Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
polymer
Polymer 47 (2006) 3565–3567
www.elsevier.com/locate/polymer

Studies on nonlinear optical parameters of bis-chalcone derivatives doped polymer

Seetharam Shettigar [a,*], K. Chandrasekharan [b], G. Umesh [b], B.K. Sarojini [c], B. Narayana [d]

[a] Department of Physics, NMAM Institute of Technology, Nitte, 574110 Karkala, Karnataka, India
[b] Department of Physics, National Institute of Technology, Surathkal, 575025 Karnataka, India
[c] Department of Chemistry, P.A. College of Engineering, Nadupadavu, Mangalore 574 153, Karnataka, India
[d] Department of Chemistry, Mangalore University, Mangalagangothri 574 199, Karnataka, India

Received 22 September 2005; received in revised form 3 March 2006; accepted 18 March 2006
Available online 4 April 2006

Abstract

Two bis-chalcone derivatives, 1,5-[di(4-methoxyphenyl)]penta-1,4-dien-3-one and 1,5-[di(4-chlorophenyl)]penta-1,4-dien-3-one were synthesized. Their SHG conversion efficiencies are reported to be 6.0 and 5.0 times that of urea and hyper polarizabilities are 9.9×10^{-30} and 10.2×10^{-30} esu, respectively. The third-order nonlinear optical properties in PMMA matrix were studied by Z-scan technique using 7 ns laser pulses at 532 nm. The nonlinear refractive index γ, nonlinear absorption coefficient β, magnitude of effective third order susceptibility $\chi^{(3)}$ and the coupling factor ρ have been investigated. The values obtained are of the order of 10^{-14} cm^2/W, 1.2 cm/GW, 10^{-14} esu and 0.2, respectively, which are comparable with the values obtained in stilbazoleum like dyes. The experimental investigation also shows that they are very interesting optical limiting materials and their optical limiting behaviour is mainly due to two photon absorption phenomenon.

Keywords: Bis-chalcones; Third order nonlinear parameters; Z-scan

1. Introduction

Photonics deals with the synergy between optics and electronics and also provides the ties between optical materials, devices and systems. The inventions of lasers and nonlinear optical phenomena [NLO] have opened up many new areas of devices and systems like frequency conversion and optical switching that are of practical interest to mankind [1]. The NLO effect in the organic molecules originates from a strong donor–acceptor intermolecular interaction, delocalized π-electron system, and also due to the ability to crystallize in noncentrosymmetric manner. Among several organic compounds reported for NLO property, chalcone derivatives are noticeable materials for their excellent blue light transmittance and good crystallizability. They provide a necessary configuration to show NLO property with two planar rings connected through a conjugated double bond [2]. Nonlinear optical (NLO) materials with large intensity dependant 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 [3].

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. Doping also enhances mechanical and thermal properties, while retaining optical transparency and NLO effects, when compared to single crystal chalcone chromophores [4]. Most recently, two-photon absorption dyes are receiving special attention because of their transmission at low incident intensity in most of the visible spectral range.

Here, we report synthesis of two bis-chalcones namely, 1,5-[di(4-methoxyphenyl)]penta-1,4-dien-3-one and 1,5-[di(4-chlorophenyl)]penta-1,4-dien-3-one and the study of third order nonlinear optical parameters of poly(methylmethacrylate) (PMMA) in presence of these molecules with single beam Z-scan technique [5].

Poly(methylmethacrylate) is a hard, rigid and transparent polymer with a glass transition temperature of 125 °C. Its

* Corresponding author. Tel.: +91 9448382169; fax: +91 8258 281265.
E-mail address: shettigarseetharam@yahoo.com (S. Shettigar).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.03.062

average molecular weight is 60,000. 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. We have, therefore, selected PMMA as the polymer into which the NLO samples are doped.

2. Experiment

The two bis-chalcones are synthesized according to the method reported in the literature [6]. The compounds are purified by recrystallization from ethanol. The structures of the compounds are confirmed by analytical and spectral data. The structures of the two compounds are given in Fig. 1. Their conversion efficiency was measured by using 8 ns laser pulses at 1064 nm. Urea was taken as the standard sample.

Each bis-chalcone sample and PMMA were taken in the powder form and mixed in the proportion 12.5–87.5 wt%. This mixture was dissolved in research grade DMF with a concentration of 10×10^{-3} mol/L. The liquid samples were taken in a quartz cell of 1 mm thickness. The Z-scan experiment was performed using 532 nm laser pulses of 7 ns duration. 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 optical limiting study was performed by keeping the sample at the focus in 1 mm thick cuvette. UV–vis spectra for the samples, obtained using UV-160A (Shimadzu) spectrophotometer, show that they have no linear absorption at a wavelength of 532 nm. Linear refractive index values of the samples used in the experiment were measured using Abbe's refractometer. Details are given in Table 1.

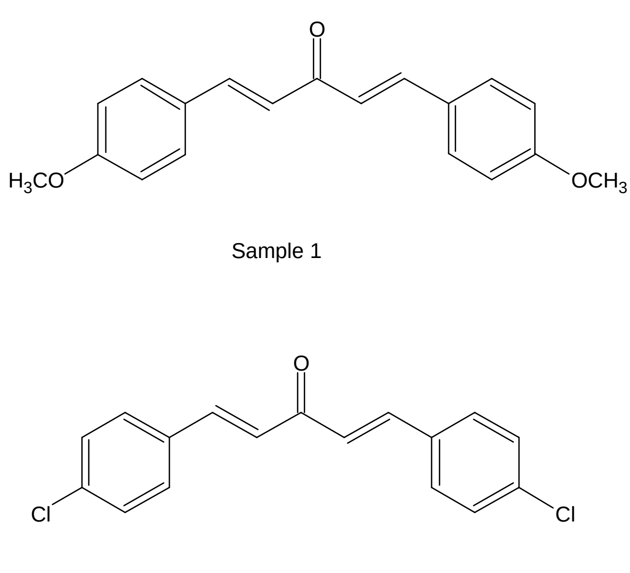

Fig. 1. Structures of bis-chalcone 1 and 2.

Table 1
Photophysical parameters of bis-chalcones doped PMMA in DMF solvent

Sample	λ_{abs}(nm) (edge)	λ_{max}(nm) (peak)	Refractive index (n_0)	Mol. wt
PMMA	380	304	1.423	60,000
Sample1 in PMMA	434	361	1.416	325 (pure sample)
Sample 2 in PMMA	413	306	1.425	303 (pure sample)

3. Results and discussion

The Z-scan technique is ideal for measuring the change in phase of a laser beam induced by propagation through a nonlinear material. It gives both the sign and magnitude of this phase change, $\Delta\Phi$, which is related to the change in the index of refraction, Δn. Fig. 2 shows the experimental closed aperture Z-scan data for sample1 doped PMMA for an input energy of 0.5 mJ. The measurement of open aperture Z-scan data shown in Fig. 3 enables the separation of nonlinear refractive index from the nonlinear absorption by dividing closed aperture data by open one [3]. Similar curves have been obtained for sample 2 doped PMMA with the same input energy.

The nonlinear absorption coefficient obtained [5] for these two samples are given in Table 2.

Figs. 4 and 5 show normalised transmittance curves for sample 1 and sample 2 doped PMMA, respectively, due to pure nonlinear refraction. The nonlinear refractive indices [5]

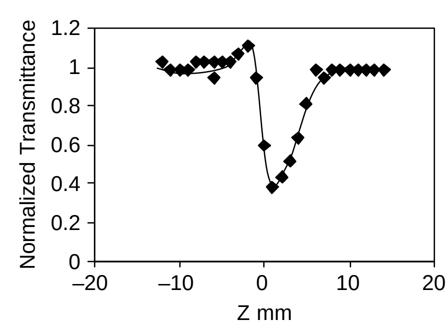

Fig. 2. Closed aperture Z-scan data of sample1 doped PMMA.

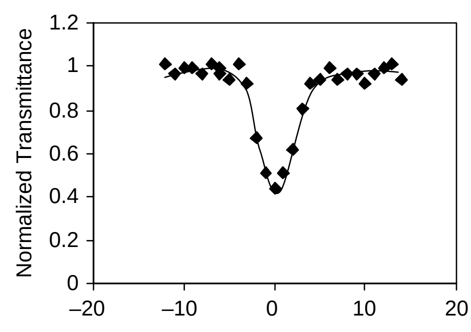

Fig. 3. Open aperture Z-scan data of sample1 doped PMMA.

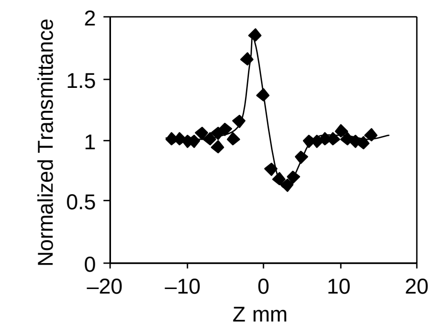

Fig. 4. Normalized transmittance curve of sample 1 doped PMMA due to nonlinear refraction.

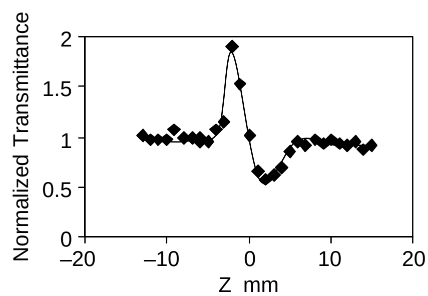

Fig. 5. Normalized transmittance curve of sample 2 doped PMMA due to nonlinear refraction.

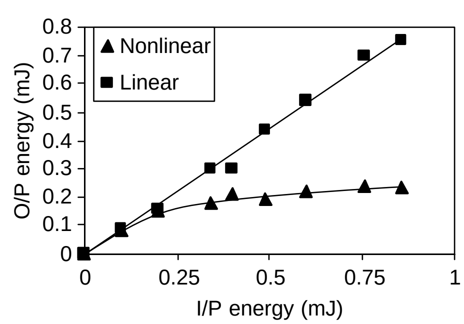

Fig. 6. Optical limiting behavior of sample 1 doped PMMA.

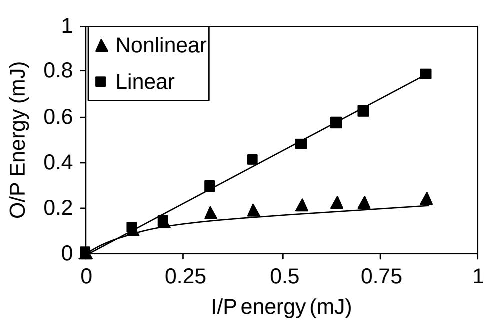

Fig. 7. Optical limiting behavior of sample 2 doped PMMA.

Table 2
Third order nonlinear optical parameters

	$\Delta\Psi_0$	$\Delta\Phi_0$	β cm/GW	γ 10^{-14} cm^2/W	$\chi^{(3)}$ 10^{-14} esu	ρ
Sample 1 in PMMA	0.795	4.267	1.36	−3.09	5.67	0.186
Sample 2 in PMMA	0.783	4.656	1.213	−3.05	5.69	0.168

obtained from above curves, the magnitude of effective third order susceptibility [7] and the coupling factor [8], ρ, of these materials are also given in Table 2. Though the nonlinearity is strong donor–acceptor intermolecular interaction, there is little or no effect on the nonlinear parameters of sample 2 when methoxyphenyl group is substituted by chlorophenyl group. Fig. 6 and 7 show the optical power limiting behavior of samples 1 and 2 doped PMMA. Both show optical limiting property may be due to two photon absorption [9]. The coupling factor is seen to be less than 1/3 (Table 2), which indicates that the nonlinearity is electronic in origin.

4. Conclusions

The optical SHG conversion efficiency and third-order nonlinearity of two newly synthesised delocalized π-conjugate systems viz., chalcone derivatives doped PMMA have been investigated. The results demonstrate they are good nonlinear materials and their third-order nonlinear parameters in polymer matrix are comparable with those for stilbazolium like dye such as *trans*-4-[2-(pyrryl)vinyl]-1-methylpyridium iodide [10]. Moreover, an easy synthesis of these materials is an added advantage over existing optical devices. Hence, these materials may be used in optical device applications in place of such dyes.

References

[1] Aggarwal MD, Wang WS, Bhat K, Penn BG, Frazeir DO. In: Nalwa HS, editor. Handbook of advanced electronic and photonic materials and devices, vol. 9. USA:Academic Press; 2001. p. 193.
[2] Indira J, Karat PP, Sarojini BK. J Cryst Growth 2002;242:209.
[3] Samoc M, Samoc A, Luther-Davies B. J Opt Soc Am B 1998;15(2):817.
[4] Tao XT, Watanabe T, Kono K, Deguchi T, Nakayama M, Miyata S. Chem Mater 1996;8:1326.
[5] Sheik-Bahae M, Said AA, Wei TH, Hagan DJ, Van Stryland EW. IEEE J Quantum Electron 1990;26:760.
[6] Vogel's text book of practical organic chemistry, 5th ed. Longman Group UK Ltd; 1989. p. 1034.
[7] Joseph WDR, Pradhan NR, Narayan Rao D. Proc National Laser Symp 2003;409.
[8] Xiadong L, Shengli G, Huitian W, Lantian H. Opt Commun 2001;197:431.
[9] Wang C, Ren Y, Shao Z, Zhao X, Zhou G, Wang D, et al. Nonlinear Opt 2001;28:1.
[10] Sun W, McKerns MM, Lawson CM, Gary MG, Zhan C, Wang D. Proc. SPIE 2000;4106:280.