, and (c) doped PMMA.

an aperture in the far-field is recorded as a function of the sample position to obtain “closed aperture” (CA) data. The measurements were repeated after removing the aperture to get the “open aperture” (OA) data. The experiment was repeated for different concentrations of the dopant in PMMA to determine the molecular second-order hyperpolarizability and also on other two doped polymeric materials.

The optical power limiting study was also performed by keeping the sample at the focus. To avoid cumulative thermal effects, data were collected in single shot mode. Before measuring this sample, the Z-scan system was calibrated using CS₂ in a quartz cell as reference. 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

material, not from the solvent or the quartz cell. All the experiments were done at room temperature.

RESULTS AND DISCUSSION

UV-visible studies

In our investigations, Ultra violet and the Visible Absorption Spectroscopy are used to identify the electronic transitions, the presence of unsaturated groups in the compounds, and the shift in the absorption peaks when doped into a polymer matrix. A UV-vis spectrum of the pure and doped samples was obtained using UV-160A (Shimadzu, Kyoto, Japan) spectrophotometer.

Figure 2 presents the absorption spectra of pure and doped PMMA in DMF solution. The study of the optical absorption spectrum of the doped NLO sample reveals two peaks one at 329 nm and the other at 389 nm, due to the π - π^* interaction and the n - π^* transitions, respectively.

When the compound is doped into PMMA, absorption edge shifts toward longer wavelength side. This increase is indicative of a slight increment in the conjugation length. The UV absorption spectrum also shows that there is negligible single photon absorption at a wavelength of 532 nm when the sydnone chalcones are incorporated in PMMA matrix. Similar effects have been observed when the dopant is incorporated with other two polymeric materials. The measured refractive index of the samples and absorption edge are given in Table I. 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.

FTIR studies

IR spectroscopy reveals information about the position of absorption peaks because of stretching vibrations of certain groups in the compound such as C=C, C-H, C=O, N=C, etc. It is also used to identify the shift in the stretching frequencies of some important groups when the compounds are doped

TABLE I
Photophysical Parameters of Sydnone Doped Polymers

Sample	$\lambda_{\text{absorption edge}}$ (nm)	Linear refractive index (n_o)
Pure PMMA	370	1.479
Doped PMMA	476	1.484
Doped PVA	245	1.416
Doped P4VP	332	1.421

RI of (a) pure PVA = 1.411; (b) pure P4VP = 1.417.

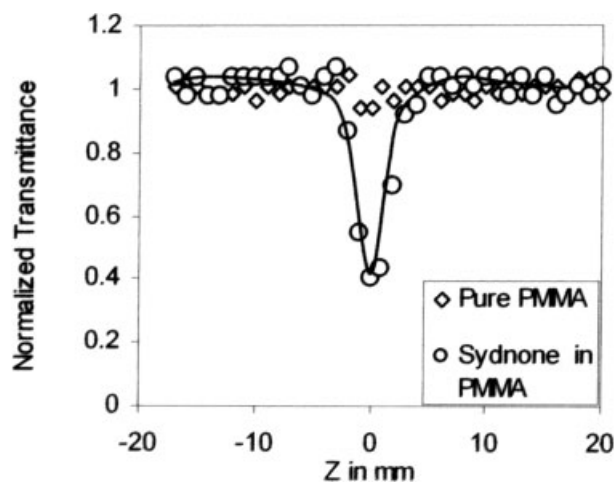


Figure 3 Open Z-scan curves of PMMA and doped PMMA.

into polymer matrix. In this work, we used FTIR-8700 (Shimadzu) spectrophotometer.

In the case of sydnone molecule doped PMMA, the FTIR spectra show shifts in the bands along with change in intensities. The absorption peak which corresponds to *N*-H stretching is shifted to 3435 cm^{-1} from 3423 cm^{-1} and the peak relating to keto group ($\text{C}=\text{O}$) of sydnone is shifted to 1732 cm^{-1} from 1757 cm^{-1} . The absorption peak corresponding to $\text{C}=\text{N}$ is shifted to 1632 cm^{-1} from 1624 cm^{-1} . In doped PVA, the absorption band associated with $\text{C}=\text{C}$ group shifts from 1650 cm^{-1} to 1646 cm^{-1} due to $\text{C}=\text{C}$ group and that for $\text{C}=\text{O}$ group shifts from 1599 cm^{-1} to 1587 cm^{-1} . In the IR spectrum of doped P4VP, the position of the absorption band for *N*-H stretch of the sydnone ring is shifted from 3423 cm^{-1} to 3390 cm^{-1} and that of $\text{C}-\text{H}$ stretching is shifted to 2930 cm^{-1} from 2926 cm^{-1} . The absorption peaks corresponding to

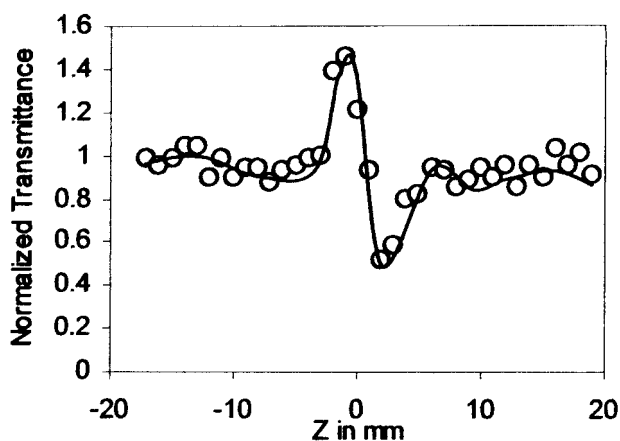


Figure 4 Normalized pure nonlinear refraction curve of sydnone doped PMMA.

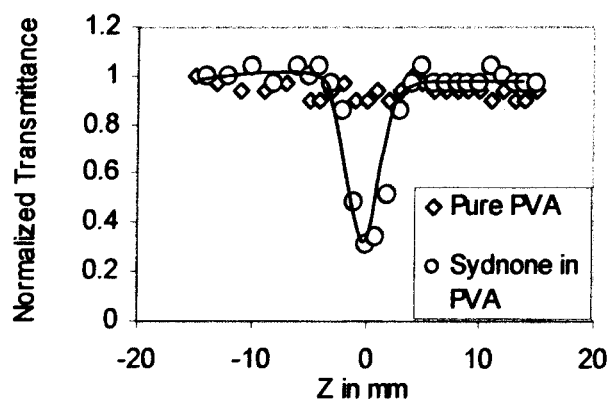


Figure 5 Open Z-scan curves of PVA and doped PVA.

$\text{C}=\text{O}$ and $\text{C}=\text{N}$ stretching occur at 1751 cm^{-1} and 1646 cm^{-1} , respectively, in the doped sample. The variation in the energy of these functional groups is indicative of good interaction between the molecules of the dopant and the matrix.^{13,16,17}

Nonlinear optical studies

Figure 3 exhibits the OA and Figure 4 represents the division of the CA by OA data obtained from Z-scan measurements for the doped PMMA. The OA curve indicates the occurrence of nonlinear absorption. In all our experiments, the nonlinear absorption behavior is attributed to the two-photon absorption (TPA).^{18,19}

The peak-to-valley configuration of the curve (Fig. 4) suggests that the refractive index change is negative, indicating self-defocusing effect. In addition, the nonlinear refraction plays a significant role in the third-order nonlinear process of the sample, which is a very attractive feature for optical switching applications. Similar curves have been obtained

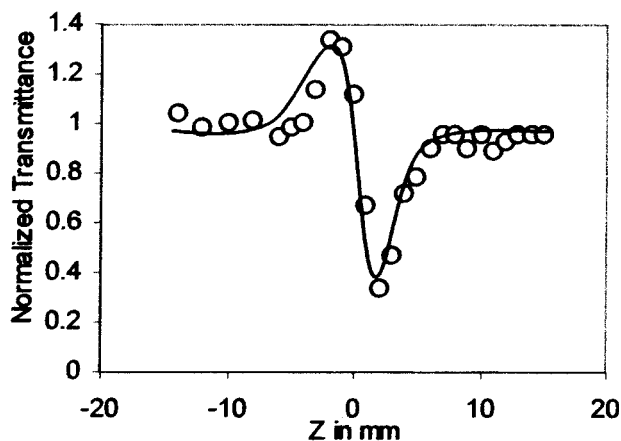


Figure 6 Normalized pure nonlinear refraction curve of sydnone doped PVA.

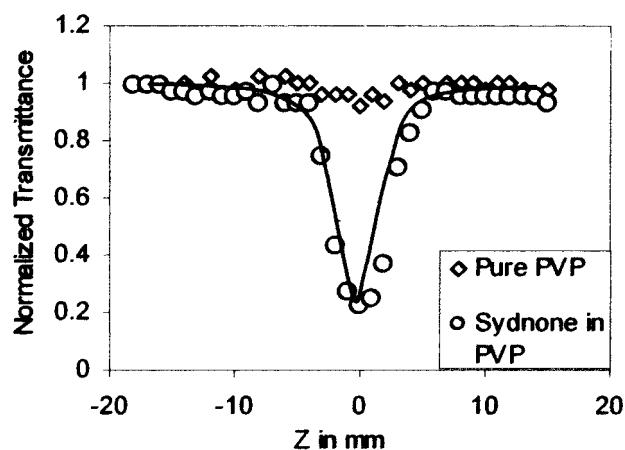


Figure 7 Open Z-scan curves of P4VP and doped P4VP.

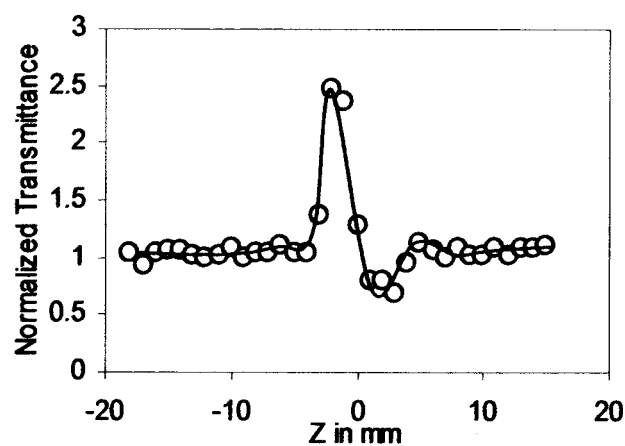


Figure 8 Normalized pure nonlinear refraction curve of sydnone doped P4VP.

when the sydnone chalcone is doped into other two polymer matrices, shown in Figures 5–8.

We obtain the nonlinear absorption coefficient values, β by fitting our measured OA transmittance values to the equation, $T(z) = 1 - \beta I_0 L / [2(1 + z^2/z_0^2)]$.²⁰ The calculated value of β for sydnone doped PMMA is 2.07 cm/GW. By knowing the concentration of the dopant, the molecular two-photon absorption cross section, σ' can be determined²⁰ and for sydnone doped PMMA it is 4.8×10^{-46} cm⁴ s/photon. The calculated values of nonlinear refractive index, n_2 ^{14,15} for doped PMMA is -3.43×10^{-14} cm²/W.

Accordingly, the real and imaginary parts of the $\chi^{(3)}$ of the sample have been calculated^{14,15} to be -1.41×10^{-13} esu and 0.36×10^{-13} esu, respectively, for doped PMMA. The same procedure was followed to calculate the nonlinear parameters of doped PVA and P4VP. The reported values in Table II were obtained by repeating Z-scan on each sample and the outcomes are in good accordance within $\pm 9\%$ accuracy. The molecular second hyperpolarizability, γ of sydnone moiety in PMMA matrix was also calculated from the concentration dependent $\chi^{(3)}$ studies, Figure 9, and is found to be 1.47×10^{-31} esu.¹⁸

The reason for the nonlinear response is the presence of *p*-tolyl group in the system. The methyl group in the phenyl ring (*p*-tolyl group) attached to sydnone does not possess an unshared pair of electrons. Hence, it is a weak electron donor. Yet, it is a *p*-director and ring activator because of positive mes-

omeric effect. 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 which results in an increase in the magnitude of the dipole moment⁸ and hence large NLO effects.

The large value of molecular second-order hyperpolarizability of the sydnone doped PMMA is because of increase in the strength of electron withdrawing group and molecular conjugation length with two aromatic methyl and phenyl systems. Therefore, it is highly probable that the obtained γ value is raised from the conjugation path of the delocalized electrons for large third-order nonlinear optical effects.^{18,21} All these nonlinear parameters are well comparable with stilbazolium derivatives, a well-known class of optical materials for photonics and biophotonics applications.²²

The doped polymers show high values of TPA cross section when compared with Rhodamine 6G listed in literatures as 10^{-48} – 10^{-50} cm⁴ s/photon.²³ The high values can be attributed to the extended conjugation effect.²⁰

Figure 10 shows the optical power limiting behavior of the pure sydnone moiety and sydnone doped polymeric materials. In pure compound, for an input energy less than 180 μ J/pulse, the output energy

TABLE II
Nonlinear Optical Parameters of Sydnone Doped Polymers

Sample	β (cm/GW)	σ' (10^{-46} cm ⁴ s/photon)	n_2 (10^{-14} cm ² /W)	Re $\chi^{(3)}$ (10^{-13} esu)	Im $\chi^{(3)}$ (10^{-13} esu)
Doped PMMA	2.07	4.83	-3.43	-1.41	0.36
Doped PVA	2.47	6.81	-3.76	-1.35	0.38
Doped P4VP	1.59	6.42	-3.86	-1.42	0.25

increases linearly. However, in excess of this energy, the output energy is nearly a constant value of 50 μJ . But for the input energy beyond 430 μJ , the compound deviates from the limiting behavior due to either damage or bleaching effect.

For an input energy less than 0.21 mJ/pulse in the case of sydnone in PMMA matrix, 0.15 mJ/pulse in PVP matrix and 0.16 mJ/pulse in PVA matrix, the output energy increases linearly. Beyond these energies, the output energy is nearly a constant value of 0.14 mJ, 0.1 mJ, and 0.07 mJ, respectively. The limiting threshold is more for the compound in PMMA matrix than other polymer matrices. It is because of the variation in delocalized electron density in the compound. Because the third-order nonlinear response arises due to delocalization of the electron, the power limiting is ascribed to the two-photon absorption mechanism.^{24,25}

Though, no much change is observed in nonlinear susceptibility of the compound with different polymer matrices, PMMA matrix is most preferred for designing components because of its better resistance to hydrolysis and good outdoor weather resistance compared with other two polymers. It is a thermoplastic and can be molten and molded into any form.

CONCLUSION

The third-order nonlinear optical properties and two-photon absorption of three different *p*-phenyl doped polymer matrices, viz., PMMA, PVA, and P4VP have been investigated by Z-Scan technique. They show negative nonlinearity in the doped form. The molecular second-order hyperpolarizability, γ obtained in sydnone doped PMMA is 1.47×10^{-31} esu. All the nonlinear parameters are comparable with stilbazolium derivatives, a well known class of optical materials for photonics and biophotonics applica-

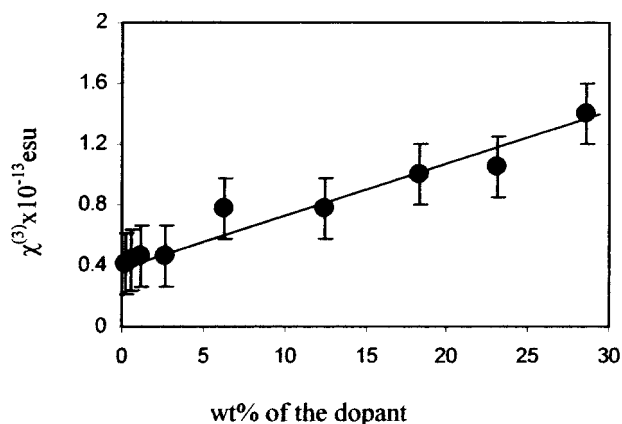


Figure 9 Concentration-dependent $\chi^{(3)}$ values of sydnone in PMMA matrix.

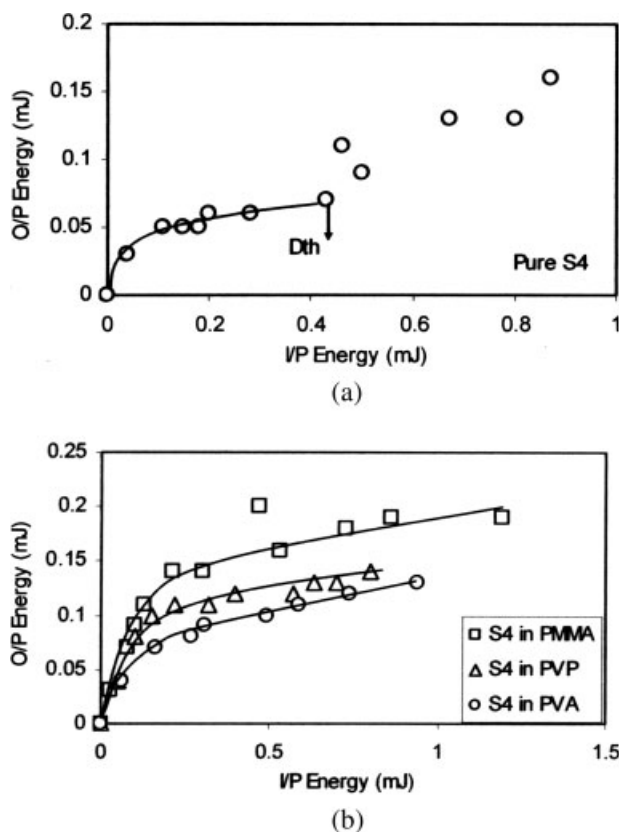


Figure 10 Optical power limiting behavior of (a) pure sydnone dopant (S4) and (b) doped polymers.

tions. It is also found that the doped PMMA has a TPA cross section at least two orders of magnitude higher than that of Rhodamine 6G (10^{-48} – 10^{-50} cm⁴ s/photon). The doped polymeric materials show good optical power limiting behavior, which is mainly ascribed to TPA. In conclusion, all the results reveal that the sydnone moiety, 2-benzylhydrazono-5-(3-*p*-tolylsydnone-4-yl)1,3,4-thiadiazine exhibits third-order nonlinear response in the polymer matrices. As a consequence the studied *p*-phenyl sydnone doped polymers can be very interesting for optical limiting applications.

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