

Study of relaxation times of polymethine dyes used for passive mode locking of solid-state lasers emitting between 750 and 850 nm

R Grigonis, N A Derevyanko, A A Ishchenko, V Sirutkaitis

Abstract. The relaxation times τ of the bleached states of polymethine dyes absorbing light in the 750–850-nm are determined by the direct pump–probe method. The effect of the dye structure and the solvent type on the relaxation time is discussed. The role of different intra- and intermolecular interactions in the relaxation of excited electronic states of the dyes is analysed. Polymethine dyes are found (with $\tau = 11 - 75$ ps) that are promising for passive mode locking in $\text{Cr}^{3+}:\text{LiCaAlF}_6$, $\text{Cr}^{3+}:\text{KZnF}_3$, and $\text{Cr}^{3+}:\text{LiSrAlF}_6$ crystal lasers.

Keywords: relaxation time, excited-state relaxation, passive mode locking, polymethine dyes.

1. Introduction

New active media based on vibronic transitions in chromium in $\text{Cr}^{3+}:\text{LiCaAlF}_6$, $\text{Cr}^{3+}:\text{KZnF}_3$, and $\text{Cr}^{3+}:\text{LiSrAlF}_6$ crystals lasing at 758, 794, and 830 nm were recently studied in paper [1]. These lasers require new passive modulators operating at the above wavelengths with short relaxation times τ of the bleached state for the generation of ultrashort light pulses. Because passive mode locking (PML) was earlier performed mainly in a ruby laser at 694.3 nm, an alexandrite laser at 725–775 nm, and neodymium lasers in the region from 1055 to 1079 nm [2], passive modulators for lasers emitting in the spectral region between 750 and 850 nm were virtually unknown. The aim of this paper is to find dyes with the short relaxation time τ which can be used for passive mode locking of new lasers mentioned above. We studied symmetric cationic polymethine dyes PD-1–PD-16 (Fig. 1).

We have chosen polymethine dyes for PML because of their spectral, luminescent, and nonlinear optical properties considered in review [2].

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2. Experimental

We used ethanol and acetone as solvents, which were purified by special methods; in some cases, methanol and deuteromethanol were also used. The relaxation time of the bleached states of dyes was measured by the direct picosecond pump–probe method. This method allows the rapid selection of dyes and solvents for the fabrication of fast optical modulators [3, 4]. For measuring relaxation times of the dyes under study, which absorbed light at 800 nm, we used an optical parametric oscillator (OPO) generating ultrashort tunable pulses. A passively mode-locked, negative-feedback neodymium glass laser was used as a master oscillator. A pump pulse repetition rate was 0.5 Hz. This laser generated a train of pulses of duration 2 ps separated by the interval of 11 ns. A pulse train consisting of approximately 180 pulses was separated from the centre of the initial train using Pockels cells.

After amplification, the pulse train was directed on a KDP crystal, where the second harmonic was generated, which was used for synchronous pumping of the OPO based on a KDP crystal. The laser radiation wavelength could be tuned from 770 to 1400 nm by rotating the KDP crystal around the OPO axis. The duration of the OPO output pulse was 1.5 ps and its energy was 0.8 μJ at 800 nm.

The pulse energy was measured with an IMO-2N power meter. The OPO radiation was incident on a beamsplitter wedge (1) (Fig. 2) where it was divided into three beams. The most intense beam was reflected with a mirror (2) to a dye cell (8). The beam reflected from the front surface of beamsplitter (1) was directed to a delay line (3) and then was also incident on a dye cell for probing a change in absorption. By choosing the probe-beam diameter two times smaller than the pump-beam diameter, the uniform excitation of the dye solution volume being probed was provided. By using a filter (4) placed in the probe beam, the ratio of the intensities of the pump and probe beams was chosen ~ 500 . It was difficult to achieve a greater intensity ratio because of the interference produced by scattered exciting radiation in the probe channel.

The experimental measurements were controlled and the data were processed with a microcomputer. The energy of pulses incident on a cell and transmitted through it was measured with photodiodes (10). These data were entered into the computer memory. The data processing included the amplitude discrimination, which limited the energy fluctuations within 30% of its mean value, the calculation of the measurement accuracy, and final data processing. The time sweep within 1000 ps was performed using a computer-

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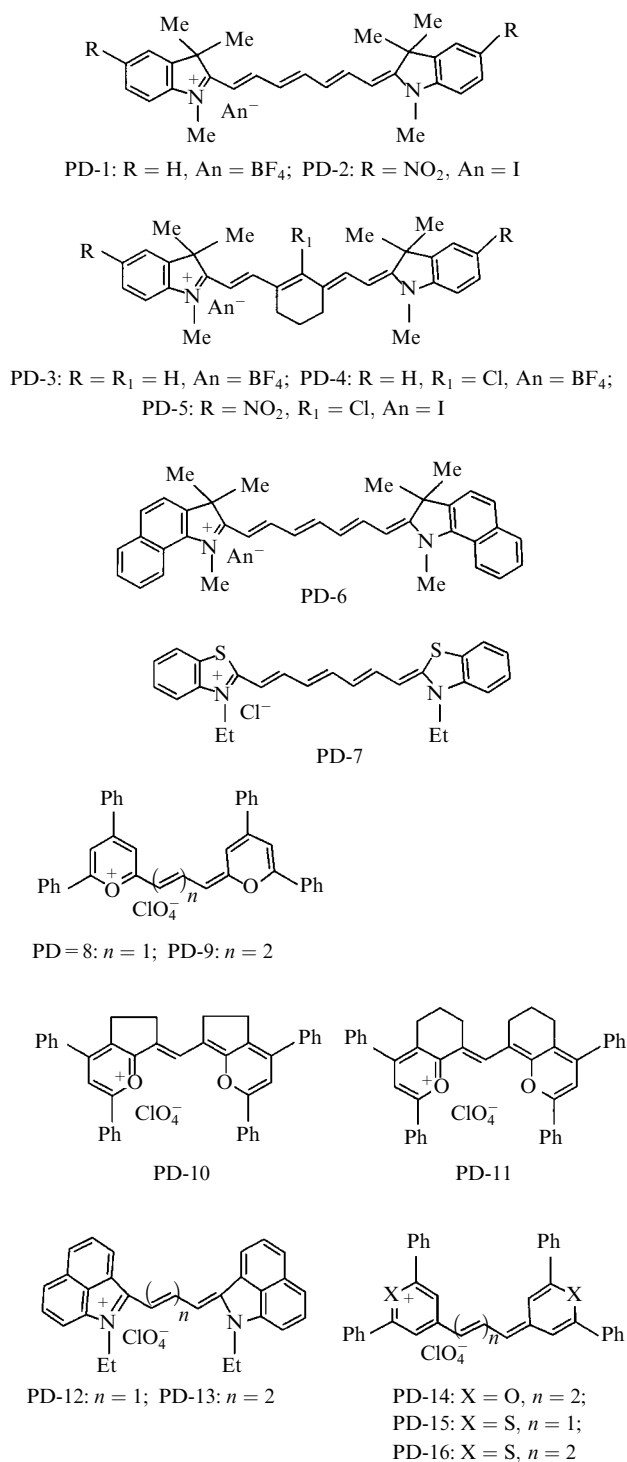


Figure 1. Structural formulas of polymethine dyes.

controlled delay line. An electromagnetic shutter (7) was used in measurements of the cell transmission upon excitation and without it. This provided the real-time measurement of a change in the optical density

$$\Delta A = \lg \left[\frac{T_0}{T(t)} \right],$$

where $T(t)$ and T_0 are the dye solution transmissions upon excitation at the instant t and without excitation, respectively.

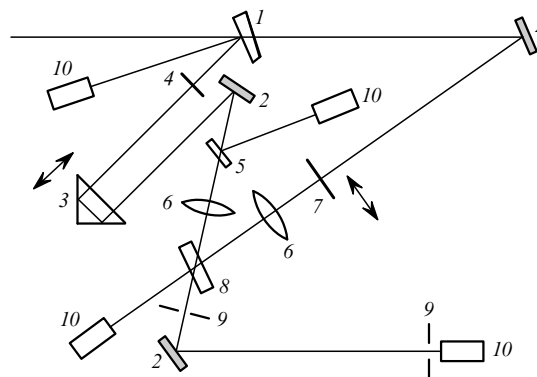


Figure 2. Scheme of the experimental setup for measuring relaxation times of dyes: (1) beamsplitter wedge; (2) mirror; (3) delay line; (4) filter; (5) beamsplitter; (6) lens; (7) shutter; (8) dye cell; (9) aperture; (10) photodiode.

3. Experimental results and discussion

The main experimental results are presented in Table 1. The table also contains the wavelengths λ_{\max} of maxima of the absorption bands of polymethine dyes and their cross sections σ_{\max} . The typical dependences of the change in the optical density on the delay time for solutions of PD-5 in ethanol and acetone are shown in Fig. 3. Note that the relaxation time of dyes PD-1–PD-16, which had different counter-ions, was independent on this ion in these polar solvents because the dyes dissociated in them [5].

Let us analyse first the relaxation times in ethanol for a group of dyes having similar structures – derivatives of indotricarbocyanine PD-1 with an unsubstituted polymethine chain. The introduction of saturated trimethylene groups into γ - and γ' -positions of this chain (PD-3 and PD-4) results in a strong increase in the relaxation time. This effect was also observed for their 5,5'-dinitrosubstituted dyes PD-2 and PD-5. The increase in τ can be explained by the increase in the chain rigidity upon cyclisation of the polymethine chain links. It is known that relaxation of the excited electronic states of polymethine dyes is mainly determined by isomerisation processes caused by rotation around the chain bonds (or rotational vibrations around them) [5].

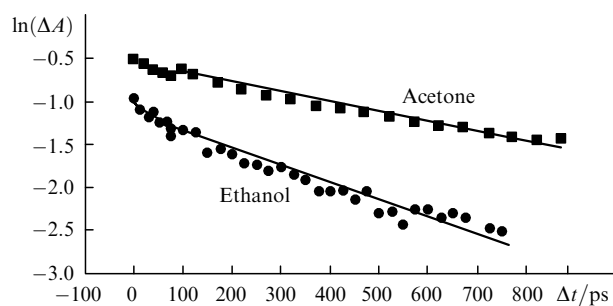
Note that benzannellation of the C6–C7 and C6'–C7' bonds of a heteroresidue of PD-1 (PD-6), which should not strongly affect photoisomerisation processes around the polymethine chain bonds, reduces the relaxation time of this compound approximately by half. Most probably, such a strong decrease in τ is caused by the enhancement of internal conversion due to a strong decrease in the $S_0 - S_1$ energy gap on passing from dye PD-1 to dye PD-6.

The bathochromic shift of the long-wavelength absorption band upon such passage is above 50 nm and λ_{\max} shifts to 800 nm, and the internal conversion begins to play a substantial role in relaxation of the excited states of polymethine dyes [5]. The role of internal conversion is also important in vinylogy series of dyes, in which the elongation of the polymethine chain by one vinylene group (an increase in n) is accompanied by the bathochromic shift of the band by 100 nm [5]. Thus, on passing from carbocyanines PD-8, PD-12, PD-15 to the corresponding dicarbocyanines PD-9, PD-13, PD-16, the relaxation time τ strongly decreases.

Similar effects are observed upon the replacement of heteroatoms without changing the length of the polymethine

Table 1. Relaxation times of the bleached state and characteristics of the long-wavelength absorption bands of PD-1 – PD-16 in ethanol and acetone.

Dye	Ethanol			Acetone		
	λ_{\max} (nm)	σ_{\max} (10^{-16} cm 2)	τ (ps)	λ_{\max} (nm)	σ_{\max} (10^{-16} cm 2)	τ (ps)
PD-1	742	8.9	306 ± 20	742	8.2	615 ± 20
PD-2	762	9.0	403 ± 20	762	9.1	1100 ± 20
PD-3	748	10.4	590 ± 25	748	10.1	–
PD-4	778	10.0	574 ± 25	778	9.3	830 ± 25
PD-5	798	7.2	508 ± 20	801	8.5	915 ± 20
PD-6	793	7.3	265 ± 15	793	6.5	480 ± 15
PD-7	765	8.5	585 ± 20	765	8.5	900 ± 20
PD-8	803	2.7	75 ± 5	796	2.5	88 ± 5
PD-9	898	3.3	13 ± 1	898	3.3	–
PD-10	861	3.8	60 ± 5	858	3.9	90 ± 5
PD-11	833	2.1	13 ± 1	833	1.9	–
PD-12	762	5.1	35 ± 3	762	5.0	20 ± 3
PD-13	861	7.3	18 ± 3	861	7.4	–
PD-14	796	9.2	453 ± 20	796	9.7	578 ± 20
PD-15	759	4.0	1060 ± 30	757	6.0	746 ± 20
PD-16	876	7.8	96 ± 10	876	7.1	90 ± 10

**Figure 3.** Dependences of $\ln(\Delta A)$ on the delay time Δt for the PD-5 dye solutions in acetone and ethanol.

chain. For example, thiopyrylocyanine PD-16, whose absorption band is strongly shifted from 800 nm to the red, has the relaxation time that is shorter almost by a factor of five than that of its oxygen analogue PD-14 with $\lambda_{\max} < 800$ nm. However, the replacement of isopropylidene groups in heteroresidues of PD-1 by sulphur atoms (PD-7) results in the increase in τ , unlike a similar replacement in the pair of PD-14 and PD-16. It seems that the increase in τ is caused by a substantial weakening of vibronic interactions, which is typical for such substitutions [6]. In the absorption region of these dyes, the internal conversion plays a minor role in the relaxation of excited states compared to vibronic interactions. It seems that for this reason the dye PD-15, which is a shorter vinylog of PD-16, has a rather long relaxation time.

The additional dissipation of the excitation energy in PD-7, PD-15, and PD-16 can be explained by the enhancement of the intersystem crossing caused by heavy sulphur atoms present in these dyes. The intersystem crossing should be more efficient in the latter dye because the distance between the singlet and triplet levels becomes smaller on passing from PD-7 to PD-15 and to PD-16. Indeed, this is observed experimentally.

The vibronic interaction is especially strong in polymethine dyes containing heteroresidues of α -pyrylium [7] and

benz[c, d]indoline [8]. The latter was used for synthesis of the well-known dye 3274u and its analogues with short τ for passively mode-locked lasers emitting at 1060 nm [9–11]. Indeed, among the dyes under study, dyes PD-8–PD-11 (α -pyrylium heteroresidue) and PD-12, PD-13 (benz[c, d]indoline heteroresidue) have the shortest relaxation times. The role of vibronic interactions in relaxation of the excited states of polymethine dyes is well demonstrated by comparing the dyes containing isomeric heteroresidues at the ends of the polymethine chain. Thus, these interactions strongly increase in α -pyrylocyanines (PD-8–PD-11) because some bonds in heteroresidues can sharply change their order (length) upon excitation [6, 7]. The replacement of these heteroresidues by isomeric heteroresidues of γ -pyrylium (PD-14) or γ -thiopyrylium (PD-15, PD-16), in which such bonds are absent, strongly weakens vibronic interactions [6, 7]. As a result, the values of τ and σ_{\max} for dyes PD-14–PD-16 are much higher compared to dyes PD-8–PD-11, while the absorption bands are much narrower (Table 1, Fig. 4).

Note, however, that α -pyrylocyanines absorb light in a longer-wavelength region (shifted to the red approximately by 100 nm) than their γ -isomers (cf. PD-9 and PD-14 Table 1 and Fig. 4). This suggests that a decrease in τ on passing from the latter to former is caused by the enhancement of internal conversion due to a strong decrease in the $S_0 - S_1$ energy gap in isomeric dyes. However, this effect is also observed for α -pyrylocarbocyanine PD-8 and γ -pyrylocarbocyanine PD-14, which have virtually the same τ (Table 1). Therefore, relaxation of the excited states of α -pyrylocyaning dyes is mainly caused by vibronic interactions.

The value of τ for dyes PD-8 and PD-9 can be further decreased by introducing saturated di- and trimethylene bridge groups to the positions 2,2', 7,7' of their chromophores (PD-10, PD-11). This cyclisation of chromophore links increases the vibronic interaction [12], internal conversion, and steric hindrance in the molecule (destroys the structure coplanarity) [13]. All these factors reduce τ . The six-link cycle enhances the vibronic interaction and internal conversion in a lesser degree than the five-link cycle [12] (the

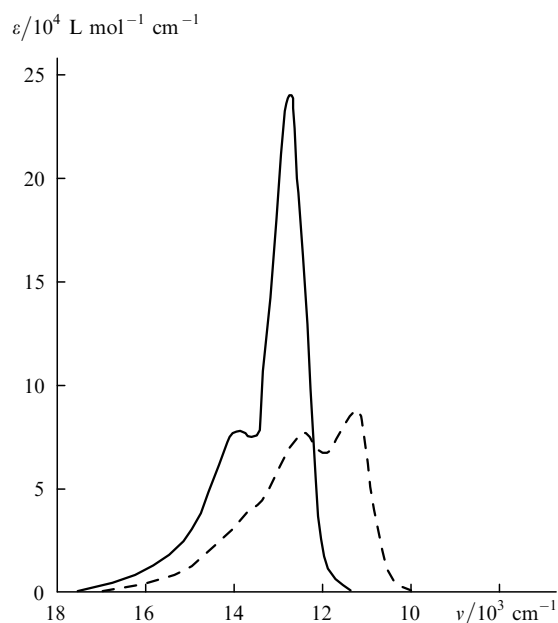


Figure 4. Extinction spectra of solutions of dyes PD-9 (dashed curve) and PD-14 (solid curve).

bathochromic shift is smaller on passing from PD-8 to PD-11 than to PD-10), but it stronger destroys the chromophore coplanarity [12]. It seems that due to the latter circumstance the value of τ for PD-11 is smaller than for PD-10.

The relaxation times of PD-1 and PD-7 were measured earlier in the nanosecond range [14–16]. It was found that $\tau = 1.13 \pm 0.08$ ns [14] and 1.2 ns [15] for PD-1 in ethanol and $\tau = 1.3$ ns for PD-7 [16]. Note that these values are substantially higher than those measured by us for the same dyes in the picosecond range (Table 1). These differences are probably explained by the fact that different intermediate relaxation states of the dyes were detected in each time range. Indeed, such states were detected in studies of instantaneous spectra [14, 17]. For example, two components with $\tau = 2.9 \pm 0.3$ ps and 300 ± 100 fs were observed in the spectra of PD-1 in ethanol recorded with the time resolution of 200 fs. Depending on the time interval, the intermediate relaxation states can be the rearranging solvate shells of dyes (dynamic inhomogeneous broadening) [5], photoisomers [5], and vibrational relaxation [17].

The relaxation time of polymethine dyes can be optimised by using solvents of different types [9, 10, 18]. Such a possibility exists for all the dyes under study (Table 1). Depending on the dye structure, the relaxation time can be changed by 1.5–2.5 times. Tricarbocyanines are most sensitive to the solution type, whereas carbocyanines are less sensitive. This is explained by the fact that the uniform charge distribution in dye chromophores is violated with increasing the polymethine chain, resulting in the enhancement of specific electrostatic interactions of charged centres of the dye with surrounding molecules [19].

The uniformity of the charge distribution is violated most strongly in tricarbocyanine PD-2 containing a nitro group in the heteroresidue, which is a strong electron acceptor. The introduction of this group reduces the electron donating properties of the indolenine heterocycle. This deviation and the elongation of the polymethine chain is accompanied by the enhancement of solvation effects [19].

For this reason, the value of τ for dye PD-2 changes most strongly on passing from ethanol to acetone compared to other dyes studied here.

The introduction of the electron-donating saturated trimethylene groups into the γ - and γ' -positions of the chain makes the charge distribution in the chromophore somewhat more uniform [12]. As a result, the sensitivity of the relaxation time of tricarbocyanines PD-3–PD-5 to the solution type decreases compared to that of the corresponding dyes PD-1 and PD-2 with the unsubstituted polymethine chain. A similar effect was observed on passing from PD-8 to PD-10 and PD-11. The charge distribution is the most uniform for the dyes based on benz[c, d]indoline [8]. For this reason, the range of variation of the relaxation time τ is minimal for carbocyanine PD-12.

It follows from the data obtained and from papers [9, 10] that polymethine dyes absorbing light in the near-IR range have, as a rule, the shortest relaxation times in alcohols. This is explained by the fact that the dye alcohol molecules can deactivate the excited states of dyes not only due to specific solvation of their charged centres but also due to the overlap of overtones of valence vibrations of the alcohol hydroxyl group with the long-wavelength electronic transitions in the dye. Indeed, the replacement of ethanol by its deuterated analogue CD₃OD results in the increase in τ from 173 to 180 ps in PD-1 and from 25 to 32 ps in PD-12. On the contrary, when methanol is used instead of ethanol, the relaxation time decreases, for example, by 2 ps for PD-1 and PD-11. This is explained by the fact that the percent content of hydroxyl groups in the methanol molecule is maximal in a homological series of alcohols. A similar effect is more distinct for dyes absorbing at 1000 nm because of a greater overlap of overtones of high-frequency vibrations of molecules of the medium with the long-wavelength electronic transition in dyes [5].

Thus, the relaxation time of polymethine dyes can be decreased by elongating the polymethine chain and introducing heteroresidues with bonds capable of changing their length upon excitation, heavy atoms, and saturated bridge groups into certain positions in the chromophore. It should be taken into account that any structural changes resulting in bathochromic shifts of the absorption bands of polymethine dyes to the region $\lambda > 800$ nm noticeably reduce the lifetime due to the enhancement of internal conversion. The value of τ can be further reduced in polar, especially hydroxyl-containing solvents.

4. Conclusions

Dyes PD-8–PD-13 are most suitable for using in passive modulators for lasers emitting in the 750–850-nm region because they have comparatively short relaxation times along with high absorption cross sections. In addition, the absorption maxima of PD-12 (760 nm), PD-8 (792 nm), and PD-11 (833 nm) virtually coincide with the maxima of emission bands of Cr³⁺:LiCaAlF₆ (758 nm), Cr³⁺:KZnF₃ (794 nm), and Cr³⁺:LiSrAlF₆ (830 nm) lasers, respectively. Therefore, these dyes can be used for passive mode locking in these lasers. It is important that passive mode locking is achieved in nontoxic alcohol solvents, in which nonlinear optical effects, for example, self-focusing are weak. Dyes PD-1, PD-7, and PD-14–PD-16 are not suitable for mode locking of ultrashort-pulse lasers because of their long relaxation times. However, they can be used for

Q -switching of solid-state lasers emitting in the region from 750 to 850 nm.

Therefore, the relaxation time of polymethine dyes can be controlled by varying the dye structure and the solvent type based on the results obtained in this paper.

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