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RAPID COMMUNICATION

Nonlinear optical absorption and NIR to blue conversion in highly stable polymeric dye rod

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Abstract A simple method for preparing transparent crack-free solid polymeric matrices is presented. Different dopants may be hosted in the polymeric matrix. The method is applied to prepare Glycidyl-methacrylate polymeric rods doped with solutions of coumarin 500 laser dye (ethanol and chloroform). The solvent's effect has appeared as a shift in the absorption and photoluminous spectral bands of the laser dye in the solid polymeric host. The prepared solid samples showed nonlinear optical response on excitation with 532 nm of nanosecond laser pulses using the open aperture z-scan technique. Each sample shows different nonlinear behavior in response to the irradiating laser beam. The theoretical fitting of the experimental data indicates that the dominant mechanism of nonlinear absorption is the two-photon absorption process. Visible amplified spontaneous emission is reported in both polymeric dye rods by NIR pumping. High photostability is reported for the samples.

1 Introduction

In recent years, the search for optical materials possessing nonlinear optical properties has grown markedly. Organics are considered as nonlinear optical candidates for wide applications in the opto-electronics and laser fields. For instance, optical limiting [1–4], optical shutters [5, 6], two-photon microscopy [7], optical data storage [8, 9], three-dimensional micro-fabrication [10], displays [11, 12], laser pulse compression and amplification (mode locking) [13–15], and tunable and up-conversion lasers [16–19]. Among the organics, coumarin dyes constitute a family of intensely fluorescent dyes which have been used as tunable blue-green laser materials [20, 21]. The basic requirement for a good nonlinear optical material is the high optical quality with large and stable optical nonlinearity in the solid state. Therefore, encapsulating dye molecules in solid matrix presents a good alternative to the liquid dyes due to their compactness and safety in handling, in addition to avoidance of toxicity, flammability, shelf aggregation, flow fluctuations, and solvent evaporation problems. Also, it can allow for composite materials of high dye concentration and novel optical properties with the ease in processing and assembling into optical devices.

Nonlinear absorption is a phenomenon defined as a nonlinear change (increase or decrease) in absorption with increasing intensity. This can be of two types: saturable absorption (SA) or reverse saturable absorption (RSA) behaviors. RSA behavior is characterized by a decrease of transmittance with increasing the input energy (valley shape), whereas the opposite happens in SA (peak shape). With increasing intensity, if the excited states show saturation (population densities in the excited and ground states are roughly equal), the transmission will show SA characteristics. SA is vital for use of dyes in optical pulse compression or amplification (mode locking). In general, RSA behavior in dyes is explained either in terms of excited state absorption (ESA) or two-photon absorption (TPA) processes depending on the location of the excitation wavelength relative to the sample's absorption band. ESA may occur from the lower excited to a higher excited state (singlet or triplet) when the population of the lower excited states is high. TPA is a third order nonlinear optical process where two photons are simultaneously absorbed to excite a molecule to a higher state of energy less than or equal to the sum of the two photons. An important application of RSA is optical limiters which used in pro-

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tecting human eyes and sensitive optical components from laser-induced damage.

Optical nonlinearities can be measured using the simple technique of z-scan [22–24]. The technique is effective particularly in measuring the nonlinear absorption and refraction. It yields both the sign and the magnitude of the nonlinearity. In this technique, a sample is moved along the z-axis through the focus of a laser beam, and the beam transmission is measured at a detector behind the focus as a function of the sample position z. It is used in two modes, the closed aperture "CA" (aperture in front of the detector) and the open aperture "OA" (without aperture). OA z-scan is sensitive only to nonlinear absorption, whereas the CA z-scan is sensitive to nonlinear absorption as well as refraction.

In this work, we first present a simple and novel method for preparing crack-free solid polymeric hosts with good optical transparency. The method is applied in preparing solid polymeric rods of Glycidylmethacrylate (GMA) doped with two solutions of coumarin500 "C500" dye (C500 in chloroform and C500 in ethanol). Absorption and reflection of the samples are measured. Laser induced fluorescence is measured at room temperature by pumping the samples at 377 nm of nitrogen laser pulses. The nonlinear absorption behavior of C500 in solid GMA polymeric host is reported, for the first time to our knowledge, using the standard single beam z-scan technique at 532 nm. Blue and green frequency up-conversion amplified spontaneous emission is observed from the solid dye samples upon pumping by NIR diode laser of nanosecond pulses. The samples displayed high photo-stability on pumping by NIR laser source. The prepared samples have the potential to replace the available liquid dye lasers.

2 Experimental

C500 laser dye and GMA polymer were procured from Exciton and Aldrich, respectively, and used without further purification. C500 in different solvents, chloroform or ethanol, was mixed with GMA. The dye concentrations were 9×10^{-3} M and 3×10^{-2} M in ethanol and in chloroform solvents, respectively. Polymerizations were carried out, without adding any initiators, by exposing the dye-polymer mixtures to ^{60}Co γ-rays source with total dose of 1 Mrad (10 kGy) [25]. The polymerized rods were immersed in distilled water for 24 h, to remove any water-soluble components, then fixed at 70°C for 24 h. The obtained rods were transparent and crack-free. Both samples are fluorescent under illumination of an UV lamp. The color of the ethanolic rod sample is blue-greenish while the chloroformic one is yellow. These rod samples will be referred to as the E sample (C500:ethanol:GMA) and F sample (C500:chloroform:GMA).

For UV-VIS-NIR measurement, the rods were cut into thin discs (∼2 mm in thickness of diameter 1 cm) and their faces were polished well to obtain smooth, uniform surfaces. The reflection and linear absorption spectra were obtained with a spectrophotometer (Burkin Elmer).

Nitrogen laser (377 nm) and diode laser (800 nm) were used as excitation sources for the polymeric dye rods. The output photoluminescence was collected using a 10 cm lens and detected by a grating spectrograph, of 1 Å spectral resolution (SPEX 750M), connected with a photomultiplier and a data scan [SPEX DS1010].

The third-order NLO properties of the samples were determined by performing OA z-scan experiments. A second harmonic Q switched Nd:YAG laser (Continuum) with pulse width of 10 ns (FWHM) was used as an excitation source at a repetition rate of 1 Hz to reduce the possible thermal accumulative effect. Each sample was moved along the z-axis through the focus of the lens (150 mm focal length). The laser energy was varied using different neutral density filters. Care was taken to prevent material optical breakdown and irreversible changes produced by laser radiation. The radius of the beam waist (w_0) has been measured using a beam profiler and was found to be 58 μm. The Rayleigh length (or diffraction length) $z_0 = \pi w_0^2/\lambda$ was estimated to be 20 mm which is much longer than the thickness of the samples (0.2 cm). The reference beam energy and the on-axis transmitted beam energy were measured simultaneously by a dual-channel energy meter to reduce the influence of laser power fluctuation. The distance between the detector and the focus of the lens was apart enough to satisfy the far-field approximation.

3 Results

The absorption and fluorescence spectra of C500-doped polymeric rods are presented in Figs. 1a and 1b. For comparison, the absorption spectrum of the blank GMA polymeric rod is displayed in the same figure by the dashed curve. No absorption is observed for the blank GMA in the whole VIS-NIR spectral range.

For the dye doped polymer, a strong broad absorption band is observed (solid curves in Figs. 1a and 1b). The absorption band maximum is located at 393 nm and ∼417 nm for sample E and F, respectively. This shift in the absorption bands is attributed to the solvents and the difference in dye concentration of each sample. It should be noted that there is no linear absorption beyond the observed absorption band up to 1100 nm for both samples.

Fluorescence spectra presented in Figs. 1a and 1b by the symbol curves. Sample E displayed a broad bandwidth of ∼80 nm with peak located at 482 nm, while F sample displayed a bandwidth of ∼90 nm with peak at 534 nm.

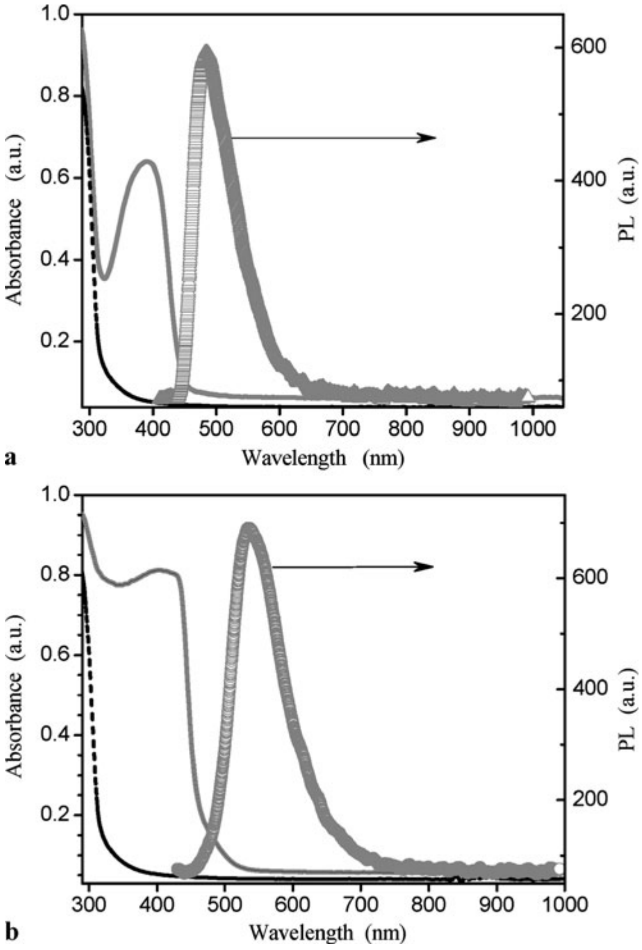

Fig. 1 Linear absorption (*solid line*) and photoluminescence (*symbols*) of (**a**) C500:ethanol:GMA sample and (**b**) C500:chloroform:GMA sample together with the absorption of the blank GMA polymeric solid matrix (*dashed line*)

Large Stokes shift is observed for both samples ($\sim$90 nm and $\sim$110 nm for samples E and F, respectively). In addition, the shift in C500 emission bands (of the two samples) is larger than the shift in the absorption bands. The small shift in the absorption spectra ($\sim$25 nm) and the large one in the emission ($\sim$50 nm) may be an indication for the higher value of the excited states dipole moments than of the ground states [21].

OA z-scan experiment was carried out to investigate the nonlinear optical properties of the prepared samples. The experiment was carried out first on the undoped solid polymeric sample. No nonlinear absorption behavior was recorded where the transmitted intensity was nearly constant with varying z.

Figure 2 depicts the OA z-scan measurements of sample E. The measurements were carried out with a 532 nm laser at irradiance 420, 660, 836 $\mathrm{MW\,cm^{-2}}$. The normalized OA transmittance measurements shows valley shapes with increasing in the valley's depth as the irradiance increased. The result is an indication of the RSA behavior of this sample.

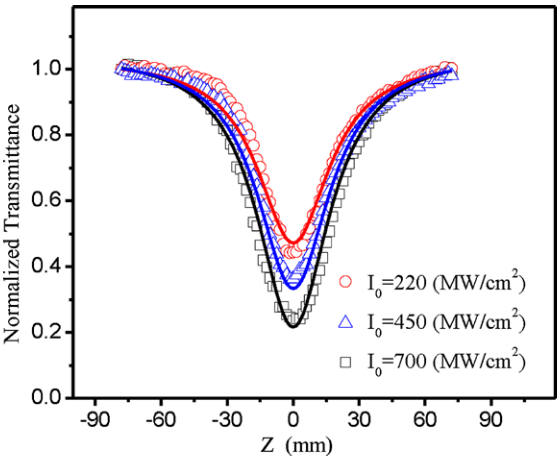

Fig. 2 Open aperture z-scan experimental data of C500:ethanol:GMA (*symbols*). *Solid lines* show theoretical fit to the experimental data. The sample displays RSA nonlinear behavior

Typical OA measurements of sample F are presented in Fig. 3 at two values of irradiance: 220 and 700 $\mathrm{MW\,cm^{-2}}$. The measurements show peak shapes which indicating the SA behavior of this sample. The observed change in the nonlinear absorption behavior of C500 dye (from SA to RSA) was reported previously for other materials, for instance: (TBA)2 Ni(dmit)2 organic, RhB laser dye, organic complex BuCu in PMMA, ruthenium and osmium complexes of modified terpyridines, zinc meso-tetra(p-methoxyphenyl) tetrabenzoporphyrin, and other materials.

In (TBA)2 Ni(dmit)2 organic material [23] showed a similar behavioral change with increasing in the irradiating intensity. The change was attributed to the fifth-order nonlinearity, as the excitation wavelength was 1064 nm and absorption peaked near 532 nm for their sample.

In RhB excited by 600 nm [24], a switchover from SA to RSA behavior was observed with increasing intensity and with increasing concentration in methanol and vice versa in water. The behavior in methanol was attributed to the localization of energy leading to resonant TPA. In water, the changeover from RSA to SA is attributed to the aggregation and fast decay times of dimers, which get populated through energy transfer. At higher concentrations, SA was attributed to enhancement of TPA due to aggregation of dye molecules, which lead to the localization of energy in the first excited S_1 state then to higher singlet states. At lower concentrations, monomers are predominant and, therefore, excitation in S_1 diffuses owing to dephasing–vibrational relaxation within S_1 state.

In "zinc meso-tetra (p-methoxyphenyl) tetrabenzoporphyrin" [26], the SA behavior was attributed due to the saturation of the first triplet state and the RSA behavior was

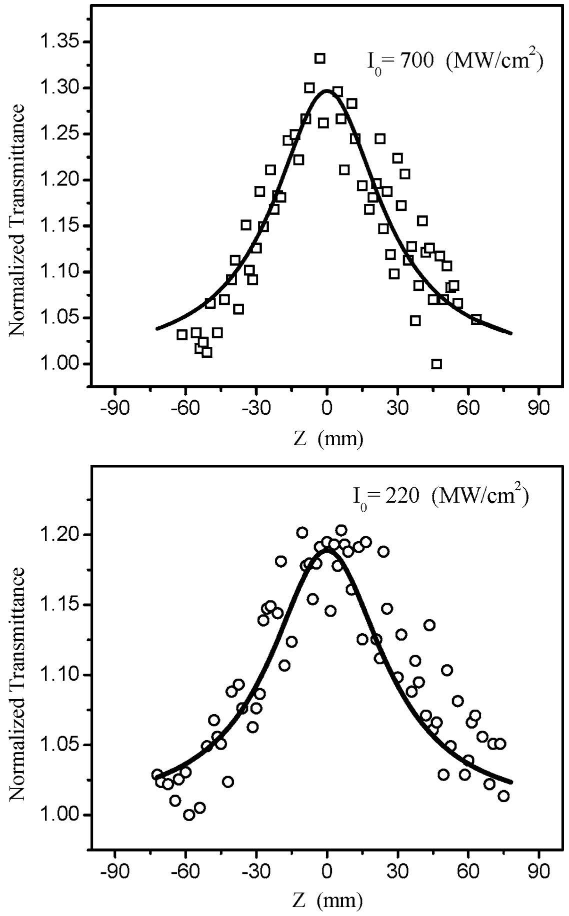

Fig. 3 Open aperture z-scan experimental data of C500:chloroform:GMA (*symbols*). *Solid lines* show theoretical fit to the experimental data. The sample displays SA nonlinear behavior

attributed to the excitation of population into higher excited triplet states at higher intensities.

The organometallic complex BuCu in PMMA thin film was pumped at 532 and 1064 nm wavelength [27]. The material showed SA at 532 nm and RSA at 1064 nm. These wavelengths were located in the near-resonant and off-resonant area of the linear absorption spectrum of the sample, respectively. The origins of the NLO properties were interpreted by the molecular structure of the material.

For ruthenium and osmium complexes of modified terpyridines [28], SA was explained as being due to the compound and the RSA portion as being due to TPA.

The most plausible explanation for the observed saturation behavior change in our samples may be attribute to the change in the dye concentration and also to the pumping laser at 532 nm, as it located off resonance with the singlet absorption band of sample E and at the lower edge of the absorption band of sample F [24]. Therefore, the greater localization of energy in sample F is expected to leads to SA behavior rather than RSA [29].

The obtained data of OA z-scan transmittance through a sample is used to calculate its nonlinear absorption coefficient. Consider that the propagation of light beam of intensity "I" through a material is given by

$$dI/dz = -\alpha I = -\alpha_0 I - \beta I^2 - \cdots \tag{1}$$

where α_0 (cm^{-1}) and β (mW^{-1}) are the linear and nonlinear absorption coefficients, respectively. The incident light intensity variation with the beam size $w(z)$ on either side of the focus ($z = 0$) is given as

$$I_{\mathrm{in}}(z, r, t) = I_0\left(\frac{w_0}{w(z)}\right)^2 e^{-t^2/\tau^2} e^{-2r^2/w^2(z)} \tag{2}$$

where $(w(z)/w_0)^2 = 1 + (z/z_0)^2$; $z_0 = \pi w_0^2/\lambda$ and τ is the laser beam pulse width.

The transmitted intensity through the sample is obtained from (1) as

$$I_{\mathrm{out}}(z, r, t) = I_{\mathrm{in}}(z, r, t)\left(\frac{\exp(-\alpha L)}{1 + q(z, r, t)}\right) \tag{3}$$

where, $q(z, r, t) = \beta L_{\mathrm{eff}} I_{\mathrm{in}}(z, r, t)$, and L_{eff} is the effective length within a sample of thickness L $\{L_{\mathrm{eff}} = (1 - \exp(-\alpha_0 L))/\alpha_0\}$. The resultant normalized transmittance for OA was derived by integrating (3) over the spatial and temporal profile of the pulse and is given by [22];

$$T(z) = \frac{1 + (z^2/z_0^2)}{q(z, 0, 0)\sqrt{\pi}} \times \int_{-\infty}^{+\infty} \ln\left(1 + \frac{q(z, 0, 0)}{1 + (z^2/z_0^2)} \exp(-\tau^2)\right) d\tau \tag{4}$$

For $|q| < 1$, this normalized transmittance can be written as [22];

$$T(z) = \frac{I}{I_0} = \sum_{m=0}^{\infty} \frac{1}{(m+1)^{3/2}} \left(\frac{-q_0}{1 + (z/z_0)^2}\right)^m \quad \text{for } |q_0| < 1 \tag{5}$$

where m is an integer and $q(z, 0, 0)$ is denoted by q_0.

The nonlinear absorption coefficient β is obtained from a best fitting performed on the obtained OA experimental measurement with (5). The imaginary part of the refractive index $\operatorname{Im}\chi^{(3)}$ and the TPA cross section (σ_{TPA}) can then be estimated from the relations,

$$\operatorname{Im}\chi^{(3)} = \varepsilon_0 c \lambda n_0^2 \beta / 2\pi \qquad \text{and} \qquad \sigma_{\mathrm{TPA}} = \beta h \nu / N_0$$

where n_0 is the linear refractive index of the sample; ε_0 is the permittivity of free space, c the velocity of light in vacuum, h is the Planck's constant, ν is the frequency of laser source, and N_0 is the number of molecules per unit volume.

Theoretical fit to the experimental data of samples E and F are represented by the solid curves in Figs. 2 and 3. It is clear that the theoretically estimated curves are matched well with OA z-scan experimental data; therefore, we may conclude that TPA is the mechanism responsible for the observed nonlinear absorption behavior.

The average estimated values for the samples' parameters are: $\beta = -1.6 \times 10^{-10}$ (mW^{-1}), $\sigma_{\mathrm{TPA}} = 386$ (GM), $\mathrm{Im}\,\chi^{(3)} = 5.8 \times 10^{-12}$ (esu) for sample E, and $\beta = 2 \times 10^{-10}\ \mathrm{mW}^{-1}$, $\sigma_{\mathrm{TPA}} = 386$ GM, $\mathrm{Im}\,\chi^{(3)} = 8.2 \times 10^{-12}$ (esu) for sample F.

It is noticed in Fig. 1 that both solid dye samples display no absorption in the spectral range from 550 to 1100 nm. However, as the nonlinear absorption property has been proved for these samples, one may speculate that two-photons of NIR radiation may be simultaneously absorbed as long as their sum energies falls within, or above, the linear absorption band of the sample. Therefore, TP pumped frequency up-conversion experiment was carried out for the laser dye rods.

A diode laser of 800 nm wavelength, 5 ns pulse duration, and repetition rate of 10 Hz was used to transversely excite the solid polymeric dye samples. The rod samples were ∼3 cm in length and 1 cm in diameter with polished two ends. The fluorescence was obtained by grating spectrograph as mentioned above. A cut off filter was employed to eliminate the NIR laser pump beam.

Typical spectra of a strong TPA induced super-radiance fluorescence (or cavity-less lasing) in the two samples are shown in Figs. 4a and 4b. For comparison, the spectrum due to one-photon fluorescence is replotted in the same figure (symbols curves). It clear that, for both samples, the bandwidth of the super-radiance spectrum is much narrower (∼8 nm) than the linear PL band (∼100 nm). It is also noticed that the emission peaks due to linear absorption (one-PA) and TPA are nearly coincidence (located at nearly the same wavelength). This is attributed due that the gain of the red-tail part of the PL does not reach the amplification threshold and the blue part of PL cannot emit due to reabsorption effect.

Photostability is an important parameter for laser dyes. It can limit its performance as an active medium in solid-state laser systems. Photostability or lifetime of laser dyes is a measure of their energy level ability of how many watt-hours can it stand without bleaching. This parameter can be indicated by measuring the number of laser pulses required to reduce the laser output intensity to half its initial value. In the present work, a measurement for the photostability was carried out for both rod samples. Each sample was pumped with 800 nm diode laser at energy level of 20 mJ and pulse rate of 10 Hz. The normalized output energy as function of number of pumping laser pulses is plotted in Fig. 5. It is clear from the figure that after 2 hours (72,000 pulses) of pumping sample E (and sample F) at the same position, the output energy dropped to only ∼79% (and ∼75%) of its initial value, respectively. This result indicates the high photostability and high laser-damage threshold of the prepared samples. This high photostability may be attributed to both the preparation method using γ-ray irradiation, which yielded dense polymeric structure, and to the low photon energy of the NIR diode laser pumping source.

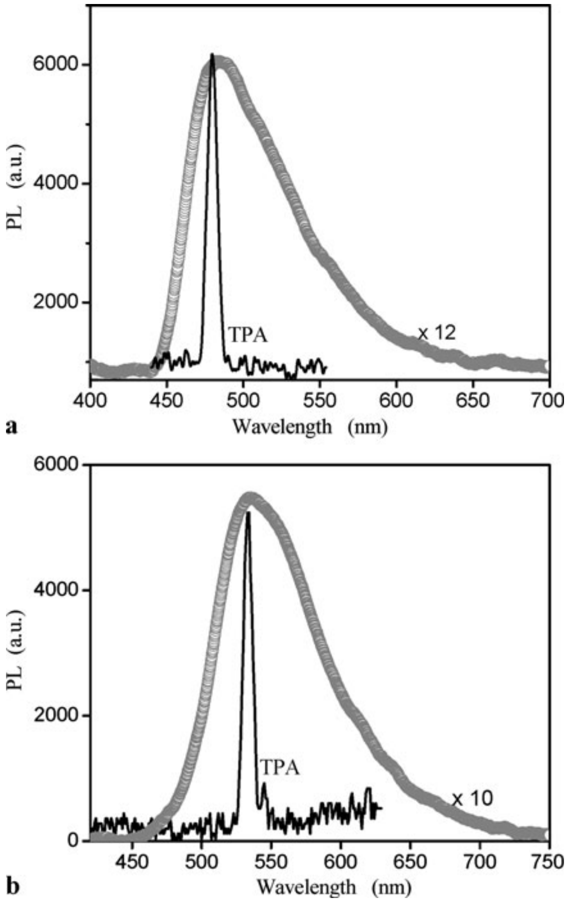

Fig. 4 **a** Fluorescence spectra of C500:ethanol:GMA rod due to one-PA at 377 nm (*symbols*) and TPA at 800 nm (*solid line*). **b** Fluorescence spectra of C500:chloroform:GMA rod due to one-PA at 377 nm (*symbols*) and TPA at 800 nm (*solid line*)

4 Conclusions

In summary, a simple and promising method for preparing highly transparent solid polymeric matrices is presented. Polymerization was carried out by exposing the liquid polymer to ^{60}Co γ-rays source. The method is applied to prepare solid GMA polymeric rods undoped and doped with C500 laser dye solutions (in ethanol and chloroform). The effect of the solvents has appeared as a shift in the absorption band and emission band of the dye. For C500:ethanol:GMA, a broad fluorescence band of width 80 nm is obtained with emission peak at 482 nm, while for C500:chloroform:GMA, a fluorescence bandwidth was 90 nm with emission peak at 534 nm.

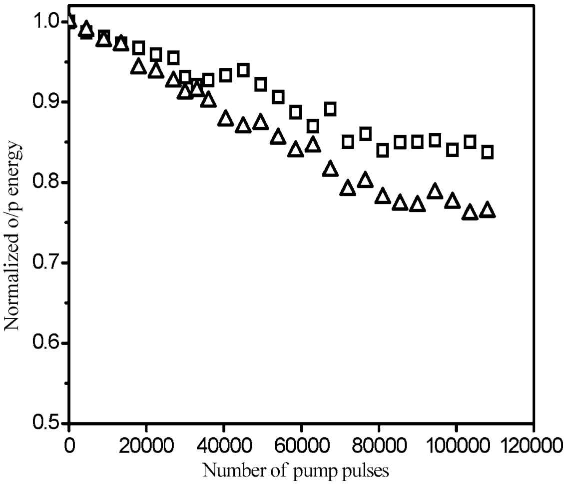

Fig. 5 Photo-stability of C500:ethanol:GMA polymeric rod (*triangle symbol*) and C500: chloroform:GMA rod (*square symbol*)

The nonlinear optical response of the samples was investigated using the open aperture single-beam z-scan technique under excitation with nanosecond laser pulses of 532 nm at repetition rate of 1 Hz. Different nonlinear optical behavior was observed in each sample. The difference in the nonlinear behavior was attributed due to the location of the excitation wavelength relative to the sample's absorption band. The excitation wavelength is located off-resonance of the absorption band of C500:ethanol:GMA sample and at the lower edge of absorption band of C500:chloroform:GMA sample. As a result, the first sample displayed RSA behavior while the second sample showed a SA behavior, respectively. It is worth mentioned that, although the C500:ethanol:GMA sample displayed RSA behavior, it was uneffective in limiting the 532 nm optical laser powers. Theoretical fitting to the measured intensities via OA z-scan indicates that the dominant nonlinear mechanism is two-photon absorption process.

TPA induced frequency up-conversion is reported by pumping the samples with 800 nm diode laser pulses of 5 ns duration. The absorption of two-NIR photons are converted to blue and green amplified spontaneous emission at 482 nm and at 534 nm in C500:ethanol:GMA and C500:chloroform:GMA rod samples, respectively.

Finally, high photo-stability is reported for both rod samples which attributed due to the preparation method using γ-ray irradiation which yielded dense polymeric structure in addition to the low photon energy of the pumping diode laser source. The prepared samples have the potential to replace the available liquid dye lasers.

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