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A study of the optical limiting properties of acid red 92 doped PMMA film using a 532 nm diode-pumped Nd:YAG laser

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Abstract

Nonlinear optical properties of acid red 92 doped PMMA film have been investigated. The measurements were performed using CW laser at 532 nm wavelength by employing Z-scan technique. The nonlinear refractive index is found to be of the order of 10^{-9} cm^2/W. Moreover, a variation of nonlinear refractive index with doping concentration is observed. Significant optical multiple diffraction rings of the sample under CW illumination at 4 mM, 8 mM and 12 mM doping concentrations were observed. The optical power limiting behavior of acid red 92 doped PMMA film was also investigated. The sample with 12 mM concentration has the best limiting effect among the other two concentrations.

Key words: Nonlinear optics, nonlinear refractive index, Z-scan technique, optical limiting, dye.

1. Introduction

Since the discovery of laser by Maiman [1] in 1960, it has been widely used in many fields, including industry, medicine, laboratory and military. While causing a great progress for the human society, it also brings a potential hazard for human eyes and optical sensors. Consequently, there is a strong need for developing optical limiters which can effectively attenuate intense, potentially dangerous optical beam, allowing only a reduced transmission to the target area, and therefore protect human eyes and optical sensors from being damaged. For the development of such devices, appropriate optical limiting materials are very important. Many materials such as metallophthalocyanines (MPcs) [2,3] and porphyrins [4-7], gold nanoparticles [8], carbon-encapsulated magnetic nanoparticles [9], dibenzylideneacetone [10], TiO_2 nanocomposites [11], cluster $[WOS_3Cu_3I(2\text{-}MePy)_3]$ [12], mercury dithizonate [13], complex Co_2L_3 [14], nickel complexes of multi-sulfur 1,2-dithiolene [15] have been widely investigated. Amongst the nonlinear materials, organic polymers are particularly attractive because of properties such as low density, mechanical flexibility and high nonlinear response [16-18]. Polymethyl (methacrylate) is a hard, rigid and transparent polymer with a glass transition temperature of 125°C. Its average molecular weight is 6×10^4. It is tougher than polystyrene. PMMA is a polar material and has a large dielectric constant. PMMA matrix is most preferred for designing components because of its better resistance to hydrolysis and good outdoor weather resistance. It is a thermoplastic and can be molten and molded into any thing we want. Its physical durability is far superior to that of other thermoplastics.

Additional dopants to the polymer matrix will modify the properties pertaining to optical, electronic and electrical conductivity behavior of polymers [19]. It gives flexibility in designing the required size and shape of the material for devices even with a small quantity of the dopant.

In this paper, xanthenes dye, namely acid red 92 was doped in methyl methacrylate (PMMA) to prepare the film samples with various doping concentrations. The investigation on refractive index nonlinearity of the acid red 92 doped PMMA film was carried out using the standard Z-scan technique. Also we investigated the self-diffraction and optical limiting properties of the sample under CW laser illumination at 532 nm wavelength.

2. Experiment and discussion

2.1 Preparation and spectrum of the sample

The molecular structure of acid red 92 is shown in Fig. 1. The matrix material is PMMA. In our experiment, firstly, the acid red 92 and PMMA were dissolved by cyclohexanone. The content of acid red 92 and PMMA in cyclohexanone is 4 mM concentration ; secondly, dissolved acid red 92 and PMMA were mixed, heated (up to 50^{o} C) and stirred for 2 hrs, thus the mixed sols of acid red 92 and PMMA were obtained. The film was prepared on a clean glass slide by the repeat-spin-coating method and dried at room temperature for 48 hrs. The other polymer films with 8 mM and 12 mM concentration were also prepared in a similar manner. The film samples have a good purity and uniform thickness. The UV-VIS (Ultraviolet-Visible) absorption spectrum of the acid red 92 doped PMMA film was recorded using an UV-VIS spectrophotometer (UV-2401 PC SHIMAZU). The optical absorption of the acid red 92 doped PMMA film shows an absorption peak at 548 nm as shown in Fig. 2.

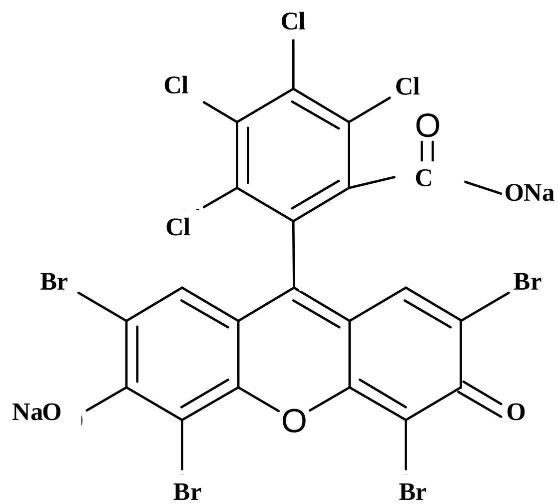

Fig. 1. Molecular structure of acid red 92 dye.

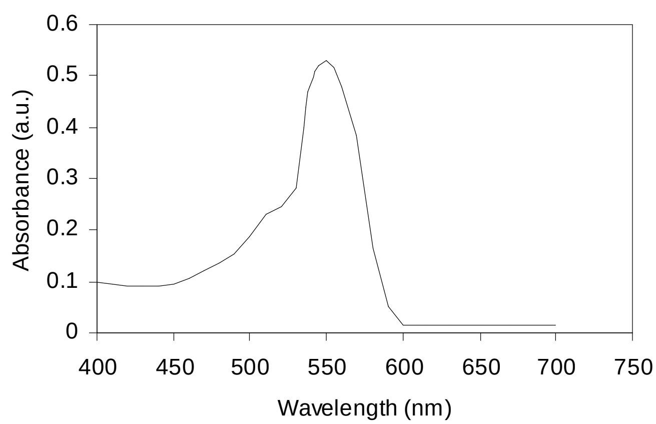

Fig. 2. UV-VIS absorption spectrum of acid red 92 doped PMMA film.

2.2 Thermal self-diffraction

The experimental setup for self-diffraction is shown in Fig. 3. A CW diode pumped Nd:YAG laser beam (Coherent, Compass 215M-50) is used as an illumination beam. The laser beam is focused by a positive lens with focal length of 3.5 cm. The sample is placed closely behind the focus and the beam is projected onto an observation screen, which is placed 20 cm away from the focal point. Then the pattern is recorded using a digital camera. Multiple concentric rings appears on the screen when the laser power exceeds a certain value (threshold value = 9 mW). The number of rings and the size of the outmost ring are both increase with increasing laser power. This indicates that they were intensity dependent. We assumed that thermally induced refractive index change is responsible for the observed diffraction. When the Gaussion beam illuminates the film, the medium absorbs the light and its temperature rises. The rises of temperature results in the change of local refractive index and thus induces the self-diffraction. A typical pattern of the diffraction rings for concentrations 4 mM and 12 mM is shown in Fig. 4.

The increasing of the number of diffraction rings and the size of the outmost ring with increasing the concentration are due to the increase in aggregation of the dye molecules at the point of focus at higher concentrations. The diffusivity extends to a larger region thereby causing more interference to take place leading to an increased number of rings.

2.3 Nonlinear optical measurement

The single beam Z-scan technique [20] was used to measure the nonlinear refractive index of the samples, where a Gaussian beam from a Nd:YAG laser of wavelength 532 nm is focused by a convex lens of focal length 3.5 cm. The sample was moved along the z-axis through the focal point. The transmission of the beam through an aperture placed in the far field was measured using photodetector fed to the digital power meter (Field master Gs-coherent). Fig. 5 shows the closed aperture Z-scan data for different concentrations of acid red 92 doped PMMA film. The peak followed by a valley-normalized transmittance obtained from the closed aperture Z-scan data, indicates that the sign of the refraction nonlinearity is negative i.e. self-defocusing. Self defocusing effect is attributed to local variation of refractive index with temperature. The nonlinear refractive index n_2 is estimated by the following equation [20]

$$n_2 = \frac{\lambda \Delta T_{p-v}}{0.812\pi(1-S)^{0.25} L_{eff} I_O} \qquad \dots (1)$$

where $L_{eff} = [1-\exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, α is the linear absorption coefficient, λ is the laser wavelength, S is the aperture linear transmittance, L is the thickness of the sample, I_o is the intensity of the laser beam at focus and ΔT_{p-v} is the difference between the normalized peak and valley transmittances for the closed aperture. In our experiment S= 0.4, I_o= 4.5 kW/cm^2 and L=1 mm. The nonlinear refractive index n_2 (cm^2/W) is calculated from the closed aperture normalized transmittance in Fig. 5. The obtained n_2 for 4 mM, 8 mM and 12 mM concentrations of acid red 92 doped PMMA film were measured to be -1.7 x 10^{-9} , -2.6 x 10^{-9} and -3.8 x 10^{-9} cm^2/W respectively.

2.4 The limiting properties of acid red 92 doped PMMA film

The experimental setup is similar to Fig. 3 where the observation screen is replaced by an aperture that is centered at the optical axis. Acid red 92 doped PMMA film with 4 mM concentration is placed at the valley behind the focal point. The input power of the laser beam and the corresponding output power through the aperture are detected by a photodetector fed to the digital power meter. So, the characteristic curve of the output power as a function of the input power can be obtained. The curve of the optical limiting characteristics under wavelengths of 532 nm is shown in Fig. 6. It can be seen that at a very low incident power, the transmittance of the sample is linearly increasing with the incident power. However, for 4 mM of sample concentration, when the incident power reaches 12 mW, the transmittance of the sample starts to deviate from linearity [defined as limiting threshold, that is, the incident power at which the transmitted power starts to deviate from linearity].

With a further increase in the incident power, the transmitted power reaches a plateau and is saturated at 1.9 mW (defined as the limiting amplitude, i.e., the maximum output power), showing the optical limiting property. A similar behaviour is observed in acid red 92 doped PMMA film with 8 mM and 12 mM doping concentrations. The limiting threshold and limiting amplitude of the film sample with 8 mM and 12 mM doping concentrations are 10, 1.48, 9 and 1.07 mW, respectively. Moreover, we can also get the regularity: the more doping concentration, the lower the threshold value, and the better limiting effect is.

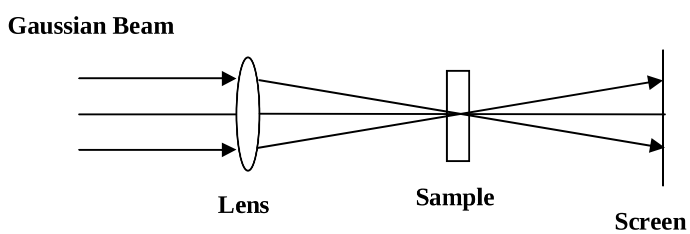

Fig. 3. Schematic diagram for self-diffraction.

(a)

(b)

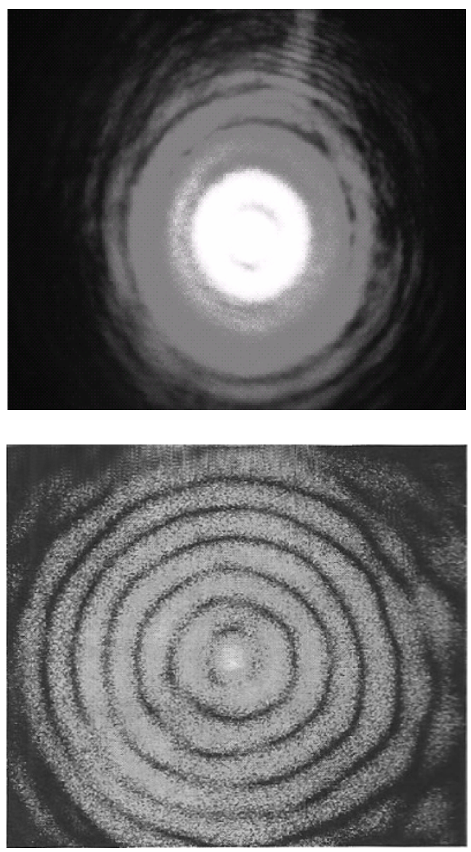

Fig. 4. A typical pattern of diffraction rings illuminated by laser beam of λ = 532 nm for concentrations: (a) 4 mM and (b) 12 mM.

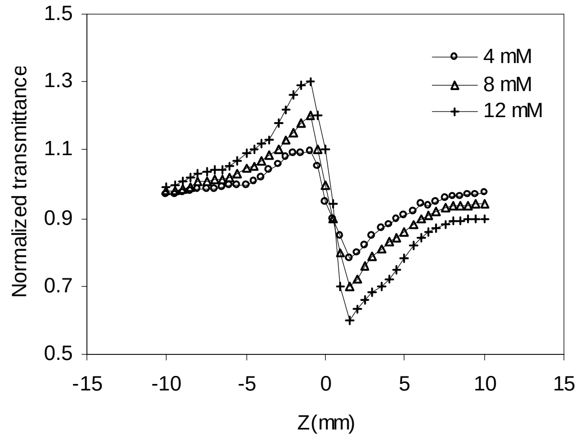

Fig. 5. Closed-aperture Z-scan data for different concentrations of acid red 92 doped PMMA film.

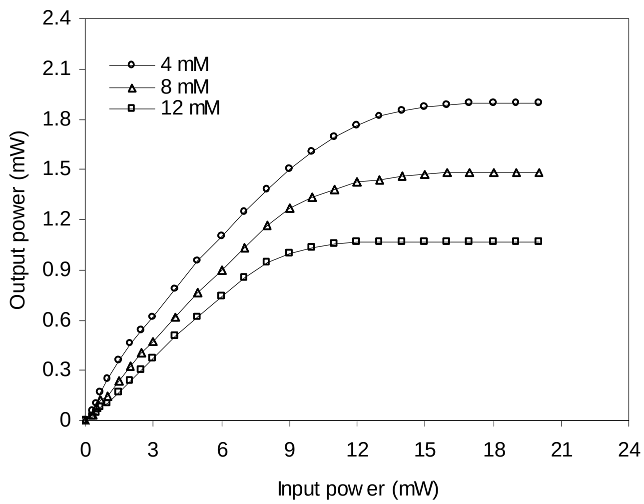

Fig. 6. Optical limiting effect of the acid red 92 doped PMMA film for different concentrations.

3. Conclusions

In conclusion, the nonlinear refractive index in the organic dye, acid red 92 doped PMMA film was investigated using a single-beam Z-scan technique under CW laser excitation at 532 nm. We also demonstrated the significant self-diffraction under CW Nd:YAG laser illumination. Both the number of rings and the size of the outmost ring are intensity dependent. Under the same incident power, laser beams with different concentrations doped film have different numbers of diffraction rings and different sizes of outmost rings. The number and the size of diffraction pattern for the sample are largest ones at 12 mM doped film. Additionally, the limiting properties of the sample demonstrate a concentration dependence. The limiting effect of the sample with 12 mM concentration is better than that of the other two concentrations.

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دراسة الخواص الحدية لفلم مطلي بصبغة acid red 92 و PMMA باستعمال ليزر Nd:YAG عند الطول الموجي 532 nm

الخلاصة

يتناول هذا البحث دراسة الخواص البصرية اللاخطيه لفلم مطلي بصبغة acid red 92 و PMMA باستعمال ليزر مستمر طوله الموجي 532 nm وتقنيه Z-scan. حيث وجد ان معامل الانكسار للفلم هو بحدود 10^{-9} cm^2/W وانه يتغير بتغير سمك الفلم.وقد تم ملاحظه حلقات حيود عندما يسلط ليزر مستمر على الفلم.وكذلك قمنا في هذا البحث بدراسة الخواص الحدية للفلم ووجدنا ان الفلم المطلي بتركيز 12 mM يمتلك افضل خواص حدية مقارنة مع التركيزين الآخرين.