

Highly efficient passive Q switches for a neodymium laser based on thiopyrylotricarbocyanine dyes

V.I. Bezrodnyi, N.A. Derevyanko, A.A. Ishchenko, A.V. Kropachev

Abstract. The spectral, photochemical and nonlinear optical properties of a group of thiopyrylotricarbocyanine dyes in a polyurethane matrix are studied and compared with well-known materials for passive Q -switching such as nickel BDN and BDNII complexes. Passive laser Q switches based on these dyes feature the high modulation efficiency (up to 76%) in neodymium lasers and high photochemical stability. It is shown that the service life of Q switches can be considerably increased by removing oxygen from a polymer matrix.

Keywords: dyes, passive laser Q switch, Q -switching.

1. Introduction

High-power laser pulses can be most simply generated by using Q -switched optical resonators. Of special interest is the use of passive laser Q switches (PLQ) because they are compact, simple, considerably simplify the design of a laser and improve its reliability. The application of organic dyes as phototropic compounds featuring reversible bleaching provides the covering of the visible and near-IR spectral ranges [1].

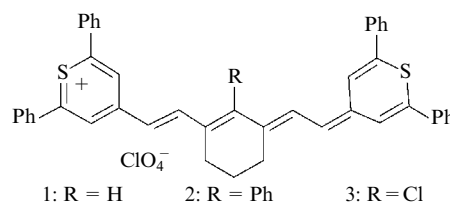
Passive Q switches based on liquid solutions of organic dyes have substantial disadvantages, for example, the necessity of using optical cells, scattering of light by optical inhomogeneities appearing in liquid during its circulation, bulky circulation systems, and the difficulty of working in the case of vibrations and zero gravity. These disadvantages are completely removed in solid Q switches based on crystals ($F_2^- : LiF$ or $Cr^{4+} : YAG$) and polymers doped with organic dyes. However, the use of colour centres in alkali halide crystals and Cr^{4+} ions for Q -switching involves a number of problems. Colour centres are rather sensitive to temperature drops and have rather long relaxation times of the bleached

state and low absorption cross sections [2], whereas Cr^{4+} ions have the anisotropy of nonlinear absorption resulting in the self-induced optical rotation [3]. Polymer solutions of organic dyes are devoid of these drawbacks [4–6]. Purposeful studies [4–6] of the mechanism of laser damage of polymer matrices have shown that it is necessary to use elastic materials which have considerable elastic deformations in a broad temperature interval. Cross-linked polyurethane described in papers [7–9] satisfy this requirement. The choice of this material is also based on criteria formulated in review [1] according to which, to obtain a high photochemical stability and radiation resistance as well as a long service life and a high bleaching degree of coloured matrices, the dye concentration in polymers should be minimal. This was provided in polyurethane that we used by its high polarity and the presence of functional groups capable of nucleophilic (electrophilic) solvate positively (negatively) charged dye molecule centres [1]. In addition, an important property of polyurethane, as shown in our experiments, is a high solubility of many organic dyes (polymethine, oxazine, xanthene, phenalenone, pyrromethene, and metalloorganic complexes) used in laser technique in polyurethane matrices without aggregation and decomposition [10]. Therefore, polyurethane is quite promising for applications in passive and active laser elements [7–10].

In this paper, we studied the possibility of highly efficient Q -switching of neodymium lasers by using PLQs based on polyurethane matrices doped with polymethine (cyanine) dyes, which have been successfully applied in high-power lasers [7–10].

2. Samples and experimental results

As phototropic centres for Q switches, we studied thiopyrylotricarbocyanines 1–3 [11] with structural formulas presented below:



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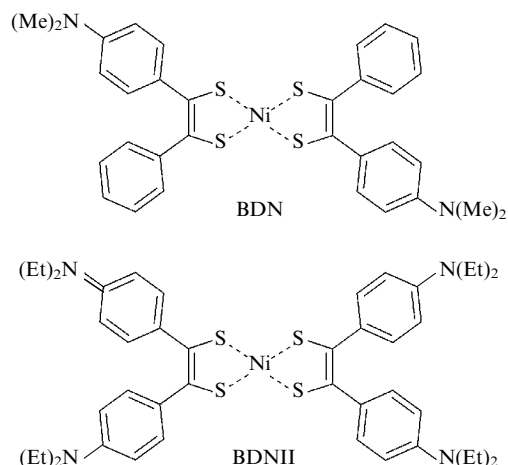
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Received 20 February 2008; revision received 8 May 2008

Kvantovaya Elektronika 39(1) 79–83 (2009)

Translated by M.N. Sapozhnikov

For comparison, we also studied well-known nickel-organic BDN and BDNII complexes [12]



which gave so far the best results among the known dyes used as passive Q switches in nanosecond neodymium lasers [7–9].

All polymer PLQs studied in the paper were triplexes with optical substrates made of K8 glass or quartz. A polymer interlayer between them was made of a urethane polymer composition – a cross-linked elastomer with high adhesion to glass, which was synthesised by polycondensation of diol with diisocyanate [7–9].

Absorption spectra were measured with a Shimadzu UV-3100 spectrophotometer. Figure 1 presents the absorption spectra of thiopyrrolycyanines 1–3 in methylene chloride and polyurethane, and Fig. 2 shows the absorption spectra of BDN and BDNII. Table 1 presents the wavelengths λ_{\max} of absorption band maxima, absorption cross sections σ and excited-state relaxation times τ in the optimal liquid solvent

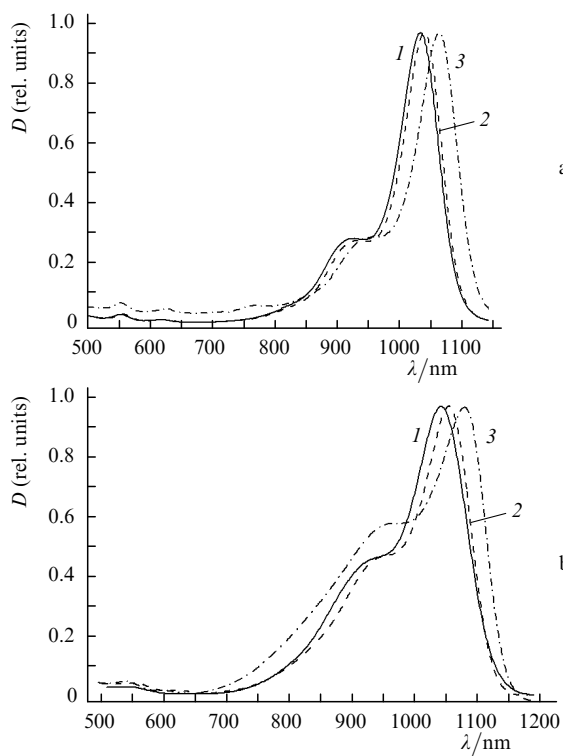


Figure 1. Absorption spectra of thiopyrrolycyanine dyes 1–3 [curves (1–3), respectively] in methylene chloride (a) and polyurethane (b).

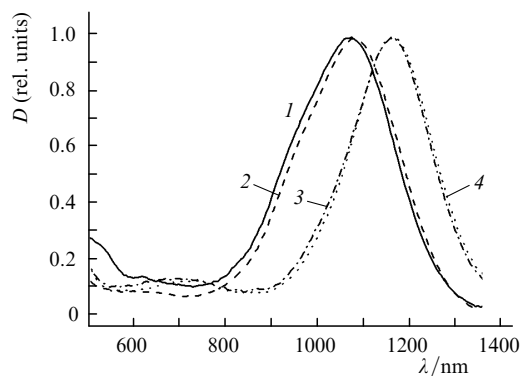


Figure 2. Absorption spectra of BDN (1, 2) and BDNII (3, 4) metal complex in methylene chloride (1, 3) and polyurethane (2, 4).

Table 1. Spectral and temporal parameters of the solutions of thiopyrrolycyanines 1–3 in methylene chloride.

| Dye | λ_{\max}/nm | $\sigma_{1060}/10^{-16} \text{ cm}^2$ | τ/ps |
|-----|----------------------------|---------------------------------------|------------------|
| 1 | 1035 | 6.7 | 55 |
| 2 | 1040 | 8.3 | 35 |
| 3 | 1065 | 11.5 | 50 |

(methylene chloride). The values of τ , determined by the method used in [13], were taken from [1].

It is known from the literature that oxygen, in particular, singlet oxygen, having a high reactivity, can oxidise laser organic dyes. It has been found that oxygen is involved in the destructive photobleaching of aminophenalenones [14] and cyanine [15] and pyrromethene [16] dyes. In this paper, we studied preliminarily the influence of oxygen on the photostability of thiopyrrolycyanine dye 2. Samples, which did not contain oxygen, were prepared in a box which was evacuated and then filled with argon at a pressure exceeding the atmospheric pressure. Polymerisation was also performed in the argon atmosphere. Samples in polymer matrices, which did not contain oxygen, also were tested for photostability under the conditions described above. Figure 3 presents the corresponding dependences.

The Q -switching efficiency was studied and resource tests in the local working region were performed by using a multimode laser. A single-lamp laser head (Kirge Inc. Model FC254KK) contained a K300 krypton-xenon flashlamp and a 5×80 -mm Nd:YAG active element with the ends AR-

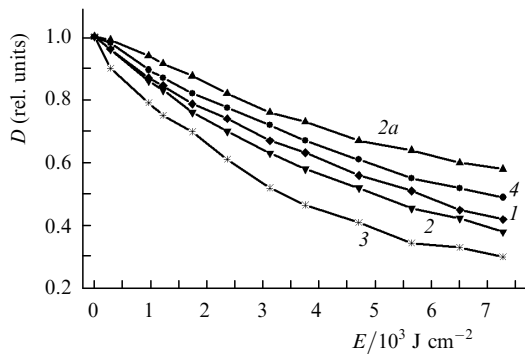


Figure 3. Dependences of the change in the optical density of dyes in polymer matrices on the radiation energy dose for thiopyrrolycyanine dyes 1–3 [curves (1–3), respectively] and BDN (4); dye 2 in the deoxygenised matrix (2a).

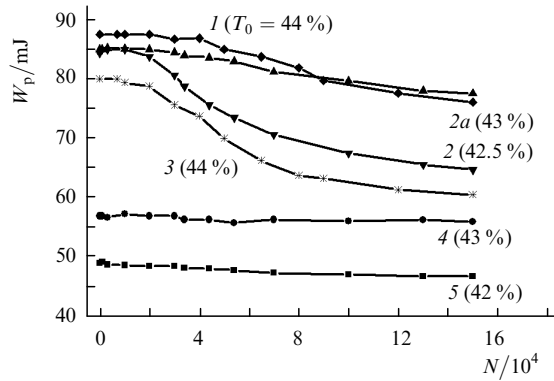


Figure 4. Dependences of a laser pulse energy on the number N of pump pulses for thiopyrylotricarboyanine dyes 1–3 [curves (1–3), respectively], BDN (4), and BDNII (5); dye 2 in the deoxygenised matrix (2a). In the parenthesis is indicated the initial transmission of Q switches.

coated at 1064 nm. The active element length irradiated by the pump light was 60 mm. The length of the resonator formed by plane mirrors ($R_1 = 99.8\%$, $R_2 = 27\%$) was 50 cm. The Q switches for resource tests also were fabricated in the form of triplexes with a polymer layer of thickness 100 μm . Optical K8 glass substrates of thickness 3 mm and diameter 30 mm were AR-coated on the external side at the operating wavelength. The initial transmission T_0 of Q switches for resource tests was in the range from 42.5% to 44%. The pump energy provided by a MIL-31 power supply was ~ 6 J. Figure 4 shows the resource dependences as functions of the laser pulse energy W_p on the number of pump pulses. Resource tests were performed in the repetitively pulsed regime at a pulse repetition rate of 12.5 Hz.

An important parameter affecting the total laser efficiency is the passive Q -switching efficiency η defined as the ratio of the output laser pulse energy, obtained by using a PLQ under study, to the output pulse energy in the free-running regime at the same pump energy. This efficiency was studied for PLQs with three different values of T_0 . Because the efficiency depends on the initial transmission [2], we tested Q switches with three different values of T_0 close to the optimal value, and Table 2 presents the average values of η . Note that the manufacturing technology of PLQs allows us to fabricate Q switches with virtually any values of T_0 .

To explain the difference in the values of η obtained for different PLQs, we measured their nonlinear transmission by using a single-mode laser. Figure 5a presents the optical scheme of the resonator of a Nd:YAG laser and the scheme for recording nonlinear transmission. The laser operating in the Q -switching regime emitted 8-ns, 24-mJ pulses. Samples

Table 2. Spectral, Q -switching, and nonlinear optical parameters of thiopyrylotricarboyanines 1–3, BDN, and BDNII in polyurethane.

| Dye | $\lambda_{\text{max}}/\text{nm}$ | T_0 (%) | η (%) | ΔT (%) |
|-------|----------------------------------|------------|------------|----------------|
| 1 | 1043 | 31; 44; 53 | 76 | 54.5 |
| 2 | 1054 | 35; 40; 54 | 74 | 53.5 |
| 3 | 1079 | 33; 45; 52 | 69 | 51 |
| BDN | 1078 | 34; 42; 51 | 51 | 36 |
| BDNII | 1150 | 32; 43; 48 | 46 | 30 |

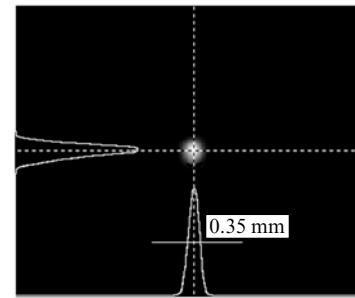
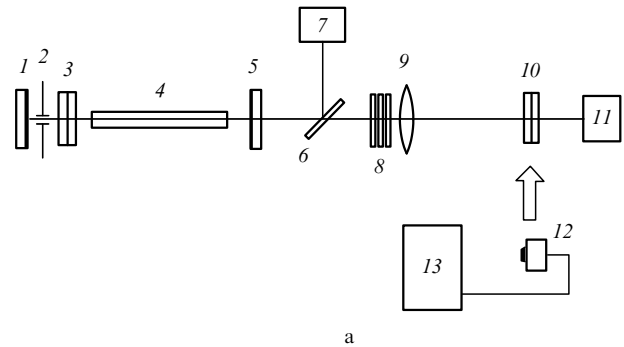


Figure 5. Experimental scheme for studying nonlinear transmission (a) and the laser beam cross section at the sample place (b); (1) highly reflecting mirror; (2) aperture; (3) PLQ; (4) Nd:YAG rod; (5) output mirror; (6) beamsplitter; (7, 11) photodiodes; (8) neutral optical filters; (9) lens; (10) sample; (12) CCD camera; (13) oscilloscope.

were located at the focus of a lens. The laser beam cross-section area in the lens focus was measured with a SPIRICON laser radiation analyser (model LBA-300PC, FTS170

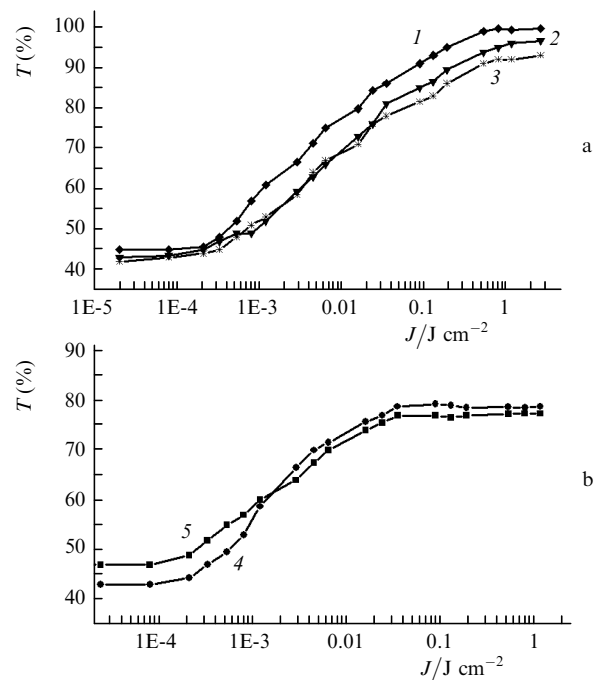


Figure 6. Dependences of nonlinear transmission on the radiation density J incident on PLQs for thiopyrylotricarboyanine dyes 1–3 [curves (1–3), respectively] (a) and BDN (4) and BDNII (5) metal complexes (b).

camera). Figure 5b shows the cross section of the laser beam incident on a PLQ whose nonlinear transmission was measured as the energy ratio of the transmitted and incident beams. The laser beam energy was determined by averaging over 10 pulses. The output signals from photodiodes were fed to a C1-104 double-beam oscilloscope. Figure 6 presents the dependences of nonlinear transmission of polymer PLQs on the incident radiation energy density.

3. Discussion of the results

The absorption bands of polymethine dyes and nickel-organic complexes in polyurethane fall in the emission region of neodymium lasers (see Figs 1 and 2). The absorption bands of dyes 1–3 in polyurethane are broader and more intense at the short-wavelength edge than in the liquid solution of methylene chloride. This is caused by the increase in the nucleophilic solvation of positively charged cationic centres by polar polymer groups [1]. This solvation suppresses considerably the aggregation of thiopyrylocyanines in polyurethane [11, 17]. Note that aggregation is suppressed even for easily associating dye 1 with the polymethine chain containing no bulk substituents preventing aggregation [17]. This is manifested in the fact that, unlike weakly polar polymers (polystyrene and polymethyl methacrylate), the absorption band shape of dye 1 in polar polyurethane is similar to that of thiopyrylocyanines 2 and 3 containing a bulk phenyl group and a chlorine atom in the chain, respectively, and is also similar to the shape of absorption bands in methylene chloride (see Fig. 1).

The shape of absorption bands of BDN and BDNII metal complexes in polyurethane are almost the same as in the liquid solution (see Fig. 2).

Polymethine dyes 1–3 and the BDN metal complex exhibit the bathochromic shift of absorption bands on passing from liquid to polymer (Figs 1 and 2), which is caused by the higher refractive index of polyurethane compared to methylene chloride. The position of the absorption band of BDNII almost does not change, which suggests that specific intermolecular interactions with the medium dominate over universal interactions (Fig. 2).

Dyes used in passive Q switches should have high absorption cross section $\sigma_d(\lambda)$ at the laser radiation wavelength so that $\sigma_d(\lambda)/\sigma_a(\lambda) \gg 1$. This is typical for thiopyrylocyanines 1–3, for which σ is approximately three orders of magnitude higher than the absorption cross section of active laser elements (Table 1). For example, $\sigma_a = 8.8 \times 10^{-19} \text{ cm}^2$ for Nd:YAG. It follows from Figs 1 and 2 that the absorption spectra of these dyes in the polyurethane matrix completely cover the spectral range of the fundamental electronic transition of neodymium lasers emitting at 1060 nm.

Coloured polymers used in Q switches should have the high dark and photochemical stability. The dark stability of new PLQs has been controlled for two years, beginning from their fabrication. No variations in their spectral parameters and Q -switching efficiency have been observed during this period. To obtain rapid information on the photochemical stability of PLQs, we irradiated PLQs manufactured on quartz substrates by a high-power xenon lamp.

One can see from Fig. 3 that the photostability of thiopyrylotricarbocyanines 1–3 in air-saturated solutions [curves (1–3)] is somewhat lower than that of the BDN dye

[curve (4)]. However, the photostability of compounds 1–3 can be considerably increased by simply removing oxygen from a polymer matrix. Kinetic curve (2a) in Fig. 3 shows that the removal of oxygen enhances the photostability of thiopyrylocyanine dye so strongly that it even exceeds that of a highly stable BDN metal complex [7].

Figure 4 shows the resource dependences of W_p on the number of pump pulses. The initial transmissions PLQs with the dyes under study were from 42.5% to 44%. The value of W_p decreased for all samples (except BDN) due to the bleaching of the dye without the damage of the polymer matrix. The Q switch based on the BDN dye proved to be most stable under the conditions pointed out above [curve (4) in Fig. 4]. The value of W_p did not change during the entire experiment (10^6 laser pulses incident at the same point of the PLQ), whereas W_p for dyes 1–3 decreased by 7%–15% under the same conditions. However, the efficiency of polymer Q switches based on thiopyrylotricarbocyanine dyes considerably exceeds that of PLQs with BDN (by a factor of 1.5) and BDNII (by a factor of 1.8) dyes, achieving 76%, which is the record value among all known polymer PLQs.

The removal of oxygen resulted in a considerable increase in the service life of PLQs [curve (2a) in Fig. 4] compared to an oxygen-containing medium [curve (2) in Fig. 4] for thiopyrylotricarbocyanine 2. Deoxygenated polymer PLQs based on this dye had almost the same initial Q -switching efficiency as that of air-saturated PLQs.

The Q -switching efficiency depends on the composition of a polymer and the optical quality of working surfaces. The problem of fabrication of polymer PLQs of the required optical quality is automatically solved by using glass or quartz substrates. Note that the manufacturing technology of such PLQs provides high quality samples, and therefore the difference in the values of η should be explained by different nonlinear optical parameters of the dyes studied.

Transmission curves presented in Fig. 6 demonstrate the nonlinear dependence of the absorption coefficient on the incident radiation power density. The bleaching amplitude is determined by the spectral parameters of dye molecules, on which the loss of radiation energy spent to maintain the bleaching state mainly depends. The residual loss and therefore the Q -switching efficiency are determined to a great extent by the interaction of intense laser radiation not only with molecules in the ground electronic state but also with molecules in the excited electronic state. The absorption spectra of the latter can be studied by special methods (laser flash photolysis), which we did not use here. The qualitative information on the spectral position of the $S_1 \rightarrow S_2$ electronic transition band can be obtained from absorption spectra in the region of the $S_0 \rightarrow S_1, S_2$ bands. It follows from Figs 1 and 2 that the absorption cross section at the $S_0 \rightarrow S_1, S_2$ transition for 1–3 dyes is lower than that for BDN and BDNII. As a result, the bleaching amplitude $\Delta T = T_{\text{sat}} - T_0$ (T_{sat} is the maximum transmission of a Q switch in the saturated state) for thiopyrylotricarbocyanine dyes 1–3 exceeds that of BDN and BDNII (Table 2). The increase in the bleaching amplitude leads to the increase in the Q -switching efficiency (Table 2).

4. Conclusions

Our investigations have shown that new PLQs based on polyurethanes doped with thiopyrylocyanines in the form of

triplexes between optical glasses provide the efficient Q -switching of neodymium lasers. The Q -switching efficiency exceeds by a factor of 1.5–1.8 that of the best polymer PLQs doped with BDN and BDNII dyes, achieving 76%. New PLQs also feature a higher degree of bleaching and a higher photostability.

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