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Original Research Article

The role of polymer host on cubical optical parameters of p-phenyl sydnone

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ABSTRACT
In this paper, it has been shown that a newly synthesised organic p-phenyl sydnone moiety may be doped into PMMA to increase its third order nonlinear optical characteristics. The findings indicate that negative nonlinearity is present in both the molecule and the molecules doped PMMA. The appearance of the p-tolyl group as well as the longer conjugation lengths are attributed to this. The addition of a moiety to PMMA significantly increases cubical susceptibility since the polymer's confirmed chain geometry has changed as a result of the addition of the moiety. The material's nonlinear absorption is due to the absorption in the excited level that is helped by two photons. The PMMA matrix portion has good optical limiting. As a result, the study shows that the sydnone molecule: PMMA is an advantageous nonlinear optical material for usages in power limiting due to its outstanding chemical and thermal stabilities and relatively significant nonresonant third-order susceptibilities.

1. Introduction

Due to its uses in modulational amplification, optical signal processing, multi-photon-pump stimulated emission, coherent limiters, fluorescence spectroscopy, and optical imaging, optical nonlinearities in materials have undergone substantial research in recent years [1]. Because of the requirement to stabilise the output laser power or intensity as well as to protect our eyes and optical sensors, studies on nonlinear optical susceptibilities lead to optical power limiting also received a lot of interest [2]. A material's nonlinear coefficient of absorption and index of refraction must be evaluated in order to evaluate it for the aforementioned uses. The Z scan method can be used to determine these two quantities. This method, which has gained widespread acceptance, has the benefit of quickly indicating the kind and sign of nonlinearity (refraction or absorption) [3, 4]. Several organic materials possessing acceptor and/or donor groups conjugated via π electronic bridge are discovered to be suitable for use in nonlinear optical device applications among the various classes of nonlinear materials [5].

An important category of mesoionic chemicals called sydnones has 1, 2, and 3-oxadiazole rings. It has the electron's sextet linked to five neighboring atoms that make up the bonding ring, as depicted in Figure 1. The partial positive charge on the ring is matched via negative charge on the exocyclic atom (O^-). The ring's emblem stands for electronic distribution. Sydnone compounds have a sizable dipole moment, which aids in their orientation under poling conditions, although it is uncertain what properties of third order nonlinear optics they possess [6]. Compared to other organic compounds with NLO characteristics, they are simple to produce.

Organic molecules are frequently doped into polymeric materials, which act as host media, for the purpose of device applications. This aids in preventing laser-induced NLO material degradation and maintains device construction flexibility. Poly(methyl-methacrylate) (PMMA) is one of the most intriguing polymeric materials that can be used as host media [7]. PMMA has the transition temperature equal to 124°C, the robust, rigid, and transparent polymer. It possess a molecular mass of 6×10^4 on average. More durable than polystyrene. A polar substance with a high dielectric constant is PMMA. Because it is a thermoplastic, it is simple to melt and form into any desired shape. Due to its extremely modest NLO parameters, PMMA cannot be employed as a stand-alone NLO medium.

In this study, utilising ns-pulsed laser at wavelength of 532 nm and the Z-scan method, we provide the third order optical properties of a newly synthesised and characterised p-phenyl sydnone, namely 2-Benzylhydrazono-5-(3-p-Tolylsydnone-4-yl)1,3,4,-thiadiazine.

2. Experimental procedure

By microwave irradiating a combination of 3-aryl-4-bromoacetylsydnone and thiocarbohydrazone, as described before [8], the sydnone chemical was created. By using a solution doping approach, about 1.3×10^{-2} g of syndnone molecules were added to 18×10^{-2} g of PMMA [9]. The solvent was DMF of research grade. For the transmission experiments, a doped polymer solution with a concentration of 5.79×10^{-2} mol/L has been produced. Owing to Z-Scan measurements, the prepared sample has been obtained in a quartz cuvette having the dimensions of 1 mm.

The light source was the Q-switched (frequency doubled) Nd: YAG laser (Spectra-Physics model: GCP 190), which generated 8 nano-second pulses at the wavelength of 532 nano-meter. A concentrated irradiance peak was held at 8.14 GW/cm^2, and the pulse energy was maintained at roughly 0.34 mJ. Making the use of converging lens of focal length 30 cm, the laser radiation was concentrated on the sample. According to estimates, the focal point beam waist was approximately 20 μm, and Rayleigh range approximately 2.5 mm. To acquire closed aperture and opened aperture analysis, the energy of the transmission through sample's length was determined in terms of the sample's length taken in Z-direction [3]. By avoiding thermal impacts, all the data were collected. Both the pure sydnone molecule and the pure PMMA in solution underwent the identical process to obtain transmission data. On the prepared samples, optical power limitation tests were run. The samples were fixed exactly at position of the spot of coherent radiation in case of these tests, and the transmitted energy was determined in terms of energy of input coherent radiation pulse.

Using a scanning spectrophotometer (Ocean Optics, SD2000) at 27°C, the linear absorption spectrum of samples was captured. Using an Abbe's Refractometer, the samples used for the experiment's linear refractive index measurements were made at wavelength of the coherent radiation pulse.

3. Results and discussion

The guest material, the host material, and the doped polymer all exhibit insignificant one photon absorption at the wavelength of 532 nm, according to absorption spectrum displayed in the Figure 2.

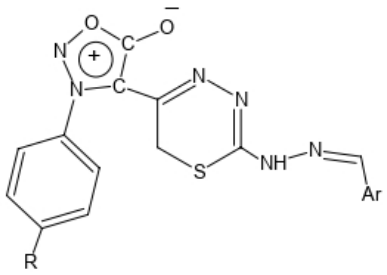

Figure 1. Sydnone compound structure, R=CH_3, Ar=Phenyl

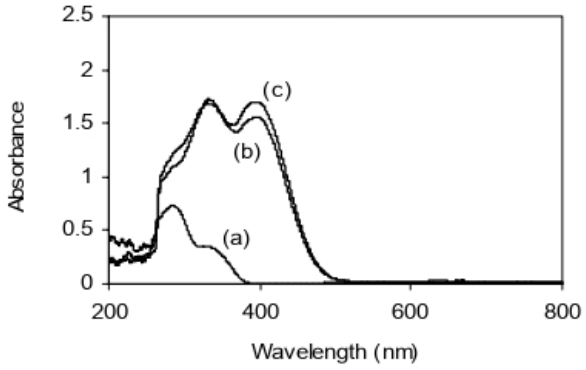

Figure 2. UV-VIS spectrum (a) Pure PMMA (b) S_1 doped PMMA (c) Pure S_1 ; S_1 is sydnone molecule

The absorption peaks are visible between 200 and 400 nm. This suggests that the molecules include unsaturated groups. Each material has two peaks as a result of the electronic transitions π- π* at longer wavelengths and n-π* at shorter wavelengths. Owing to transfer of the electrons from the site of the dopant to the site of the matrix when phenyl sydnone is added to a PMMA matrix, the absorption peaks of PMMA shift towards longer wavelengths. This increase in electron delocalization is indicated by the red shift of the absorption peak wavelength. Table 1 lists the samples' measured refractive indices.

Figures 3 through 5's depictions of the Z-scan spectra of sydnone-doped PMMA samples exhibit the peak-to-valley pattern consistent with the (-) nonlinear refraction coefficient. Pure sydnone moieties have also produced comparable spectra. Under the identical experimental circumstances, there is no detectable nonlinearity in PMMA. At room temperature, all of the trials were conducted.

The calculated magnitudes of Re $\chi^{(3)}$, Im $\chi^{(3)}$, and n_2 determined via the expressions [3, 10]:

$$\mathrm{Re}\,\chi^{(3)} = 2n_0^2\varepsilon_0 c n_2 \text{ and } \mathrm{Im}\,\chi^{(3)} = \frac{n_0^2\varepsilon_0 c\lambda}{2\pi},$$

β and σ' are presented in Table-1.

These values have been determined by performing many Z-scan measurements for all samples, and it was discovered that the values remained stable across all trials. The calculated magnitudes of Re $\chi^{(3)}$ and Im $\chi^{(3)}$ for pure sydnone molecules are 1.41×10^{-13} e.s.u. and 0.358×10^{-13} e.s.u., respectively, while the calculated magnitudes of Re $\chi^{(3)}$ and Im $\chi^{(3)}$ for sydnone molecules doped PMMA are -0.929×10^{-13} e.s.u. and 0.326×10^{-13} e.s.u., respectively, estimated from the Z-scan data. Large π delocalization length and enhanced effective conjugation are the causes of the large nonlinear refraction coefficient. No unshared electrons exist in p-tolyl group connected to sydnone. Yet it functions as a ring activator and p-director. The methyl group connected to the conjugate system is known to display the electron pumping effect in addition to a unique form of resonance known as no-bond resonance (also known as hyperconjugative) that includes delocalization of the σ electrons. As a result, the phenyl ring linked with sydnone has a higher electron density.

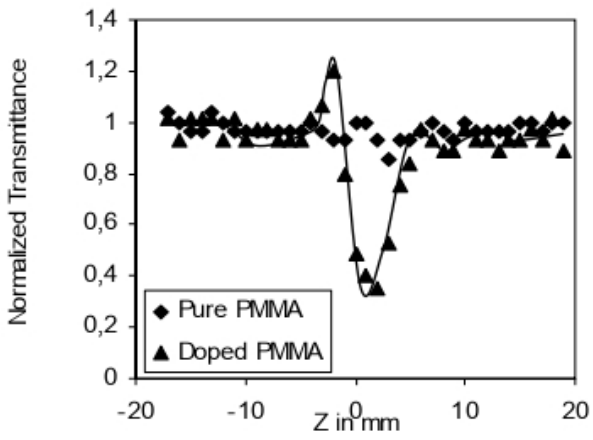

Figure 3. Z-Scan plot of pure PMMA and doped PMMA (closed aperture).

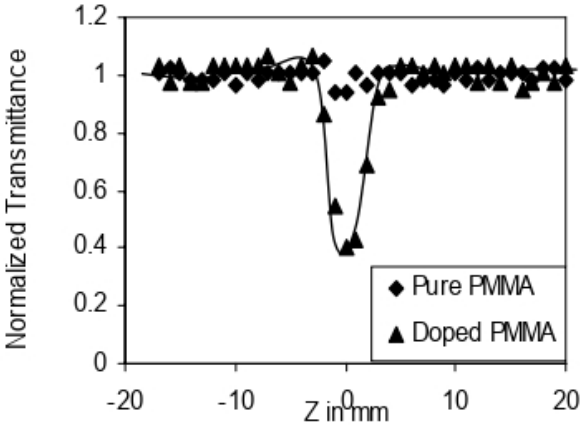

Figure 4. Z-Scan plot of pure PMMA and doped PMMA (open aperture).

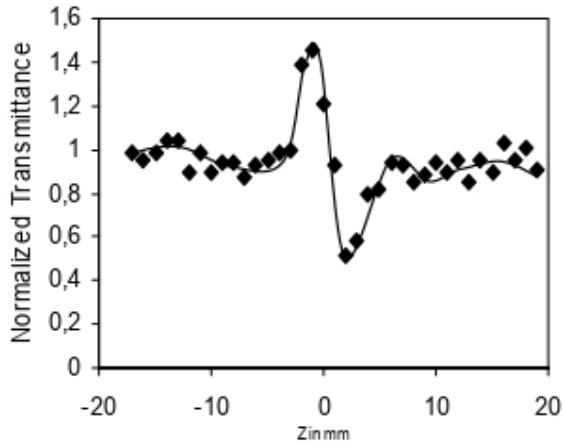

Figure 5. Pure nonlinear refraction plot (normalized) for Sydnone doped PMMA.

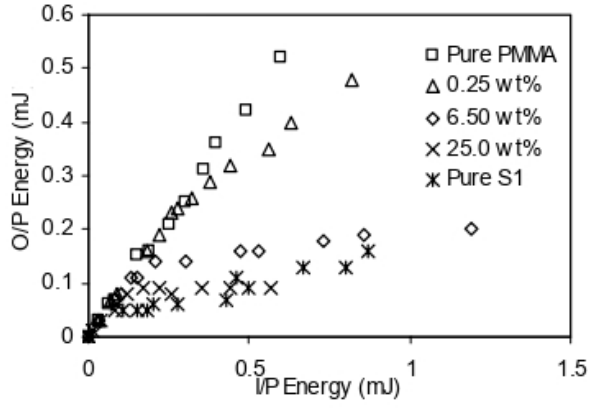

Figure 6. Measured output energy versus input energy for sydnone doped PMMA.

As a result, the donor gives the sydnone acceptor a higher donation of π–electrons. As a result, adding electron's donor to the phenyl ring causes the dipole moment's amplitude to grow, producing significant nonlinear susceptibilities [7]. PMMA that has been sydnone-doped has greater values of $\chi^{(3)}$ than pure dopant. This is because the charge transfer mechanism that occurs during doping might alter the conformation of the chain geometry. These small-scale changes to the chains' geometry have a significant impact on the electrical property because the electron-phonon coupling is strong [11, 12].

Table 1. Calculated values of nonlinear optical parameters of *p*-phenyl sydnone doped PMMA (dopant conc.: 6.5 wt %, solvent used: DMF)

Sample	η_0	n_2 ($\times 10^{-18}$ m^2W^{-1})	Re$\chi^{(3)}$ ($\times 10^{-13}$ esu)	Im$\chi^{(3)}$ ($\times 10^{-13}$ esu)	β (cm/GW)	σ' ($\times 10^{-46}$ cm^4.s/photon)
Pure sydnone molecule	1.480	-2.25	-0.93	0.326	1.87	1.75
Sydnone doped PMMA	1.479	-3.43	-1.41	0.358	2.07	4.86

The two photon induced transmissivity is described by [13]

$$T_{(Io)} = \frac{\ln[1+\beta L_{eff} I_o]}{\beta L_{eff} I_o},$$

where $L_{eff} = \frac{1-\exp(\alpha_L)}{\alpha}$.

In above equation, L stands for sample's length, while I_0 represents the laser's initial input intensity. $L_{eff} = L$ when linear absorption is at its limit, $\alpha \to 0$. Fitting the measured transmittance values to the aforementioned expression, which is shown in Table 1, yields the nonlinear absorption coefficient. Since it has been hypothesised that the excited state absorption affects nanosecond measurements, the nonlinear parameters—also known as the net TPA cross-section are calculated using [13, 14], $\beta = \sigma_2^{'} N_A dx \times 10^{-3} h\nu$. Here N_0 stands for molecular density of TPA compound, d is the TPA compound's concentration in the solution, N_A is the Avogadro constant, and $h\nu$ is the incident photon's energy. The calculated magnitudes of $\sigma_2^{'}$ are also given in Table 1.

Figure 6 depicts the sydnone doped PMMA's optical power limiting behaviour for 7 ns laser pulses. The output energy rises linearly for PMMA with 6.5 wt% sydnone and input energy < 0.22 mJ/pulse. Higher input energies, however, cause the output energy to saturate at almost a constant value of 0.12 mJ. The damage threshold for pure molecules occurs at 0.43 mJ, and the limiting threshold drops as the dopant concentration rises. Due to bleaching, it exhibits linear response at higher energy.

The contribution of excited singlet - singlet and triplet - triplet transitions for different optical pulse lengths causes the optical-limiting behaviour. Because of the rapid inter-system crossing rate, singlet-singlet absorption dominates the power limiting response for pico-second laser pulses and triplet-triplet absorption for nano-second pulses [13, 14]. For usage in optical peak power stabilisation, this quality is ideal. To facilitate with increasing the signal-to-noise ratio of laser pulses, an optical component composed of this sort of material can be utilised.

The values obtained in trans-4-[2-(pyrrl)vinyl]-1-methylpyridium iodide (PVPI), one of the best known

nonlinear absorptive materials for broad band optical limiting applications, are found to be consistent with the experimentally measured nonlinear characteristics reported in Table (1) [15].

4. Conclusions

In this paper, it has been shown that a newly synthesised organic p-phenyl sydnone moiety may be doped into PMMA to increase its third order nonlinear optical characteristics. The findings indicate that negative nonlinearity is present in both the molecule and the molecules doped PMMA. The appearance of the p-tolyl group as well as the longer conjugation lengths are attributed to this. The addition of a moiety to PMMA significantly increases cubical susceptibility since the polymer's confirmed chain geometry has changed as a result of the addition of the moiety. The material's nonlinear absorption is due to the absorption in the excited level that is helped by two photons. The PMMA matrix portion has good optical limiting. As a result, the study shows that the sydnone molecule: PMMA is an advantageous nonlinear optical material for usages in power limiting due to its outstanding chemical and thermal stabilities and relatively significant nonresonant third-order susceptibilities.

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References

[1] M. Yin, H.P. Li, S.H. Tang, W. Ji, Determination of nonlinear absorption and refraction by single Z-scan method, *Appl. Phys. B* **70** (2000) 587-591.

[2] T.C. Lin, G.S. He, Q. Zheng , P.N. Prasad, Degenerate two-/three-photon absorption and optical power-limiting properties in femtosecond regime of a multi-branched chromophore, *J. Mater. Chem*. **16** (2006) 2490.

[3] M.S. Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W.V. Stryland, Sensitive measurement of optical nonlinearities using a single beam, *IEEE J. Quant. Electron*. **26** (1990) 760-769.

[4] X.B. Sun, X.Q. Wang, Q. Ren, G.H. Zang, H.L. Yang, L. Feng, Third-order nonlinear optical properties of bis(tetrabutylammonium)bis(5,5-dithiolato-1,3-dithiole-2thione)copper, *Mater. Res. Bullet*. **41** (2006) 177-182.

[5] A.A. Andrade, S.B. Yamaki, L. Misoguti, S.C. Zilio, D.Z.T. Atvars, Two photon absorption in diazobenzene compounds, *Materials* **27** (2004) 441-444.

[6] J.O. Morley, Nonlinear optical properties of organic molecules. 19. Calculations of the structure, electronic properties, and hyper polarizabilities of phenylsydnones, *J. Phys. Chem*. **99** (1995) 1923-1927.

[7] H.M. Zidan, Electron spin resonance and ultraviolet spectral analysis of UV-irradiated PVA films filled with $MnCl_2$ and CrF_3, *J. Appl. Poly. Sci*. **88** (2003) 104-111.

[8] B. Kalluraya, G. Rai, Environmentally benign reaction: synthesis of sydnone chalcones under solvent-free conditions, *Ind. J. Chem*. **42B** (2003) 2556-2557.

[9] S. Shettigar, K. Chandrasekharan, G. Umesh, B.K. Sarojini. Studies on nonlinear optical parameters of bis-chalcone derivatives doped polymer, *Polymer* **47** (2006) 3565-3567.

[10] M. Samoc, A. Samoc, B.L. Davies, Femtosecond Z-scan and degenerate four-wave mixing measurements of real and imaginary parts of third-order nonlinearity of soluble conjugated polymers, *J. Opt. Soc. Am. B* **15** (1998) 817-825.

[11] C.W. Spangler, T.J. Hall, L.S. Sapochak, P.K Liu, Polaron and bipolaron formation in model oligomeric extended π -electron systems: studies towards the rational design of electroactive polymers for non-linear optics applications, *Polymer* **30** (1989) 1166-1169.

[12] R. Vijaya, Y.V.G.S. Murti, G. Sunderarajan, T.A. Prasad Rao, Degenerate four-wave mixing in solutions of pure and iodine-doped polyphenylacetylene, *Opt. Commun*. **76** (1990) 256-260.

[13] G.S. Hee, C. Weder, P. Smith, P.N. Parsad, Optical power limiting and stabilization based on a novel polymer compound, *IEEE J. Quant. Electron*. **34** (1998) 2279-2285.

[14] W. Sun, C.C. Byeon, M.M. McKerns, C.M. Lawson, S. Dong, D. Wang, G.M. Gray, Characterization of the third-order nonlinearity of ≅$(CH_3$ –TXP)Cd]Cl, in Power Limiting Materials and Devices, C.M. Lawson, ed., *Proc. SPIE* **3798** (1999) 107–116.

[15] F. Guo, W. Sun, D. Wang, L. Zhao, Z. Lu, Y. Nie, Optical limiting of pentaazadentate metal complexes for picosecond pulses in solution, *Appl. Opt*. **40** (2001) 1386-1388.