# Optical limiting of nanosecond laser radiation by polymethine dyes

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Nonlinear absorption by four polymethine dyes excited by focused radiation of a Nd:YAG laser second harmonic ($\lambda$ = 532 nm) has been investigated experimentally. Good limiting effect in solutions and a polymer matrix has been demonstrated. Spectra of reverse saturable absorption on the nanosecond time scale were recorded (pump-probe experiment). Comparison of the experimental data on reverse saturable absorption with the results of theoretical quantum chemical investigation was carried out ($S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ absorption).

## Introduction

Investigation of the optical limiting effect in different materials opens new possibilities for applying such materials as limiters of laser radiation to make it safe for optical sensors, human eyes, etc. Among nonlinear optical phenomena leading to efficient optical limiting, the RSA (reverse saturable absorption) mechanism is now being extensively studied. The RSA-based limiters are characterized by fast response $< 10^{-9}$ s and high extinction coefficients.

Many organic compounds limit laser radiation just by this mechanism, and the best studied among them are Fullerenes, porphyrins, and phthalocyanines.[1–6] Polymethine dyes also possess good limiting properties.[7,8] Dyes of this wide class that are used for optical limiting are characterized by high transparency in the visible spectral region and strong reverse saturable absorption in a wide spectral range.

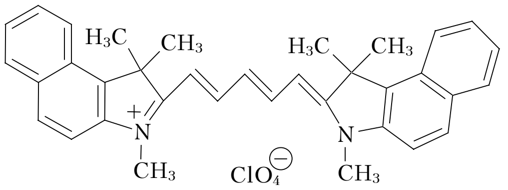
This paper presents some results on the limiting properties of four polymethine dyes studied in different solutions and in a polymer matrix. For explanation of the limiting effect, we invoke experimental spectroscopic results, in particular, concerning the reverse saturable absorption and the results of quantum-chemical calculations.

## 1. Materials, experimental and theoretical methods

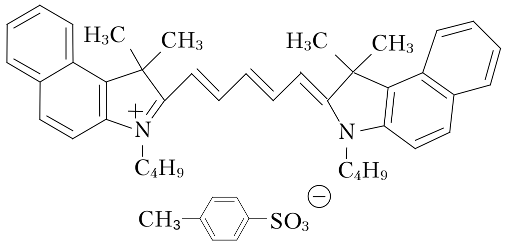
The polymethine dyes (Fig. 1) produced by Alfa-Akonis (Dolgoprudnyi) were characterized by high purity and therefore used without additional purification. P3 and P4 compounds have the same structure formula, but are synthesized in different ways.

Propylene glycol carbonate (PGC) of Aldrich Chemical Co. and ethyl alcohol (ethanol) of spectroscopic quality were used as solvents.

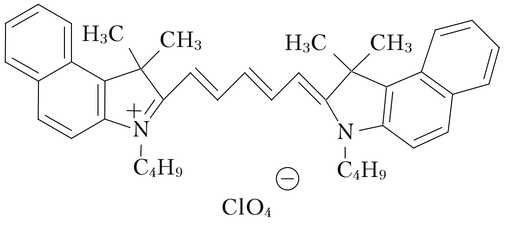
P1



P2



P3 (red species)



P4 (green species)

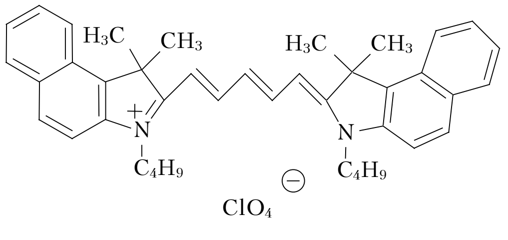


**Fig. 1.** Structure formulas of the molecules under study.

Polymer samples (dye-doped polymethylmethacrylate (PMMA)) were produced from methyl methacrylate (MMA) (Merck) by the technology described in Ref. 9. Finished samples were polished manually.

The concentration of polymethine dyes varied from $5 \cdot 10^{-5}$ to $2 \cdot 10^{-4}$ mol/l.

The spectral-luminescent characteristics were studied by standard methods with a Specord M-40 spectrophotometer and a Hitachi-850 spectrofluorimeter.

Nonlinear transmittance was examined with a setup shown in Fig. 2. The second harmonic radiation of a Nd:YAG laser ($\lambda_{exc} = 532$ nm, $E_{pulse} = 6$ mJ, $\tau_{1/2} = 6$ ns, $f = 1$ Hz) was focused with a spherical lens of the focal length $F = 350$ mm onto a quartz cell or a polymer sample with the thickness $L = 5$ mm. The cross section diameter of the pump beam at the cell length was 0.5 mm. The power density of exciting radiation varied from 1 to 400 MW/cm$^2$ ($\approx 6$ mJ/cm$^2$–2.5 J/cm$^2$); the radiation was attenuated with neutral-density filters. The energy radiation passed through and incident on a sample was measured with a KTP-2 microcalorimeters calibrated against an IMO 2N calorimeter. The aperture of the microcalorimeters was an order of magnitude larger than the cross section of the incident laser beam.

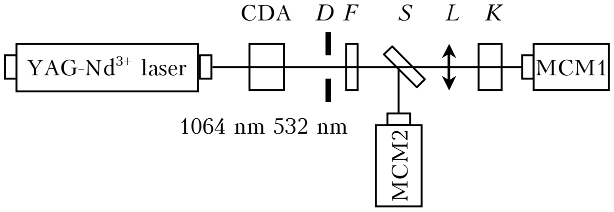


**Fig. 2.** Experimental setup for studying nonlinear absorption by organic molecules: nonlinear crystal for second harmonic generation (CDA); diaphragm *D*; neutral-density filter *F*; beam splitting plate *S*; spherical lens *L*; cell with a solution analyzed or a solid-state sample *K*; KTP-2 microcalorimeters MCM1 and MCM2.

In calculating the extinction coefficient, we took into account reflection from cell walls (surface of the polymer sample), as well as absorption and scattering of the exciting radiation by solvent (polymer) molecules. Thus, the extinction coefficient $\mathrm{KO}_W$ was calculated as

$$\mathrm{KO}_W = T_0 / T_W,$$

where $T_0$ is the initial linear transmittance of the analyzed object at the wavelength of exciting radiation (532 nm) as measured using a dual-beam spectrophotometer (with the allowance made for reflection from the sample surface and solvent absorption); $T_W$ is the nonlinear transmittance of the sample at the power density of exciting radiation $W$ with the allowance for reflection from the sample surface and solvent nonlinear absorption at this power density of the radiation.

Reverse saturable absorption was studied with a laser flash-photolysis setup. Solutions of polymethine dyes were excited with pulsed radiation of an exciplex XeCl laser ($\lambda_{rad} = 308$ nm, $t_{1/2} = 12$ ns, $E_{pulse} = 40$ mJ) at the power density of 20 MW/cm$^2$ achieved by use of focusing cylindrical lenses. Fluorescence of solutions of some organic fluorophores was used as a probe radiation. Fluorescence was excited using the same exciplex XeCl laser. Thus, there was no need in synchronization of the pump and probe beams. The optical delay line (1–20 ns) allowed us to make separation of short-lived (existing only during the pump pulse) $S_1 \rightarrow S_n$ and long-lived (for example, $T_1 \rightarrow T_n$) absorption. The probe pulse energy density did not exceed 1 μJ/cm$^2$. Spectra were recorded with a REAL (Novosibirsk) spectrometer based on a CCD array connected to a personal computer. This setup allowed us to study the reverse saturable absorption in the spectral region of 350 to 650 nm.

The reverse saturable absorption at a certain wavelength was estimated through the optical density $D(\lambda)$ as

$$D(\lambda) = \log[I_{unexc}(\lambda)/I_{exc}(\lambda)],$$

where $I_{unexc}(\lambda)$ and $I_{exc}(\lambda)$ are the intensity of the pump radiation with the wavelength $\lambda$ passed through unexcited and excited samples. The quantum-chemical calculation of the P1 dye was carried out by the Intermediate Neglect of Differential Overlap (INDO) method with spectroscopic parameterization.[10] Using this method, we calculated the electronic $S_0 \rightarrow S_n$-, $S_1 \rightarrow S_n$- and $T_1 \rightarrow T_n$ absorption spectra, as well as the oscillator strengths and rate constants of electronic transitions.

## 2. Results and discussion

### 2.1. Spectral-luminescent properties of polymethine dyes

The spectral-luminescent characteristics of the molecules under consideration were studied in two solvents: ethanol and PGC, and in the PMMA polymer matrix. It should be noted that absorption and fluorescence spectra in the above solvents (matrix) vary only slightly. Table 1 presents the absorption and fluorescence wavelengths, as well as the molar and the quantum yield of fluorescence of polymethine compounds in ethanol.

**Table 1. Spectral-luminescent characteristics of polymethine dyes in ethanol**

| Species | $\lambda_{abs}$, nm | $\varepsilon \cdot 10^{-5}$, liter·M$^{-1}$·cm$^{-1}$ | $\lambda_{fl}$, nm | $\eta_{fl}$, rel. units |
|---|---|---|---|---|
| P1 | 678 | 2.0 | 727 | 0.14 |
| P2 | 680 | 1.8 | 760 | 0.16 |
| P3 | 683 | 1.8 | 753 | 0.17 |
| P4 | 683 | 1.8 | 743 | 0.15 |

It can be seen from Table 1 that the spectral characteristics of all the four molecules considered are quite close. Also, it is worth noting high molar extinction coefficient [$\varepsilon = (1.8 - 2.0) \cdot 10^5$ liter·M$^{-1}$·cm$^{-1}$] of polymethine molecules. Figure 3 depicts the experimental absorption spectrum of the P1 compound in ethanol (curve *1*) and calculated peaks of electronic transitions from the ground state (vertical lines) for an isolated molecule.

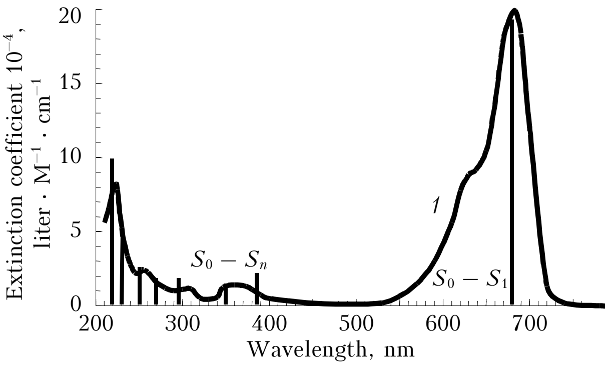


**Fig. 3.** Absorption spectrum of P1 polymethine dye.

One can see a close agreement between the experimental and calculated data. The peak of the longwave absorption band lies in the red part of the spectrum – near 678 nm. All over the visible spectrum $\lambda > 400$ nm, absorption is low, as well as the quantum yield of fluorescence $\eta_{fl} < 0.2$. Therefore, these compounds are promising as a basis for optical limiters operating in the visible spectrum.

## 2.2. Reverse saturable absorption

Figure 4 depicts the optical density induced during the pump pulse in the spectral region of 360–580 nm for the P1 and P3 dyes. In the spectral ranges < 360 and > 580 nm there is strong absorption from the ground state, which hampers recording of the reverse saturable absorption. One can see that the strong reverse saturable absorption lies in the range of 400–570 nm (curves *1*, *2*). Two peaks near 420 and 540 nm can be seen. Similar spectra are also observed for the P2 and P4 compounds.

In studying the reverse saturable absorption using a delay line (15 ns), it was found that the induced optical density $D$ decreased significantly (curve *3*) after the completion of the pump pulse.

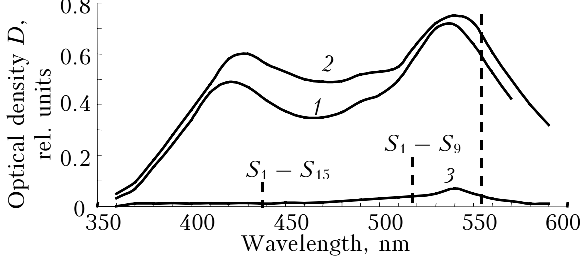


**Fig. 4.** Reverse saturable absorption of polymethine dyes: calculated absorption $S_1 \to S_n$ peaks of the P1 compound (dashed vertical lines); optical density $D$ induced by XeCl laser radiation in ethanol solutions of P1 (curve *1*) and P3 (curves *2*, *3*) compounds as measured without a delay (*1*, *2*) and with a 15 ns delay (*3*).

Thus, the reverse saturable absorption likely arises in the channel through singlet states. The data of quantum-chemical calculations also favor this conclusion. The main channel for deactivation of the $S_1$ state is the internal conversion (rate constant $k_{ic} = 6 \cdot 10^8$). The probabilities of singlet-triplet conversion and radiative $S_1 \to S_n$ transition are lower ($k_{st} \approx k_r = 2 \cdot 10^8$). Besides, according to calculated data, there are no intense $T_1 \to T_n$-transitions in the spectral range of 350–580 nm analyzed. Experimental and calculated spectra of reverse saturable absorption are in a good agreement. The studies of the reverse saturable absorption showed that the polymethine dyes must have good limiting properties in the spectral region > 350 nm.

## 2.3. Restriction of optical limiting

To study the limiting properties of polymethine dyes, we used radiation of a Nd:YAG laser second harmonic of nanosecond duration, whose wavelength (532 nm) lies just near the peak of the reverse saturable absorption (540 nm). Linear transmittance of the samples at the wavelength of pump radiation was $T = (70 \pm 5)\%$. It was found that the nonlinear absorption of the compounds studied started at the power density $W \ll 1$ MW/cm$^2$ and at 10 MW/cm$^2$ the extinction coefficient approaches two and even higher. Table 2 shows the extinction of laser radiation in different solvents and in PMMA at the pump power density of 100 and 400 MW/cm$^2$. The P1 and P2 compounds were subject to significant decoloration in the process of polymerization, therefore in Table 2 there are no data on the limiting properties of these molecules in PMMA.

**Table 2. Extinction of YAG-Nd$^{3+}$ laser second harmonic radiation (532 nm) by polymethine dyes; 70% linear transmittance of the samples; KO$_{100}$, KO$_{400}$ are the extinction coefficients at $W$ = 100 and 400 MW/cm$^2$**

| Compound | Solvent (matrix) | | | | | |
|---|---|---|---|---|---|---|
| | ethanol | | PGC | | PMMA | |
| | KO$_{100}$ | KO$_{400}$ | KO$_{100}$ | KO$_{400}$ | KO$_{100}$ | KO$_{400}$ |
| P1 | 7.0 | 11 | 5.5 | 8.0 | – | – |
| P2 | 7.2 | 13 | 7.0 | 12 | – | – |
| P3 | 8.1 | 14 | 10 | 14 | 7.2 | 14 |
| P4 | 7.7 | 14 | 7.6 | 12 | 6.1 | 10 |

The highest extinction coefficient was obtained in ethanol solutions. The P3 compound is the best limiter for laser radiation (KO$_{400}$ = 14), and the limiting efficiency is almost independent of solvent. The high extinction coefficient was also obtained for the P3 compound and in PMMA, which is very important, because this is of greatest interest from the viewpoint of creation of optical limiters.

The photostability of the P3 compound in the polymer was studied. At excitation by radiation with the wavelength of 532 nm, the molecular photostability of the compounds studied is $\approx 10^{-5}$ molecules/photon. The polymer sample with the P3 dye was irradiated by 100 pulses in 1 s and the power density $W = 200$ MW/cm$^2$, and the limiting properties ($KO_W$) of the sample kept unchanged. Irradiation by a larger number of pulses in 1 s led to formation of microdamages on the sample surface. The following studies were carried out with a short-focus lens ($F = 60$ mm). The lens focus was 5 mm behind the rear surface of the sample. The power density of the incident radiation was $W = 100$ MW/cm$^2$, and the extinction coefficient was KO = 22. In this case, no damage was observed at irradiation by 500 pulses in 1 s.

## Conclusion

The results of investigation of nonlinear absorption of polymethine dyes in solutions and PMMA showed that the limiting of laser radiation occurs by the RSA mechanism in the channel through singlet states. The highest extinction coefficient KO = 14 for the radiation with the wavelength of 532 nm in the scheme with a long-focus lens was obtained for the P3 compound. The high values of extinction coefficient, weak linear absorption, and strong reverse saturable absorption in the region of 400–560 nm observed for the analyzed molecules in solutions and PMMA (P3 and P4 compounds) make them promising for creation of broadband limiters for visible optical radiation.

It is planned to conduct further investigations into nonlinear properties of P3 and P4 dyes in solutions and PMMA by *z*-scan methods and to study the effect of the pump radiation wavelength on KO.

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