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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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