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Nonlinear optical studies of bromothymol blue in liquid and solid media

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ABSTRACT

The third-order nonlinear optical properties are used in high speed telecommunications, optical limiters and optical computers. The purpose of the study is to determine the third-order nonlinear characteristics of bromothymol blue dye in both polymer and liquid mixtures. The samples are prepared by dissolving dye of different concentrations in methanol and ethanol and thin film was prepared by bulk polymerization technique. The spectral characteristics of the dye are studied by recording the absorption and fluorescence spectra of the dye doped in poly(methylmethacrylate) modified with additives ethanol and methanol and the dye in MMA with additives (liquid mixture). The spectral results of the dye doped polymer rod are compared with dye in liquid mixture. The nonlinear measurements of the dye in liquid and polymer medium were performed using CW Nd:YAG laser of wavelength 532 nm by employing Z-scan technique. The closed Z-scan of the samples exhibited a negative nonlinear refractive index, which is larger in magnitude in solid film compared to that in solution. The open Z-scan in solution and solid samples displayed reversible saturable absorption.

1. Introduction

The protection of sensitive optical equipment has been the focus of much attention in recent times. Of great importance is the protection of human eye from potentially harmful intense beams. A large number of compounds have been synthesized to realize nonlinear susceptibilities far larger than the inorganic optical material [1]. In this paper we report the synthesis, characterization and nonlinear optical properties of bromothymol blue dye doped polymer and compare it with dye doped monomer. Nonlinear optical properties of polymer solution were studied by means of a Z-scan set-up. Nonlinear optical effects can be employed for the design and performance of optical limiter. It has been showed that optical limiting can be used for the protection of eyes and sensors from intense lasers [2].

Solid matrix used as lasers get rid of many of the common problems associated with static or flowing liquid systems. The most frequently used polymeric material is poly(methylmethacrylate) (PMMA) [3]. Review of literature showed most of the work on dye doped polymers was done with rhodamine dyes [4] and pyromethane dyes [5]. Some work was reported on coumarin dyes [3] and on dye IR140 [6].

In this paper, the fabrication of dye bromothymol blue doped polymer films of concentration 0.03, 0.05 mm, its spectral parameters and the study of nonlinear refractive index under the Nd:YAG laser excitation are reported. The properties of the dye in liquid medium are compared with that in the solid matrix.

2. Materials and methods

2.1. Synthesis of dye doped polymer

Bromothymol blue, a triarylmethane dye, supplied by Exciton, USA, is chosen for the study. The molecular structure of the dye is shown in Fig. 1. Thin layer chromatography (TLC) test confirms the absence of any impurities in the dye. Methylmethacrylate (MMA) is used as a monomer for synthesizing dye doped polymer film. Initial MMA compositions are cleared of foreign inclusions. Spectroscopic grade ethanol and methanol are used as additives. The dye doped polymer film (DDP) is synthesized using thermal bulk

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Table 1
The spectral parameters of the dye in ethanol and methanol.

S. no.	Name of the dye	Solvent	Wavelength λ_{max} (nm)	Absorption α
1	Bromocresol purple (BCP)	Methanol	423	0.961
2	Bromocresol purple (BCP)	Ethanol	421	0.692

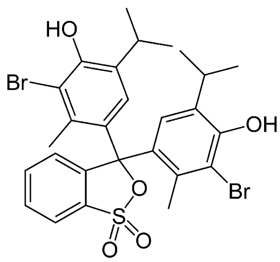

Fig. 1. Chemical structure of bromothymol blue.

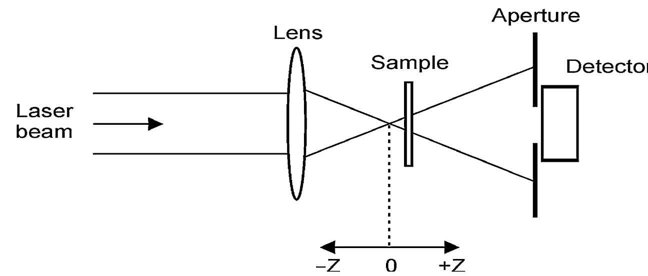

Fig. 3. Schematic diagram of closed Z-scan set-up.

free radical polymerization [7] of dye concentrations 0.03 mM and 0.05 mM. The internal optical qualities of polymer films are checked by passing the laser beam of 5 mW He–Ne laser (632.8 nm) through these films. No dispersion or distortion of the He–Ne laser beam was observed.

2.2. Spectral characteristics

The UV–vis absorption spectrum of the dye in liquid medium and the solid matrix (PMMA + nBA) was obtained using Hitachi U2900 spectrophotometer. This spectrum is shown in Fig. 2. The spectral parameters such as absorption-peak wavelength and absorption co-efficient are tabulated in Table 1.

3. Nonlinear studies

The closed Z-scan [8] set-up, developed by Sheik Bahae et al. is used to characterize the nonlinear optical properties of the dye in different mixtures. It is based on intensity dependent refractive index and includes variation of refractive index as a function of incident beam irradiance of the sample. The set-up is shown in Fig. 3. A Gaussian beam from Nd:YAG laser (λ: 532 nm, power: 50 mW) was focused by a convex lens of focal length 35 mm and passed through the sample. A 1 mm wide optical cell containing the dye in solvent is translated across the focal region along the axial direction, that is the direction of the propagation laser beam. The transmission of the beam through an aperture placed in the far field is measured using photo detector fed to the digital power meter (Field Master Gs-coherent). For an open aperture Z-scan, a lens to collect the entire laser beam transmitted through the sample replaced the aperture. The same was repeated for the polymer sheet of thickness 1 mm. Figs. 4 and 5 provide the closed Z-scan and open Z-scan traces of sample. These figures provide not only the magnitude of real and

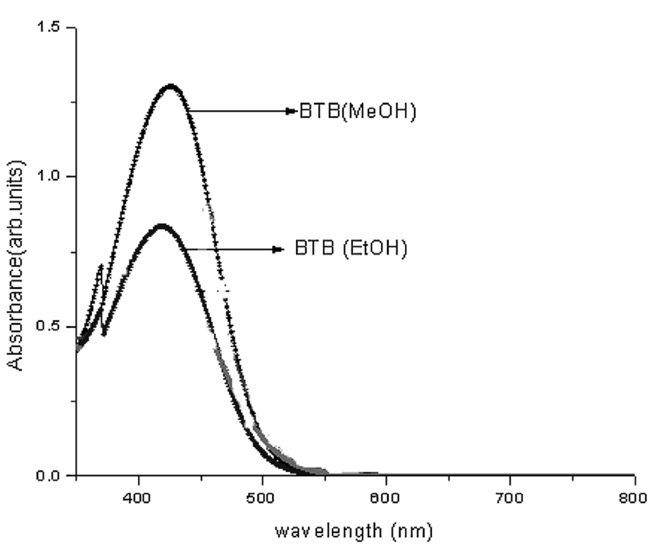

Fig. 2. UV–vis absorption spectrum of dyes in various solvents.

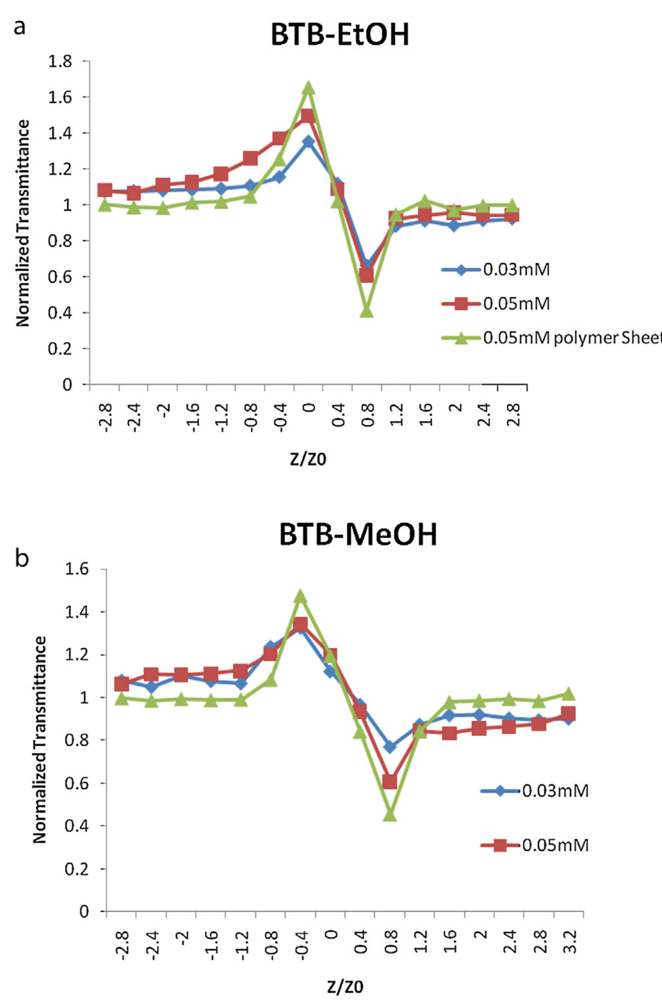

Fig. 4. (a) Closed Z-scan of BTB–EtOH. (b) Closed Z-scan of BTB–MeOH.