Polymer dye laser pumped with green semiconductor lasers

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Abstract. **We report the results of experiments on quasi-longitudinal pumping of a polymer dye laser by two green (λ = 513 nm) pulsed laser diodes. The lasing thresholds, efficiency, and photostability of pyrromethenes in various polymers are studied. The efficiency of dye lasers based on pyrromethene 567 and pyrromethene 580 with a three-mirror cavity with partial astigmatism compensation exceeds 20 %.**

Keywords: polymer dye laser, diode pumping, pyrromethenes, photostability.

1. Introduction

In recent years, the use of semiconductor laser diodes for pumping of various lasers has become a world trend. This tendency is also observed for wavelength-tunable lasers. Successful experiments were performed on diode pumping of colquirite [1] and Ti:sapphire [2] lasers. This was stimulated by the progress in the development of high-power visible diode lasers based on gallium nitride. Attempts to use laser diodes for pumping dye lasers (DLs) have been undertaken for many years, but the efficiency of these lasers was extremely low [3–9]. The appearance of cw blue diodes with a nominal power of 1.7 W made it possible to achieve a polymer DL efficiency of 9 % [10]. The DL in [10] was pumped by 100-ns pulses of two such diodes with an-order-of-magnitude excess over their acceptable current.

In 2013, the Nichia company developed a high-power green laser diodes (λ = 520 nm, P = 1 W), which led to a significant advance in investigations of diode pumping of lasers based on Ti:sapphire because radiation at λ = 520 nm is most suitable for pumping this crystal [2, 11]. An efficiency exceeding 15 % was achieved in [11, 12] using these diodes both in cw and mode-locking regimes. Green diodes (λ = 520 nm) in many cases are more preferable for pumping DLs than blue diodes (λ = 445 nm). This is related first of all to the fact that

the most efficient laser dyes, such as rhodamines and pyrromethenes (PMs), have absorption peaks at wavelengths close to λ = 520 nm and almost do not absorb at λ = 445 nm. The use of two multimode green diodes allowed us to tune laser wavelength within the range $\Delta\lambda$ = 145 nm and achieve record-high (exceeding 25 %) efficiency for diode-pumped dye-solution lasers [13]. However, solid-state DLs, which do not require liquid circulation systems, are much more convenient for practical applications.

To date, there are several known solid matrices for laser dyes, namely, polymers of various compositions [14], sol–gel glasses [15], and microporous glass–polymer composites [16]. The lasing efficiency and photostability of an active element (AE) strongly depend on the matrix composition and the active dye. As a rule, it is necessary to optimise the matrix composition for a particular dye. Pumping of dyes with laser diodes requires rather sharp focusing of diode beams with a large angular aperture to overcome the lasing threshold, because of which the AE should be thin. In the case of quasi-longitudinal pumping and focusing by a lens with the focal length f = 18 mm [13], we used a liquid layer 0.2 mm thick; the efficiency at larger thicknesses was noticeably lower. From this viewpoint, the most appropriate matrices are polymers, because they allow one to fabricate AEs by different methods with different thicknesses, from 150 nm [17, 18] to 25 cm [19].

In the present work, we report the results of experiments on using green semiconductor lasers for pumping polymer samples with different compositions and doped with different laser dyes.

2. Experiment

Previously [13], we studied a series of dyes in several solvents with low lasing thresholds and high efficiencies under pumping by green diodes. In the present work, we studied the lasing characteristics of these dyes in different polymer matrices.

Active elements for diode-pumped polymer DLs are glass–polymer–glass triplexes with component thicknesses of 2.6, 0.07–0.11, and 2.6 mm, respectively. The process of fabrication of each sample consisted of the following stages. First, 5 % solutions of polyvinylbutyral (PVB), polybutylmethacrylate (PBMA), and a copolymer of butylmethacrylate (BMA) with methacrylic acid (MAA) (BMA:MAA ratio 9:1) in mixtures of ethanol:toluene (4:1) for PVB and ethylacetate:toluene (4:1) for PBMA and BMA:MAA were prepared. A plasticiser – dibutyl sebacate (DBS) – with a concentration corresponding to 25–30 vol % in the dried polymer film was introduced into the polymer solutions. The dye amount was chosen so that the AE optical density at the pump wavelength (513 nm) was 2.0 ± 0.2. The solutions were

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thoroughly mixed until complete dissolution of dyes and filtered through a Schott glass filter.

The filtered solution was dropped onto the centre of a horizontally positioned optical glass $20 \times 20 \times 2.6$ mm in size using a dosator. The film was dried first at a temperature of $50-60\,^{\circ}$C and then at $105-110\,^{\circ}$C. The dried film was covered by the second optical glass with 100-μm calibration spacers preliminarily fastened to the glass plate corners. The triplex was placed into a press mould and then in a drying box for formation at a temperature of $100 \pm 5\,^{\circ}$C for 30 min. After completion of formation, the press mould was slowly cooled to room temperature and then the triplex was withdrawn.

The advantages of triplexes consist in the following: they are easy to fabricate (without using spin coating [20]), the polymer is protected from environmental factors, and the optical quality of the AE surfaces is determined by the used glasses.

The scheme of a polymer DL pumped by two pulsed green laser diodes is shown in Fig. 1. The studied polymer samples are quasi-longitudinally pumped (the pump beam passes beside one of the spherical mirrors and is incident on the AE at an angle of $\sim43°$) by two NDG7475 multimode semiconductor lasers with a pulse duration of 200 ns. The pulse repetition rate was 2 Hz. The average wavelength of the semiconductor lasers under these conditions was 513 nm. The spectra of these lasers are presented in Fig. 2.
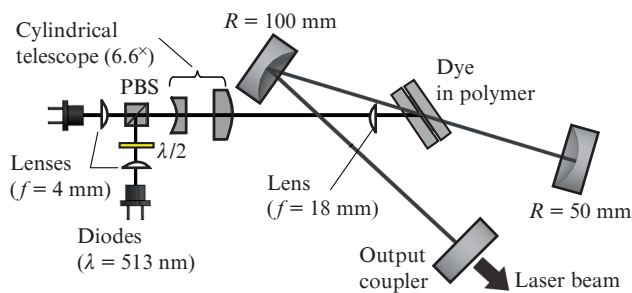
Figure 1. Scheme of a diode-pumped polymer DL (PBS is a polarisation beam splitter).
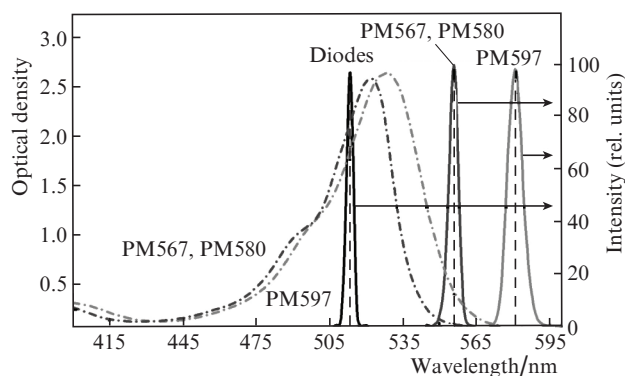
Figure 2. Absorption spectra of PM567, PM580, and PM597, as well as emission spectra of pump diode lasers and the polymer DLs.

The triplex was placed in the region of the cavity waist at a Brewster angle to the axis of the cavity formed by two highly reflecting spherical mirrors (radii of curvature $R = 50$ and 100 mm, reflection coefficients $r > 0.99$ in the spectral range of $400-750$ nm) and a plane output coupler with $r \approx 0.87$ at the lasing wavelength. This cavity has low intracavity losses and a small mode size in the waist ($\sim30 \times 30$ μm) and allows one to use dispersive elements in the compensating channel. The cavity length was ~30 cm. The beams of each diode were collimated using G2 aspherical lenses ($f = 4$ mm). Using a half-wave plate, the polarisation of one of the diodes was rotated by 90°, and then the beams were superimposed by a polarisation beam splitter. The combined beam was expanded along the 'slow' axis by a cylindrical telescope, after which the pump radiation was focused by an aspherical lens with $f = 18$ mm into a spot $\sim20 \times 40$ μm in size. The maximum absorbed pump energy was 0.75 μJ, and the power density on the AE did not exceed $\sim6 \times 10^5$ W cm^{-2}. The laser energy was measured using a calibrated photodiode with an integrating circuit and a digital oscilloscope. The lasing characteristics of dyes in polymers and ethanol (methanol) solutions were compared at identical parameters of cavities and pump radiation.

3. Results and discussion

The results of our investigations for the best dye–polymer pairs are listed in Table 1. Figures 3a, 3c, and 3e show the dependences of the laser energy on the pump diode energy absorbed in the AE for lasers based on PM567, PM580, and PM597 dyes in PBMA, BMA:MAA, and PVB polymer matrices, as well for DLs based on the same dyes in ethanol or methanol solutions. Such well-known dyes as DCM, rhodamine 6G, and rhodamine 110 in our polymer matrices demonstrated lower photostability and higher lasing thresholds or lower efficiency than in ethanol, methanol, DMSO, or benzyl alcohol (their characteristics are not given in Table 1). However, PM567, PM580, and PM597 laser dyes in polymer matrices showed the lasing characteristics comparable with their characteristics in solutions. The AE photostability was estimated as the number of pump pulses absorbed at one point of the polymer after which the lasing energy decreases with respect to the initial energy by two times. The photostability of polymer samples with PMs is rather high, $10^3 - 10^5$ pulses at the maximum pump energy of 0.75 μJ.

The measured photostabilities of the studied polymer samples are presented in Figs. 3b, 3d, and 3f. The photostability in all cases was measured under identical conditions, i.e., at an absorbed pumped energy of 0.75 μJ and a pulse repetition rate of 2 Hz. It should be noted that a decrease in the pump energy, as well as an increase in the optical density of samples, leads to a considerable increase in the photostability, while an increase in the pulse repetition rate decreases the photostability of samples.

The photostability for PM567 lies within the range of $1.3 \times 10^3 - 10^4$ pulses and strongly depends on the choice of the polymer matrix. The efficiencies and lasing thresholds for PM567 in polymers and ethanol solution differ insignificantly and only slightly depend on the polymer matrix. The obtained results indicate that the best polymer matrix for diode-pumped PM567 dye is PBMA.

The PM580 dye in the studied polymers showed excellent results, i.e., its lasing characteristics in polymer samples and ethanol solution almost coincide. The highest efficiency was demonstrated by PM580 in PVB, where the lasing efficiency was 25% and the slope efficiency was 41.4%. The photostability of this dye in PVB was $\sim5 \times 10^3$.

The sample of PM597 in the BMA:MAA polymer matrix showed the highest photostability (about 10^5 pulses) among

Table 1. Results of investigation of polymer samples with diode pumping.

| Dye | Polymer matrix | | Dye layer thickness/µm | Threshold pump energy/µJ | Slope efficiency (%) | Efficiency (%) | Photostability/ 10^3 pulses |
	Polymer	DBS plasticiser (vol%)					
PM567		ethanol (EtOH)	200	0.28	43.3	26.7	–
PM567	PVB	30	80	0.33	36.9	20.3	3.5
PM567	PBMA	30	98	0.29	36.5	22.7	10
PM567	copolymer BMA:MAA	25	73	0.32	41.8	22.9	1.3
PM580		ethanol (EtOH)	200	0.32	46.3	26.8	–
PM580	PVB	30	116	0.30	41.4	25.0	4.7
PM580	copolymer BMA:MAA	30	110	0.30	38.2	23.4	2
PM597		methanol (MeOH)	200	0.38	34.6	17.4	–
PM597	PVB	30	100	0.37	30.7	15.5	17
PM597	copolymer BMA:MAA	30	102	0.35	25.0	13.5	100
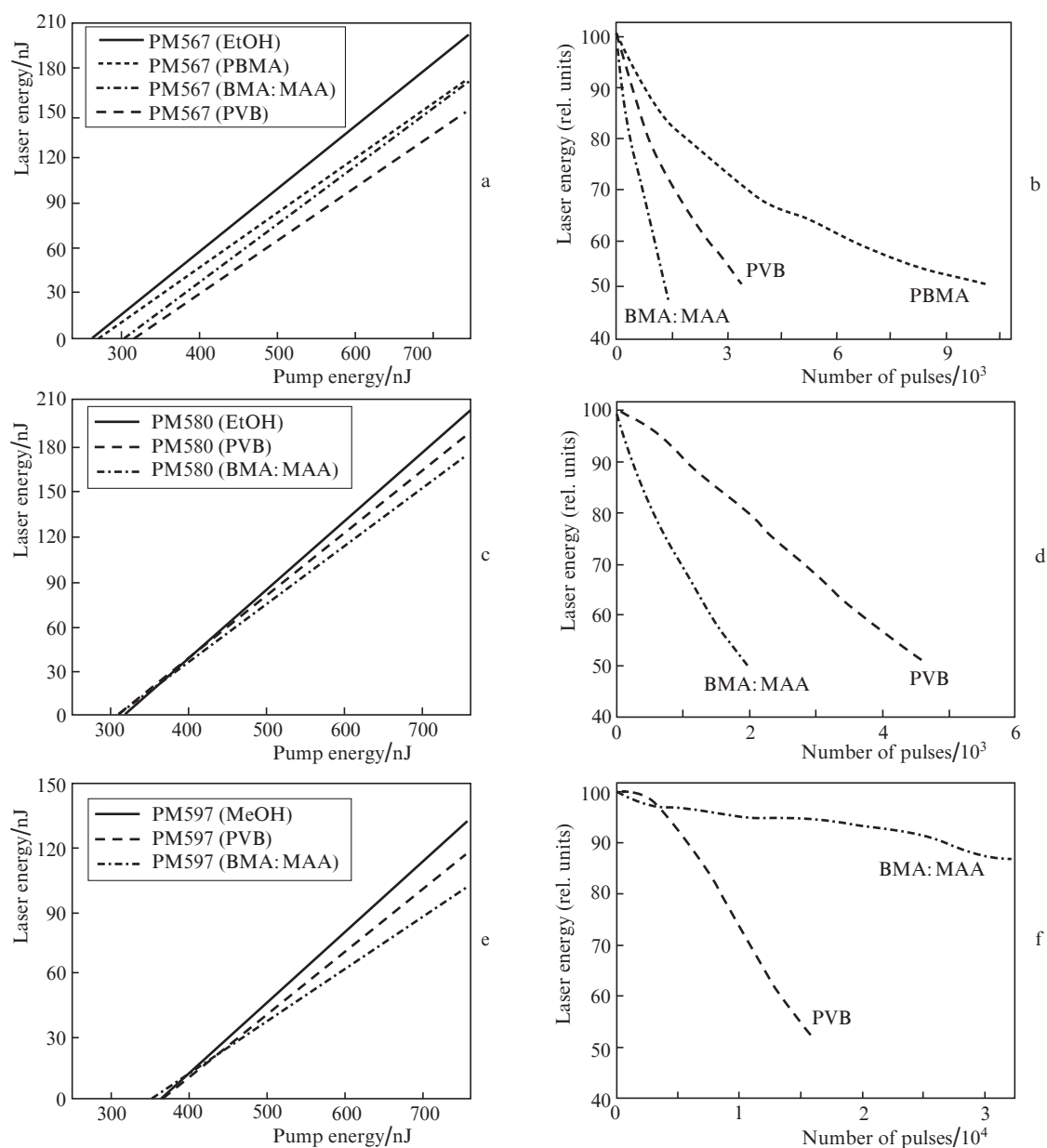
Figure 3. Dependences of the output energy on the pump energy for lasers based on (a) PM567; (c) PM580, and (e) PM597 dyes in solutions (EtOH, MeOH) and polymer matrices (PBMA, BMA:MAA, PVB), as well as the dependence of the laser energy on the number of laser pulses for different polymer matrices doped with (b) PM567, (d) PM580, and (f) PM597.

the studied samples, while the highest efficiency was achieved for a triplex with PVB.

4. Conclusions

The lasing characteristics of diode-pumped polymer DLs have been studied. Glass–polymer–glass triplexes with a dye embedded into the polymer were used as AEs. It is determined which dye–polymer pairs are most efficient under pumping by green ($\lambda \approx 513$ nm) pulsed diodes. The best results are obtained for laser dyes of the pyrromethene class. The lasing thresholds are found to be 0.29–0.38 μJ at the output mirror transmission $T = 0.13$. The slope efficiency for different polymer matrices was 25%–42%, which is several times higher than the data given in the literature for diode-pumped polymer lasers. The maximum efficiency was obtained in the case of a PVB polymer matrix plasticised by DBS with a concentration of 25–30 vol%. The efficiencies of PM567 and PM580 dyes in this matrix exceed 20%, which is rather close to the efficiencies for ethanol solution. The best photostability was demonstrated by PM597, whose energy decreased by two times after absorption of $\sim 10^5$ pump pulses at one point of the polymer at a pump energy of 0.75 μJ (twofold excess over the lasing threshold). Thus, our results demonstrate that high-power green diodes can be used for efficient pumping of polymer DLs.

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