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Nonlinear optical and thermal properties of BCP: PMMA films determined by thermal self-diffraction

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ABSTRACT

The third-order nonlinear optical properties of Bromocresol purple (BCP): PMMA films are determined by means of thermal self-diffraction using continuous-wave (cw) diode laser beam with a wavelength of 473 nm and a laser power output of 40 mW. The magnitude of the nonlinear refractive index, n_2, is determined based on the diffraction ring patterns obtained as a result of thermal self-diffraction induced by self-phase modulation. The results indicate that BCP: PMMA films have large nonlinear refractive index, n_2, for near resonance absorbance under 473 nm excitation. This happens since the energy of the excitation at 473 nm is nearer to the gap energy of the BCP: PMMA films, hence it is expected that the linear absorption and the nonlinear optical properties of this medium to be large at this wavelength. The nonlinear refractive index, n_2, the change in refractive index, Δn, and the thermo-optic coefficient, dn/dT, are in the order of 10^{-5} cm^2/W, (0.0088–0.039), 10^{-5} K^{-1} respectively.

1. Introduction

The search for new nonlinear optical (NLO) materials with high optical nonlinearities is gaining interest from the point of view of research and industry. Recently, there has been a growing interest in the third-order nonlinear optical properties of dye-doped polymer materials owing to their large nonlinear refraction values, which are interesting for the applications in optical storage, optical-limiting, optical switching and fiber communication systems [1–3]. To have strong second order (NLO) properties, the compound must possess a large first order molecular hyperpolarizability and also must crystallize in a noncentrosymmetric structure to have nonzero second order susceptibility. Besides the strong nonlinear optical response the NLO materials must also fulfill some other requirements such as good transparency and high thermal stability [4]. It has been generally understood that the second order molecular nonlinearity can be enhanced by large delocalized π-electron systems with strong donor and acceptor groups [5]. Highly conjugated organic compounds can easily be crystallized into noncentrosymmetric structures when their molecular conjugation systems are substituted with the bromo (Br) group. Thus these compounds not only have large first order molecular hyperpolarizability value but also usually have fairly strong power second harmonic generation (SHG). Bromo group is an effective group for the microscopic second order nonlinearities. Moreover, the bromo group can also obviously improve the transparency and the thermal stability of compounds [5,6]. Bromocresol purple (BCP) dye is one of the sulfonephthalein dye group where the central carbon atom is joined by three phenyl rings. BCP dye widely used as acid base indicators to monitor transformations as a function of pH of medium. The color of the BCP is yellow in weakly acidic solutions and turns to red when the pH is raised. The acid form is singly charged ion, and the base form has two negative charges (see Fig. 1b). The color change is ascribed to the rehybridization of atoms from the unsymmetric resonance system to the symmetric form [7]. The color change in BCP dye can also be brought about by changing the polarity of the medium, since the more polar basic form is stabilized readily in a polar environment. In other word, in a nonpolar solvent like chloroform the BCP dye exists mainly in their neutral form and exhibits their characteristic absorption [8,9]. BCP dye molecule has significant second order hyperpolarizabilities and its value decreases as the dielectric constant or polarity of the solvent decreases. In chloroform the value of second order hyperpolarizabilities is equal to 80×10^{-30} esu [7], this value of second order hyperpolarizabilities in chloroform makes BCP dye a promising material for use in dye-doped polymeric system.

In case of nonlinear refractive index based optical devices there is also the need for high and fast NLO material in order to achieve the desired change in optical beam characteristic with an interaction length as short as possible, and with the rapid response time [10]. One of the most interesting polymeric media is Poly (methyl methacrylate). It is hard, rigid and transparent polymer with a glass transition temperature of 125 °C. PMMA is a polar material and has a

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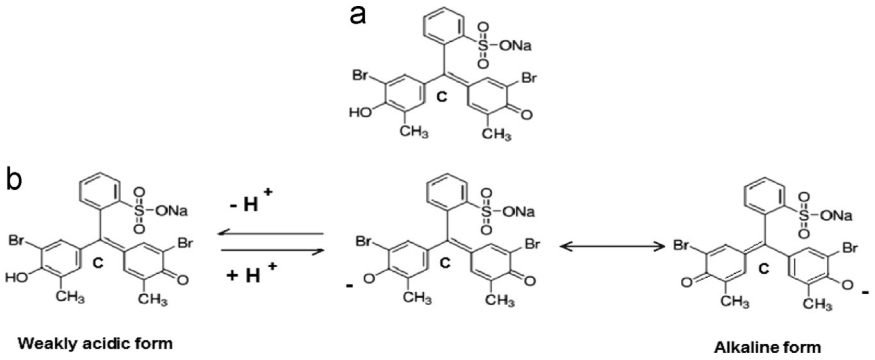

Fig. 1. (a) The chemical structure of Bromocresol purple (BCP) dye. (b) Structure change of BCP dye with change of pH of the medium.

large dielectric constant. It is a thermoplastic and can be molten and molded into desired form [11]. Despite its advantages, PMMA by itself have low nonlinear refractive index. To enhance the third order NLO properties of PMMA we mix it with a highly nonlinear optical material such as BCP dye and to have a high transparency films we use chloroform as a solvent.

When a laser beam propagates through a material with a nonlinear refractive index, several nonlinear effects can be observed. The physical mechanism that creates an intensity dependent refractive index in the medium can have different origins such as heat, charge carriers, etc. [12]. The refractive index of the medium can be altered by the thermal effects produced by the absorbed laser energy along the path of the laser beam. In this process, light energy is absorbed by the medium and then transferred to heat by nonradiative decays of the excited state, leading to an increase of local temperature in a sample [13]. This phenomenon has been explored extensively in recent years, in connection with problems involving the nonlinear interaction of laser beams in different media [14]. As a result, a nested array of diffraction intensity rings can be observed in the far-field due to the thermal effects. The number of rings depends generally on the on-axis nonlinear phase shift suffered during its passage through the sample [15]. By measuring the relative phase shift of a laser beam in the far field, the refractive index change, Δn, and effective nonlinear refractive index, n_2,of the sample can be determined [16]. The temperature profile produces a refractive index gradient in the sample related to the thermo-optic coefficient, dn/dT. The interplay between the nonlinear response of the materials with an intensity dependent refractive index and divergence of the propagating beam may illustrate spatial self-phase modulation [17].

Thermal self-diffraction technique is one of the photothermal techniques; it is based on the use of electromagnetic radiation to induce nonradiative-excitation of excited states resulting in change in temperature of the test sample. The present work reports on a technique based on the thermal self-diffraction due to thermally induced self-phase modulation (SPM) effects to determine the thermo-optic coefficient, dn/dT, and the nonlinear refractive index, n_2, of Bromocresol purple dye: PMMA films.

2. Samples preparation and UV-visible spectroscopy

The chemical structure of Bromocresol purple (5′,5″-Dibromo-o-cresolsulfon-phthalein) dye is shown in Fig. 1a. The Bromocresol purple (BCP) dye: doped Poly (methyl methacrylate) (PMMA) films are prepared as follows: BCP dye and PMMA are dissolved separately in chloroform then the solution of BCP dye and that of PMMA are mixed completely. After stirring for 30 min, the mixed solution is spread on a clean glass slide uniformly and dried at room temperature for 24 h. The content of BCP dye and PMMA in chloroform are (C1: 0.14 mM) concentrations; other two concentrations

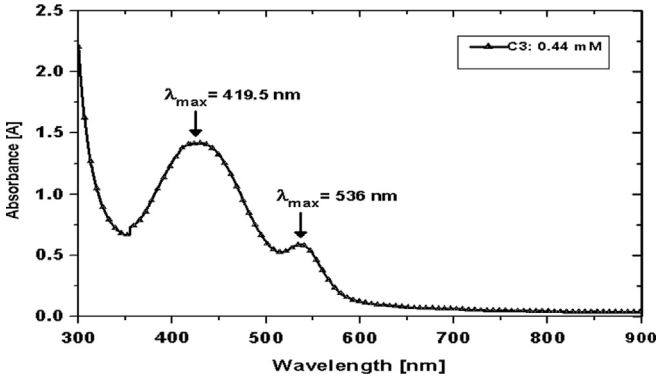

Fig. 2. The absorption spectrum of BCP: PMMA film for 0.44 mM concentration.

(C2: 0.29 mM, C3: 0.44 mM) of BCP are prepared by the same method. The films samples have good purity and uniform thickness. Thicknesses of the films were measured using a digital micrometer type CT 200–521 and is found to be 25 μm. The absorption spectra of the films are measured at normal incidence in the spectral range (300–900) nm using Cecil ReflectaScan Reflectance Spectrophotometer CE-3055. The absorption spectrum of 0.44 mM concentration is shown in Fig. 2 where the two absorption peaks are located at 419.5 and 536 nm.

3. Experimental setup

In the experimental setup (Fig. 3), a Gaussian beam of a TEM_{00} mode diode laser (SDL-473 nm-40 T) was focused onto the sample by a lens of focal length (+200 mm). BCP: PMMA film of thickness 25 μm was placed between the lens and the focal point (195 mm away from the lens). The radius of the laser beam at the sample of (96.5 μm) was calculated using the equation $(1.22f\lambda/\omega)$, where f is the focal length of the lens, λ is the wavelength of diode laser and ω is the laser beam radius at the lens.

After the laser beam passed through the sample, it diverges in to a nested array of diffraction rings, which illuminated the screen (30 × 30 cm). The distance between the screen and the sample was (1000 mm) to observe and record the diffraction ring patterns. The images of the diffraction rings pattern were recorded by a CMOS digital camera (Sony Cyber-shot DSC-WX1/B 10 MP), with an exposure time of 30 frame/s.

4. Results and discussion

4.1. Photochemical kinetics

During the experimental, when a BCP: PMMA photopolymer material is illuminated by light of a suitable wavelength of