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Z-scan studies of third-order nonlinear optical and optical limiting properties of chalcones doped Poly(methyl methacrylate) thin films for visible laser protection

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ABSTRACT

In the present study, third-order nonlinear optical properties of three chalcone derivatives, (2E)-3-(4-methoxyphenyl)-1-(4-nitrophenyl)prop-2-en-1-one (**MNC**), (2E)-3-(4-methylphenyl)-1-(3-nitrophenyl)prop-2-en-1-one (**ML3NC**) and (2E)-3-(3,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (**DMMC**) doped Poly(methyl methacrylate) (**PMMA**) thin films are reported. The thin films were prepared using spin-coating technique at three different doping concentrations. Surface roughness and linear optical properties of the films were studied by atomic force microscopy (AFM) and UV-Vis-NIR absorption spectrum, respectively. The intermolecular interactions of the chalcones were studied using Hirshfeld surface analyses (HSA). The third-order nonlinear optical (NLO) properties of the films were investigated by using Z-scan technique with DPSS continuous wave (CW) laser excitation at 532 nm. All the films exhibited strong nonlinear absorption (NLA) behavior, and the obtained nonlinear absorption coefficients (β) increases with doping concentration of chalcones. Further, we observed the optical limiting property for all the films, which is mainly originated from two-photon absorption (TPA) mechanism. The calculated third-order nonlinear absorption coefficients (β), imaginary part of third-order nonlinear susceptibilities (Im $\chi^{(3)}$) and the optical limiting (OL) thresholds of the films are in the order of 10^{-5} cm/W, 10^{-8} esu and 10^{3} J/cm^{2}, respectively. The results revealed that the chalcones doped PMMA thin films are promising materials for optical limiting applications in visible region.

1. Introduction

Nonlinear optical (NLO) properties of chalcone derivatives have been studied since many years for their potential applications in nonlinear optics such as frequency doubling, all-optical switching and optical limiting (OL) [1–4]. The carbonyl group functionality in conjugation with the adjacent donor/acceptor substituents forming the charge transferring bridge made the chalcones as exceptional candidates for biological and nonlinear optical applications [5–10]. One can enhance the NLO behavior of chalcones by substituting different donor/acceptor substituents or by increasing the conjugation length of the bridge [11–14]. However, the direct use of this kind of organic materials for device applications is limited due to the lack of photophysical stability as well as mechanical and thermal properties. This can be overcome by doping the organic materials into other materials that possess strong photophysical properties [15–18]. The polymer doped materials can enhance the stability while retaining their NLO properties and linear optical transmittance [19–24]. In this case, we have chosen Poly(methyl methacrylate) (PMMA) polymer as a suitable host material. It is a hard, rigid, and transparent polymer with a large dielectric constant (2.9 at 1 MHz). Its physical strength is superior to that of other thermoplastics, and can be molded into anything we desire. Moreover, the chalcone derivatives are thermally stable upto their melting points, which is near to the glass transition temperature of the PMMA matrix (125 °C) that makes them suitable candidates for doping.

Recently, we have reported the combined experimental and theoretical investigations on the molecular structures and nonlinear optical properties of (2E)-3-(4-methoxyphenyl)-1-(4-nitrophenyl)prop-2-en-1-one (MNC), (2E)-3-(4-methylphenyl)-1-(3-nitrophenyl)prop-2-en-1-one (ML3NC) and (2E)-3-(3,4-dimethoxyphenyl)-1-(4-methoxyphenyl) prop-2-en-1-one (DMMC) [25–28]. They possess strong two-photon absorption and negative nonlinear refraction under femtosecond laser regime. Interestingly, they can be used for optical limiting applications owing to their strong two-photon absorption in the near IR region of the electromagnetic spectra. These results, and the intensive use of continuous wave laser beams in the visible region have motivated us to investigate the third-order nonlinear optical properties and optical limiting mechanism of thin films of these three chalcones doped PMMA

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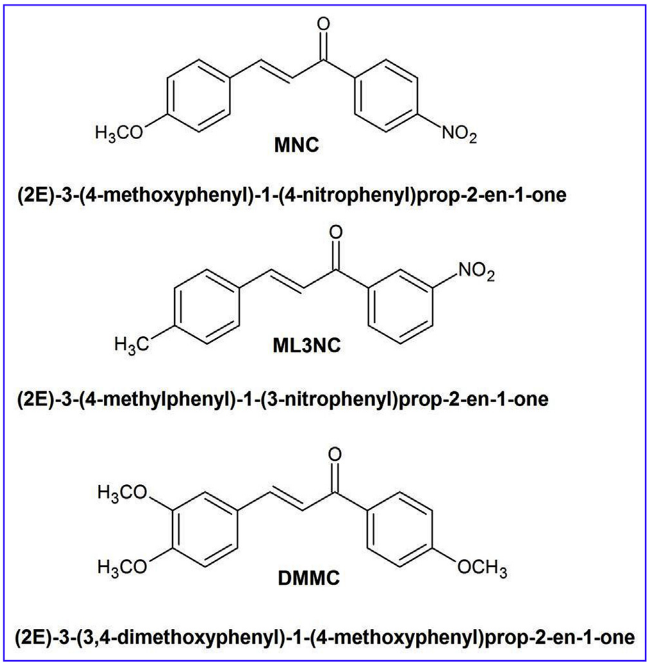

Fig. 1. The molecular structures of **MNC**, **ML3NC** and **DMMC** chalcone derivatives.

polymer under CW laser at 532 nm. The thin films of chalcones doped -PMMA polymer at three different concentrations were prepared using spin coating technique. The intermolecular interactions in the crystals, surface morphology and linear optical properties of the films were also studied.

2. Experimental

2.1. Synthesis of chalcones

The chalcone derivatives, **MNC**, **ML3NC** and **DMMC** having methoxy, methyl and nitro as the anchoring groups were synthesized by the condensation reaction between appropriately substituted benzaldehydes (0.01 mol) with acetophenones (0.01 mol) in ethanol (60 mL) in the presence of a catalytic amount of NaOH solution [25–27]. After vigorous stirring for 1–3 h, the reaction mixture was poured into ice-cold water (500 mL) and left to stand for overnight. The resulting precipitate was filtered, washed with distilled water and dried. Finally, pure chalcones were obtained through repeated recrystallization of crude solids from acetone. In the synthesized chalcones (Fig. 1), methoxy, dimethoxy, and methyl groups are electron donors while nitro group is an electron acceptor. Further, there is an electron acceptor C=O group which is present in the middle of the bridge. Hence, the synthesized molecules belong to D–A–A (**MNC** and **ML3NC**) and D–A–D (**DMMC**) systems.

2.2. Film preparation and characterization

MNC, ML3NC and DMMC chalcones - doped PMMA thin films with three doping concentrations by weight (10, 20, 30 wt%) were prepared using spin coating technique. Initially, MNC, ML3NC, DMMC and PMMA samples were weighed separately, and dissolved in DMF solvent. Then, the two solutions were mixed completely, filtrated and was spread by spin-coater (2500 rpm, 30 s) (**spinNXG-P1,** programmable spin coater, APEX Instruments Co PVT LTD, Kolkata, India) on a clear glass substrate (2.5 × 2.5 × 0.1 cm). Finally, the annealing of the prepared films was done at 60 °C for about 2 Hrs. The obtained thin films were found to be stable, moisture free and have uniform thickness.

The linear optical absorption studies were carried out by using a **Cary 300** UV-Vis-NIR spectrophotometer in the wavelength region of 200–900 nm. The optical band gaps (E_g) were measured with the help of Tauc's plot by using the linear absorption data. The surface roughnesses of the thin films were analyzed using an atomic force microscopy (Nanosurf AG-easy Scan AFM).

2.3. Z-scan measurements

The third-order nonlinear optical properties of chalcones – doped PMMA thin films were determined using open aperture Z-scan technique [29] with a continuous wave (CW) diode-pumped solid-state (DPSS) laser of Gaussian beam profile having 532 nm wavelength. The beam size and the intensity of the laser at the focus point are measured to be 27 μm and 1.81×10^8 W/m^2, respectively. The Z-scan measurement of thin medium condition is fulfilled since the sample thickness is less than the Rayleigh range (Z_0 = 4.15 mm). The films were scanned across the focus of the lens along the Z-axis direction (laser beam propagation). The cross section of the laser beam coming out of the sample was controlled by placing an aperture of variable diameter in the far field. All the transmitted intensity through the sample was collected in the open aperture Z-scan experiment. The digital electric control unit attached with all the detectors is connected to the computerized Z-scan program. The experimental set-up used in the present study was shown schematically in our earlier report [30]. Further, we performed the Z-scan experiment on pure glass substrate and did not observe any nonlinearity. Hence, the measured NLO parameters are purely from the chalcones doped PMMA thin films only.

3. Results and discussion

3.1. AFM analyses

To examine the influence of chalcones doping concentration on PMMA polymer matrix morphology, and the topography of the thin films were investigated using AFM technique. The AFM images of the thin films are plotted on x and y scales in the 5 μm range (Fig. 2). It is observed from the images that the surface roughness of the pure PMMA films is found to be larger, and it decreases with doping percentage.The measured roughness parameters of the AFM images show the average height of the image profile. The calculated values of R_a and R_q judges the roughness of the films (Table 1). R_a is the arithmetic average of the absolute values of surface height deviation measured from the mean plane, and R_q is the root mean square average of height deviation taken from the mean image data plane. It is found that R_a and R_q values decrease with the doping concentration of the chalcone derivatives. The observed highest values 5.3 & 8 nm in pure PMMA film suggests the greater surface roughness. Whereas, the observed lowest values 0.29 & 0.33 in MNC-30% sample indicate the smaller surface roughness. The average heights of the AFM image profile peaks and the valleys of the films are shown in Fig. 3.

3.2. Linear optical absorption

UV–Vis–NIR study helps to understand the types of optical transitions, the transparency and optical band gap of any materials. The NLO materials must exhibit a lower cut-off wavelength and wide optical transmittance window for practical usage in optoelectronic devices. The recorded UV-Vis-NIR absorption spectrum of the thin films in the wavelength range of 200–900 nm is shown in Fig. 4. The films are highly transparent in the near IR and visible region (450–900 nm) and have the maximum absorption in the region 300–337 nm, which corresponds to the π→π* transition. However, the absorption edge of the films is slightly changed with few nanometers of wavelength, and absorption found to be increased with doping concentration.

The optical band gap (E_g) of the material is strongly related to the