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Characterization of nonlinear optical parameters of polymethine dyes

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ABSTRACT We investigated nonlinear refraction, nonlinear absorption, and saturable absorption of polymethine dyes by the Z-scan technique ($\lambda = 1064$ nm). The analysis of simultaneous appearance of several nonlinear optical processes in dye solutions excited by picosecond pulses was carried out. The saturable absorption was analyzed taking into account various models. Nonlinear refractive indices, nonlinear absorption coefficients, and saturation intensities of various polymethine dyes were measured.

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1 Introduction

Applications of polymethine dyes in laser physics require their various optical parameters to be investigated. Whereas the optical characteristics of such dyes are well defined [1], the analysis of their ultra-fast nonlinear response has not yet received appropriate attention and is of great importance. Previously it was shown that the nonlinear susceptibilities of a number of organic dyes possessing double-conjugated bonds are comparable with those of resonant susceptibilities of atoms [2, 3]. Such molecules with double-conjugated bonds are highly attractive as the nonlinear media. For instance, the delocalization of π-electrons in fullerenes causes the large value of the nonlinear susceptibility [4, 5].

The high-frequency Kerr effect, reverse saturable absorption, multi-photon absorption, and saturable absorption are the main nonlinear optical processes during propagation of ultra-short laser pulses through such dyes. The last process plays a crucial role in achieving the passive mode-locking (PML) conditions of ultra-fast pulse generation. Variations of nonlinear optical characteristics of dyes due to such factors as intense light interaction, solvents, temperature, etc., lead to the changes of the parameters of laser radiation propagating through such media. During their lifetime the irreversible changes in polymethine dye mode-lockers [6] lead to their nonlinear optical parameter variations (saturation intensities, nonlinear absorption coefficients, etc.).

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In this paper, we present our investigations of various nonlinear optical characteristics of polymethine dyes using the Z-scan technique.

2 Experimental set-up

Picosecond radiation from a Nd:YAG laser ($\lambda =$ 1064 nm, $\tau = 55$ ps) was used in our studies of dye solutions. The investigated sample (a 5-mm-thick quartz cell filled with dyes dissolved in ethanol, QC) was mounted on a translation stage TS controlled by a computer that moved the sample along the Z axis through the focal point of the focusing lens (25 cm focal length lens, FL, Fig. 1). Laser pulse energy was measured by the calibrated photodiode PD1. A 1-mm aperture A transmitting 3% of laser radiation was fixed at a distance of 120 cm from the focal plane (closed-aperture scheme). Output radiation propagated through this aperture was measured by the photodiode PD2. The closed-aperture scheme allowed us to determine the sign and the magnitude of the nonlinear refractive index (γ) using a normalized transmission trace $T(z)$.

The open-aperture Z-scan scheme (without aperture A) was used for the measurements of the nonlinear absorption coefficient (β). The detector PD2 in that case was kept at such a distance from the sample that allowed us to measure all transmitted radiation to determine the dependence of the sample's transmission on the intensity of laser radiation [7].

In these experiments we used a Gaussian beam that was filtered in a spatial filter. The divergence of radiation before the focusing lens was chosen to be 0.5 mrad. The beam-waist radius ω_0 (at $1/e^2$ intensity level) was measured to be 63 μm. We also provided the calculations of beam-waist

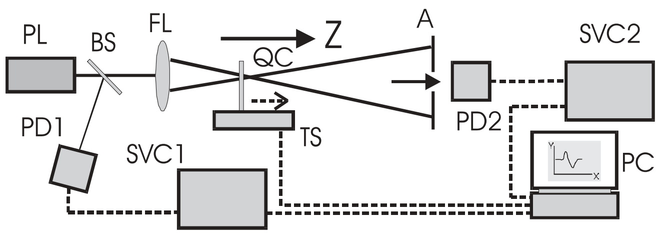

FIGURE 1 Experimental set-up. PL: picosecond laser; FL: focusing lens; QC: quartz cell with dye solutions; PD1 and PD2: photodiodes; SVC1 and SVC2: stroboscopic voltage converters; TS: translation stage; PC: personal computer; A: aperture; BS: beam splitter

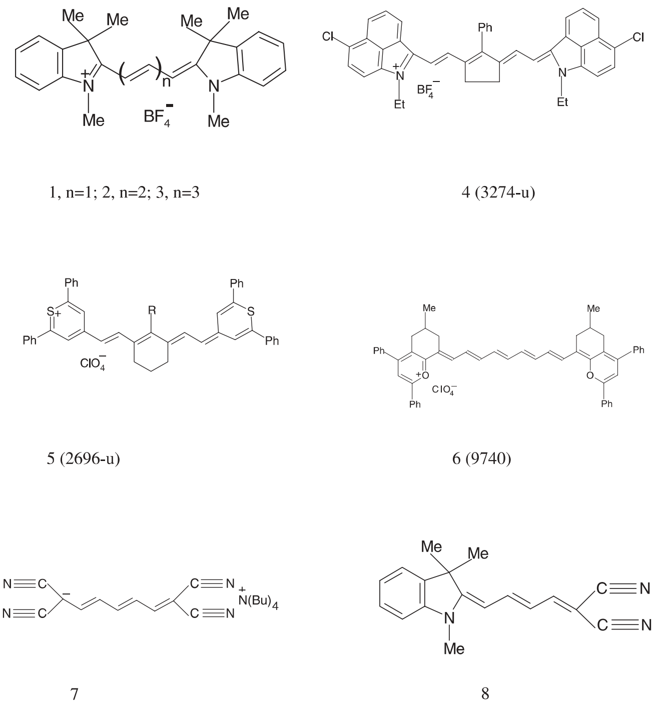

FIGURE 2 The structures of polymethine dyes (frequently used dye numbers are presented in brackets)

radius in accordance with the next feature of the closed-aperture Z-scan technique. The distance (Δz) between the maximum and the minimum of the function $T(z)$ is related to the spatial characteristics of the focused Gaussian radiation in the focal plane by the formula $\Delta z \approx 1.7 z_0$, where $z_0 = 0.5 k\omega_0^2$ is the diffraction length of the beam and $k = 2\pi/\lambda$ is the wave number. The calculated ω_0 size ($\omega_0 = 60\,\mu\text{m}$) in that case was close to our straight measurements of beam-waist radius. Thus, the analysis of the normalized transmission allows us to calculate the spatial parameters of the focused radiation to within high accuracy, assuring accurate determination of nonlinear optical parameters of the samples.

Dye structures (dyes 1–8) are shown in Fig. 2. These dyes can be characterized as possessing different ionic states, namely cationic (dyes 1–6), anionic (dye 7), and neutral (merocyanine dye 8). The analysis of their optical characteristics was presented in [1, 6].

3 Results and discussion

Figure 3 shows the normalized transmittances as functions of sample position in the closed-aperture Z-scan scheme for cationic dyes (1, 3) and the neutral one (8). One can see that, along with Kerr-nonlinearity influence, nonlinear absorption takes place. In that case the transmittance curve of closed-aperture Z-scan observes a suppression of a peak and an enhancement of a valley.

One of the advantages of the Z-scan technique is the possibility of separation of the contributions of several nonlinearities when they are presented simultaneously. In general, when both nonlinear refraction and absorption are presented, the normalized transmittance (T) of samples placed in the closed-aperture Z-scan scheme can be written as follows:

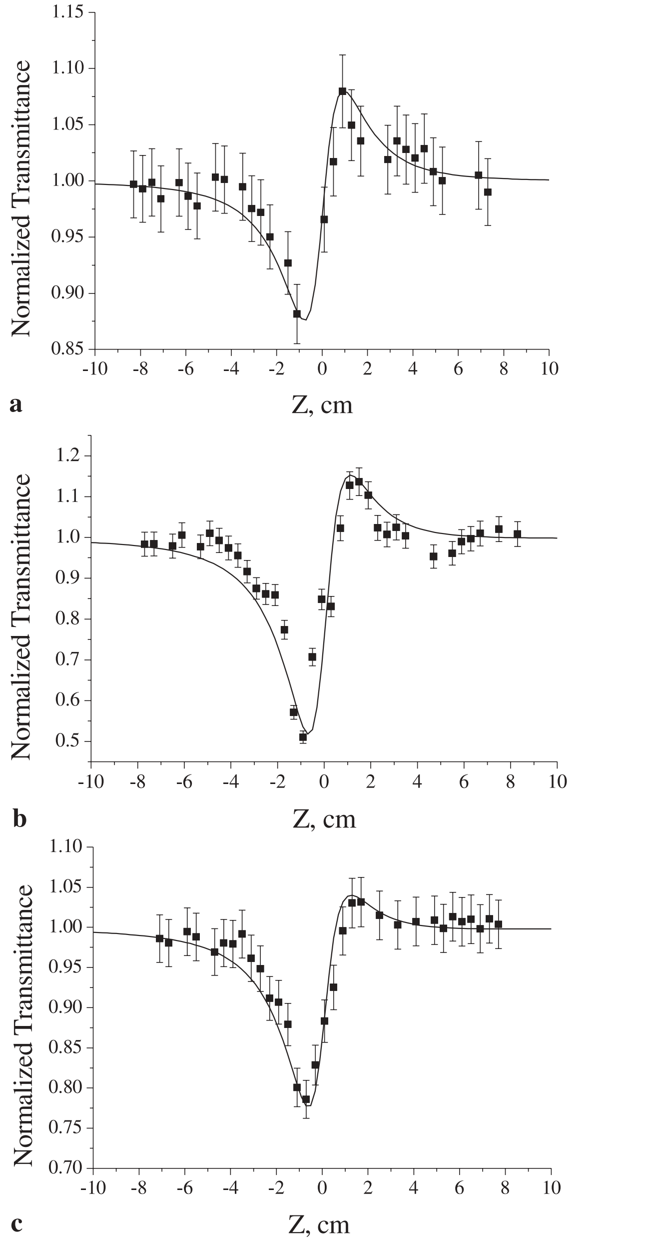

FIGURE 3 The normalized transmission dependences for solutions of dyes 8 (**a**), 3 (**b**), and 1 (**c**) measured in the closed-aperture Z-scan scheme. *Solid lines* are the theoretical fits

$$T = 1 + \frac{4x}{(x^2+9)(x^2+1)}\Delta\Phi_0 - \frac{2(x^2+3)}{(x^2+9)(x^2+1)}\Delta\Psi_0\,, \quad (1)$$

where $x = z/z_0$, $\Delta\Phi_0$ and $\Delta\Psi_0$ are the parameters determining phase shift near the focal point as a result of nonlinear refraction and nonlinear absorption respectively, $\Delta\Phi_0 = k\gamma I_0 L_{\text{eff}}$, $\Delta\psi_0 = \beta I_0 L_{\text{eff}}/2$, I_0 is the laser-radiation intensity at the focal point, $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ is the effective length of the sample, α_0 is the linear absorption coefficient, and L is the sample length. Introducing the coupling factor ϱ, which is the ratio of imaginary to real parts of the third-order susceptibility ($\varrho = \beta/2k\gamma$), one can get the relation between $\Delta\Phi_0$ and $\Delta\Psi_0$ ($\Delta\Psi_0 = \varrho\Delta\Phi_0$). Equation (1) in that case can be rewritten in the following form [8]:

$$T = 1 + \frac{2(-\varrho x^2 + 2x - 3\varrho)}{(x^2+9)(x^2+1)} \Delta\Phi_0 \,. \quad (2)$$

The theoretical $T(z)$ curves were fitted to our experimental data using (2). In particular, the best fitting for dye 1 was observed at $\varrho = 0.35$ and $\Delta\Phi_0 = 0.6$. After fitting of ϱ and $\Delta\Phi_0$ we consequently found γ and β. The same calculations were carried out for other dye solutions. We also made independent β measurements of these dyes using the open-aperture Z-scan technique. One can obtain the data on nonlinear refraction and nonlinear absorption coefficients of material in some particular cases from the closed-aperture Z-scan. An open-aperture Z-scan can be performed to test the results obtained with the nonlinear curve fitting using (2).

In Fig. 3, one can see the theoretical curves calculated by (2) taking into account the mutual influence of two nonlinear optical effects. The open-aperture Z-scan scheme was applied for the comparison with the results of β calculations obtained in the closed-aperture scheme (dye 2, Fig. 4). β was calculated using the relation [9, 11]

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \,, \quad (3)$$

where $q(z) = \beta I(z) L_{\mathrm{eff}}/[1+(z_0^2/z^2)]$ and $I(z)$ is the radiation intensity. Fitting (3) to our experimental data (Fig. 4, solid line) one can find β.

β of dye 2 was measured using this technique to be $(3.3 \pm 0.7) \times 10^{-13}\,\mathrm{cm\,W^{-1}}$ at 2.5×10^{-3} mol/l concentration, which is close to our calculations of the nonlinear absorption coefficient taking into account the fitting of (2) to our closed-aperture measurements of dye 2 solution ($(3.0 \pm 0.6) \times 10^{-13}\,\mathrm{cm\,W^{-1}}$). The mechanisms of nonlinear absorption can be both two-photon absorption and reverse saturable absorption.

The calculations reported earlier showed that some of organic dyes (tetracene, paraterphenyl, pentacene) possess considerable third-order Kerr-induced nonlinearities [10]. The search for new materials possessing high nonlinear refractive nonlinearities is of current interest due to the possibility of practical applications of such media as optical limiters based on the Kerr effect. We present here the closed-aperture $T(z)$ measurements of dye 6 solution (Fig. 5) as an example of a dye possessing relatively strong nonlinear refraction (at comparable concentrations). One can see here an almost symmetric picture relative to the focal point, with the initial appearance of saturable absorption ($|T_{\mathrm{p}} - 1| > |T_{\mathrm{v}} - 1|$).

The results of γ and β measurements of the investigated samples as well as their linear absorption coefficients are presented in Table 1. Nonlinear absorption coefficients presented in Table 1 were measured using the closed-aperture Z-scan technique. We compared these β measurements with ones derived from open-the aperture scheme and found both data coinciding within the errors of our experiments. Note that we observed the linear increase of nonlinear optical parameters following with the growth of molar concentration of dye solutions. The results of dye 7 investigations have shown the absence of nonlinear optical processes in that solution.

The changes in polymethine chain length in the dyes 1–3 lead to the absorption-band shift of about 100 nm. We have compared the figures of merit γ/C (C is the molar concentration) of these solutions ($0.9 \times 10^{-17}\,\mathrm{m^2\,W^{-1}\,l\,mol^{-1}}$, $2.2 \times 10^{-17}\,\mathrm{m^2\,W^{-1}\,l\,mol^{-1}}$, and $2.3 \times 10^{-17}\,\mathrm{m^2\,W^{-1}\,l\,mol^{-1}}$ for dyes 1, 2, and 3 respectively). Such change of their nonlinear optical properties can be explained by the spectral absorption variations of these dyes.

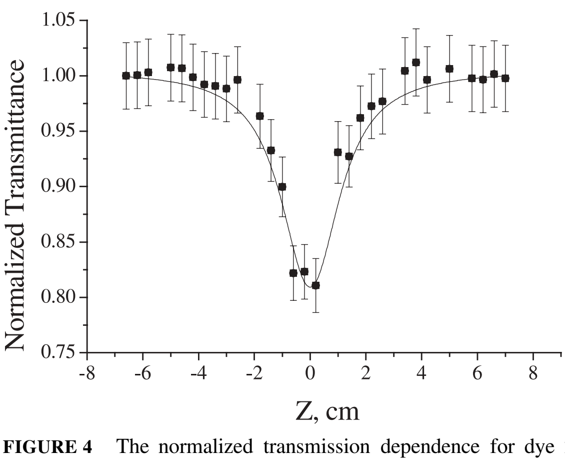

FIGURE 4 The normalized transmission dependence for dye 2 solution measured in the open-aperture Z-scan scheme. *Solid line* is the theoretical fit

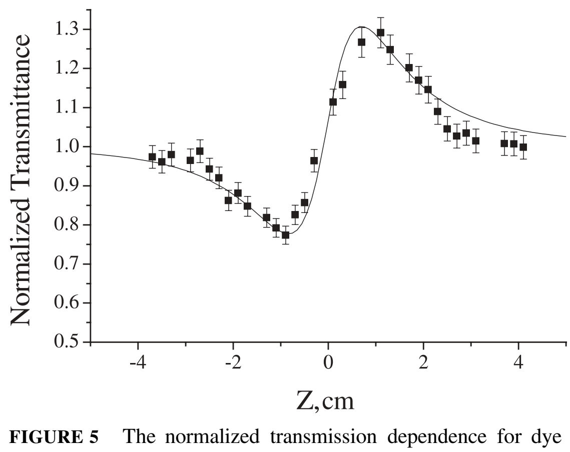

FIGURE 5 The normalized transmission dependence for dye 6 solution measured in the closed-aperture Z-scan scheme. *Solid line* is the theoretical fit

Dye	C (10^{-3} mol/l)	α_0 (cm^{-1})	γ (10^{-20} m^2 W^{-1})	β (10^{-13} cm W^{-1})	I_{sat} (W cm^{-2})
1	2.8	0.78	2.6 ± 0.52	2.3 ± 0.46	
2	2.5	0.27	5.6 ± 1.2	3.0 ± 0.6	
3	2	0.27	4.5 ± 0.9	1.7 ± 0.34	
4	2	5.81			4×10^8
5	1.3	5.41			3.4×10^6
6	1.6	3.04	65 ± 13		3.4×10^6
8	4.5	1.92	2.7 ± 0.54	0.5 ± 0.1	

TABLE 1 Nonlinear optical parameters of polymethine dye solutions

Comparing the cationic dye 1 and the neutral dye 8 that have the same γ values, one should note that the former dye possesses stronger nonlinear absorption relative to the latter. The reason for this behavior seems to be due to the difference of their spectral absorption while the charge conditions of dyes have a negligible influence on their optical nonlinearities.

The dye 5 is of especial interest among the investigated samples. The effective laser generation in a broad range ($\lambda_G = 1150\,\text{nm}$, $\Delta\lambda = 80\,\text{nm}$) [12] observed in this dye embedded in polyurethane and alcohol makes it suitable for PML due to its strong saturable absorption and for ultra-short laser-pulse generation due to broadband lasing characteristics. These properties require the investigation of nonlinear optical processes in this dye that provide valuable information about the phase modulation due to both the Kerr effect and laser-radiation redistribution as a result of inhomogeneous nonlinear absorption and saturable absorption. Below we present the studies of saturable absorption in dye 5 alcohol solutions using the open-aperture Z-scan scheme.

An open-aperture Z-scan scheme is insensitive to the nonlinear refraction, and such Z-scan traces are expected to be symmetric with respect to the focal plane ($z = 0$). Separate γ measurements of dye 5 using the closed-aperture Z-scan technique have shown the absence of self-interaction processes (self-focusing and/or self-defocusing). So, we assumed that the influence of nonlinear refraction in this dye was negligible.

Figure 6 presents the normalized transmission dependences of dye 5 solution ($C = 1.3 \times 10^{-3}\,\text{mol/l}$) using different laser-radiation intensities. Note that at low intensities the characteristic dependence of saturable absorption was observed showing the transmission increasing with the intensity growth. With further intensity growth, the $T(z)$ dependence was broadened and at highest intensities the influence of additional nonlinear optical processes was observed that can be attributed both to reverse saturable absorption and nonlinear absorption. One can determine from these dependences the intensity range at which efficient saturable absorption can be achieved without the influence of nonlinear absorption (see the inset in Fig. 6).

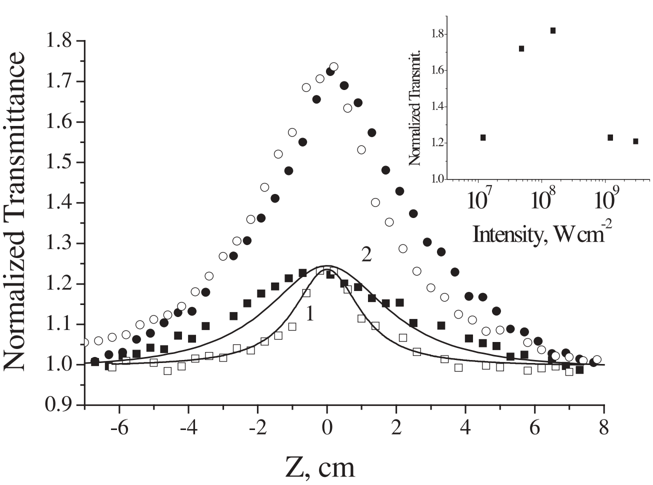

FIGURE 6 The normalized transmission dependences for dye 5 solution measured in the open-aperture Z-scan scheme at different radiation intensities at the focal plane (□: $1.2 \times 10^7\,\text{W cm}^{-2}$; ● : $4.8 \times 10^7\,\text{W cm}^{-2}$; ○: $1.5 \times 10^8\,\text{W cm}^{-2}$; ■: $1.2 \times 10^9\,\text{W cm}^{-2}$. *Solid lines* are the theoretical fits at minimal (1) and maximal (2) intensities of laser radiation. *Inset*: maximal normalized transmission dependence as function of radiation intensity

We fitted these Z-scans assuming various saturable absorption models that were analyzed in [13–15]. We analyzed the theoretical transmission curves by the same way as was done in [13]. The best fits with experimental results for dye 5 solution were observed using the kinetic model when the saturation is considered in terms of depletion of the ground-state concentration [13, 14] in the case of low intensities (Fig. 6, curve 1), and a two-level model considering the inhomogeneously broadened states [15] at high intensities (Fig. 6, curve 2). Saturation intensities (I_{sat}) were derived from these fits both for dye 5 and other dyes possessing saturable absorption features (see Table 1).

The dye 5 possesses high temporal stability. The application of this dye as a saturable absorber for PML in a Nd:YAG laser led to the generation of mode-locked 48-ps pulses. The high absorption coefficient at the wavelength of Nd:YAG laser generation allows us to hope that this dye can be simultaneously used both as a lasing medium and a saturable absorber.

4 Summary

We presented results on nonlinear optical parameter investigations of polymethine dyes in alcohol solution. Nonlinear refractive indices, nonlinear absorption coefficients, and saturation intensities were measured at the wavelength of 1064 nm using the Z-scan technique. The simultaneous presence of several nonlinear optical processes was analyzed. The analysis of saturable absorption in dye 5 solution was carried out at different laser intensities.

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