Effect of Polymer Host on Third Order Nonlinear Optical Properties of Newly Synthesized Organic Liquid Crystal

Seetharam Shettigar[*], G. Umesh[#], P. Poornesh [#], Y.L.N. Murthy[$]
** Department of Physics, NMAM Inst. of Technology, P.O.Nitte – 574110, Karkala, Karnataka, India*
Fax:+91 8258 281265, E mail: shettigarseetharam@yahoo.com
[#] Department of Physics, National Institute of Technology, Surathkal, - 575025, Karnataka, India
[$] Department of Organic Chemistry, Andra University, Visakapatnam, A.P., India.

ABSTRACT
We report the investigation of third order optical nonlinearity of 2,4,6-tri-(p-hyptoyoxylphenyl) pyrilium tetraborate doped PMMA using nanosecond laser pulses at 532nm wavelength by employing Z-Scan technique. To see the effect of polymer host, the results have been compared with the pure dopant. The material shows a large negative nonlinearity with real and imaginary parts of $\chi^{(3)}$ are - 3.31×10^{-14}esu and 0.73×10^{-14}esu respectively. Excited state absorption cross-section is found to be 3.41×10^{-48} cm^4.s/photon in PMMA host. The magnitude of third order nonlinear parameters increases when the compound is doped into PMMA matrix because of change in the conformation of chain geometry as a result of charge transfer processes. The values are comparable with a best known nonlinear liquid crystal molecule namely, 4-cyano-4'-n-pentylbiphenyl in the nematic phase. Hence, these molecules can be suitably used as nonlinear optical materials in PMMA matrix for device applications.
Key words: nonlinear optics, pyrilium esters, Z-Scan, doped polymer .

1. INTRODUCTION

In recent years studies on optical nonlinearities in materials have become more interesting because of their useful application in integrated optics such as optical modulation, optical information, two-photon-pumped lasing, optical limiting, fluorescence excitation microscopy and imaging [1].To asses a material for the above application, one must characterize its nonlinear refractive index and two photon absorption coefficient. These two parameters may be determined by Z scan technique. This technique is an increasingly popular method and has the advantage that it immediately indicates the sign and type of the nonlinearity (refraction or absorption) [2,3].

Liquid crystals (LC) are known to exhibit large optical nonlinearities which have been the subject of considerable study in recent years, from both experimental and theoretical points of view. So far, almost all the research has been focused on thermotropic liquid crystals (TLC) [4,5]. Since LC molecules typically have delocalized π-electrons, they are believed to be potential sources of fast and large nonlinearities. Due to bulk anisotropy of nematic LC, nonlinear optical parameters (e.g., nonlinear refractive index n_2 and nonlinear optical absorption, β) are expected to depend on the geometrical configuration between the light polarizing direction ($\vec{E}$) and the nematic director $\hat{n}$ **.**

Several techniques have been developed to measure the nonlinear optical refractive index n_2 (nonlinear interferometry, degenerate four-wave mixing and ellipse rotation, among others). These techniques are sensitive but usually require relative complex experimental apparatus. The single-beam Z-scan technique, an application developed by the CREOL group[2], is simple (from the experimental point of view) and sensitive in measuring both the nonlinear refraction and nonlinear absorption. It is a powerful and straightforward technique to study nonlinear properties of materials in different time scales.

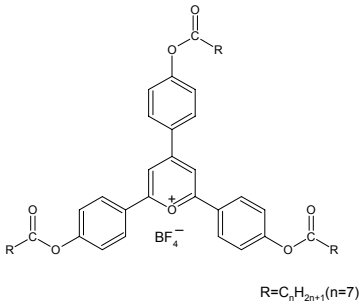
In this paper we report the measurement of third order nonlinear optical coefficients of a polymeric material doped with newly synthesized organic liquid crystal compound, 2,4,6-tri-(p-hyptoyoxylphenyl) pyrilium tetraborate (THPTB) by Z-Scan technique using 532nm output of a Q-switched Nd-YAG laser, prospective of reaching a compromise between good processability and high nonlinear properties of the material.

2. EXPERIMENTAL

The compound was synthesized [6] by adding boron trifluoride-etherate (0.65ml) to a mixture of P-OH acetophenon (0.5ml) and p-OH benzaldehyde (0.25ml).The reaction was refluxed at 100°C for 2hrs; ether was distilled from the reaction mixture. The reaction mixture was dissolved in acetone and the product was precipitate by the addition of ether. The product was obtained as crystalline solid and purification was done by

column chromatography. The compound belongs to the thermotropic liquid crystal which exhibit mesophases at two transition regions. Its structure is shown in Fig.1.

Figure 1. Structure of the compound.



To prepare the sample, initially 7.5wt% of molecules and 92.5wt% PMMA are dissolved separately at room temperature. Research grade DMF was used as solvent. The solutions are then mixed uniformly by stirring them together for an hour. Thus a doped polymer solution of concentration 6.2×10^{-4} mol/L was prepared for the transmission measurement purposes.

The sample was taken in a quartz cell of 1mm thick and Z-scan experiment was performed using 532nm laser pulses of 7ns 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 energy used was 0.58mJ.The experiment was also performed on pure dopant. Care was taken to avoid cumulative thermal effects. All the measurements were made at room temperature.

The UV absorption spectrum of the sample shows that there is no specific absorption band at a wavelength of 532nm when the liquid crystal molecules are incorporated in PMMA matrix, implying that the molecules can be considered as no linear absorption at experimental wavelength.

3. RESULTS AND DISCUSSION

Z–Scan data shown in fig.2 reveals that the sample, prepared in liquid form, has a large negative nonlinear refraction coefficient. For pure compound it is -0.57×10^{-14} cm^2/W and the value increases to -0.89×10^{-14} cm^2/W when doped into the polymer. The real and imaginary parts of $\chi^{(3)}$ for pure compound are found to be -2.0×10^{-14} esu and 0.23×10^{-14}esu, respectively. For doped PMMA, the values have been increased to -3.31×10^{-14}esu and 0.73×10^{-14}esu, respectively. For pure compound the effective TPA cross sections is 1.15×10^{-48} cm^4.s/photon and in PMMA host, the value increases to 3.41×10^{-48} cm^4.s/photon. The molecular second hyperpolarizability of sydnone molecule doped PMMA is obtained to be 1.29×10^{-32} esu. The values of the third order nonlinear parameters are given in Table1.

Thermotropic liquid crystals are usually organic compounds and these compounds interact weakly through van der Waals forces. Carbon atoms can form two types of bonds: covalent σ - bonds, spatially localized and π–bonds, regions of delocalized electronic charge. The electronic density of π–bonds is much more mobile than that of the σ–bond. So, the nonlinear optical properties mainly depend on the change of polarizability of the electrons in the π–bonding orbitals. Hermann *et al*.[7] have shown that the nonlinear optical properties of organic compounds with electrons π in their structures are bigger than those of the saturated compounds with the same number of carbon atoms.

The compound THPTB belongs to the pyrilium salt which is an ionic solid. When the transfer of π electron takes place from the oxygen atom in the pyrane compound to the phenyl ring, the salt will reach the equilibrium state by forming a +ve borate ion. The released π-electrons from the oxygen will be taking part in conjugation by resonance phenomenon. Thus the presence of electron donor (oxygen) or ring activator into the phenyl ring results in an increase in the magnitude of dipole moment which leads to large nonlinear susceptibility. Thus the nonlinear optical response is mainly due to the π-electrons of the benzene rings. The negative nonlinear refraction is due to the change in the density of the medium, which overcomes the positive sign of the transient orientational nonlinearity[8].

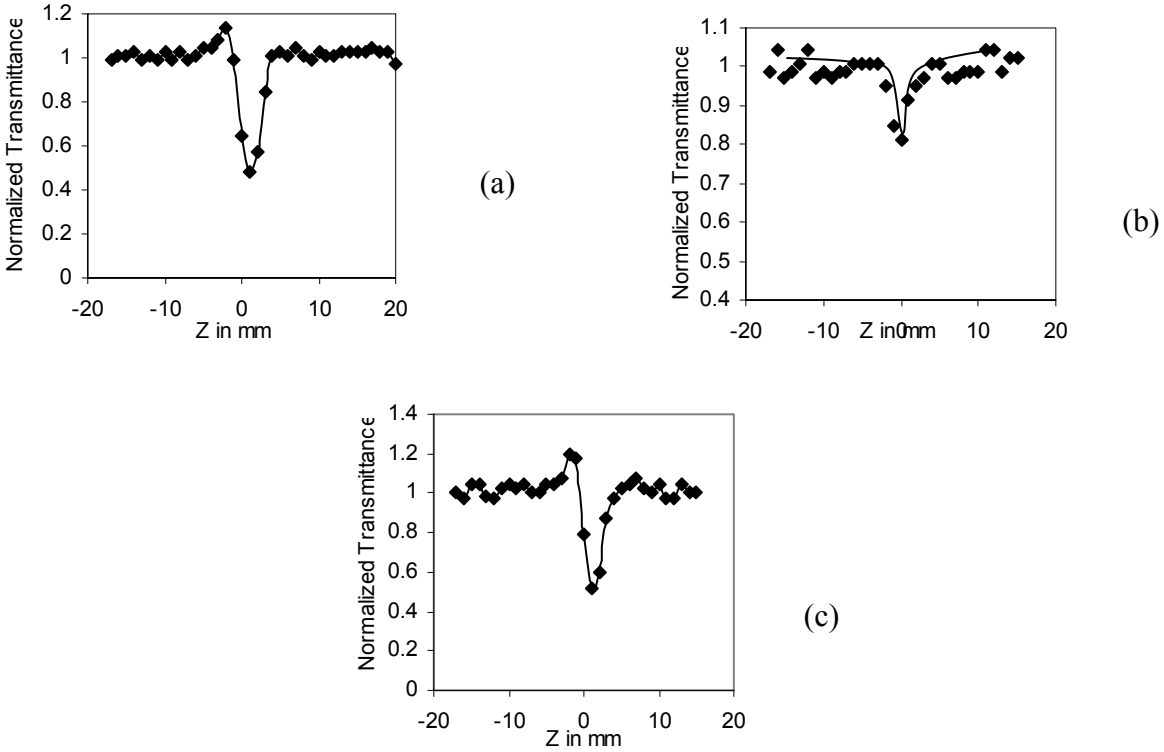


Figure 2. Z scan curves of THPTB doped PMMA (a) Closed (b) Open and (c) Pure nonlinear refraction.

The magnitude of third order nonlinear parameters increases when the compound is doped into PMMA matrix because of the change in the conformation of chain geometry as a result of charge transfer processes. The electron-phonon coupling being strong, these local geometric modifications of the chains, markedly affect the electronic property[9,10]. The values are comparable with one obtained in the case of a best known nonlinear liquid crystal molecule namely 4-cyano-4'-n-pentylbiphenyl in the nematic phase[8]. The effective TPA cross-section is comparable with the values reported in the literature for rhodamine 6G. Therefore these molecules can be suitably used as nonlinear optical materials in PMMA matrix for device applications.

Table 1. Nonlinear optical parameters of THPTB doped PMMA (concentration of the dopant : 7.5wt%).

	β cm/GW	σ'_{ex} 10^{-48} cm^4.s/Ph	n_2 10^{-14} cm^2/W	$\chi_R^{(3)}$ 10^{-14}esu	$\chi_I^{(3)}$ 10^{-14}esu	$\chi^{(3)}$ 10^{-14}esu	ρ
Pure THPTB	0.156	1.15	0.57	2.00	0.23	2.09	0.113
THPTB doped PMMA	0.464	3.41	0.89	3.31	0.73	3.393	0.222

4. CONCLUSION

Many of the basic properties involved in the nonlinear optical processes have been investigated for 2,4,6-tri-(p-hyptoyoxylphenyl) pyrilium tetraborate(THPTB) both in pure and also by doping in PMMA matrix by employing Z – scan technique. The magnitude of nonlinear parameters has been increased in PMMA matrix because of the change in the conformation of chain geometry. The values are comparable with one obtained in the case of a liquid crystal molecule namely, 4-cyano-4'-n-pentylbiphenyl in the nematic phase. The effective TPA cross-section is comparable with the values reported in the literature for rhodamine 6G. Therefore these molecules can be suitably used as nonlinear optical materials in PMMA matrix for device applications.

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