Lasing properties of active medium based on sulforhodamine 101 incorporated into commercial polyurethane compound

S.V. Nikolaev, V.V. Pozhar, M.I. Dzyubenko

Abstract. **The lasing properties of polymer matrices based on commercial polyurethane compound activated by sulforhodamine 101 dye are studied. Lasing with an efficiency of 26 % and pulse energy of 76 mJ is obtained using microsecond transverse pumping at a wavelength of 587 nm. The service life (time of operation to a decrease in the output energy by 50 % upon excitation by 0.3 J cm^{-2} pulses) amounts to 2500 pulses. A particular attention is given to the bichromatic lasing spectra of the samples tested. Based on the experimental data a model explaining the two-band emission spectrum is proposed and discussed.**

Keywords: *dye, laser, solid-state dye laser, polymer matrix.*

1. Introduction

The development of new active media for solid-state dye lasers (SSDLs) is a promising line of research in laser physics. The main requirements for these media are the high pump conversion efficiency and a long service life of the active element. Many studies on this subject were devoted to the synthesis and improvement of new polymer and hybrid materials for the solid base of laser elements, which would possess necessary optical and thermophysical properties, and to the search for the most efficient and resistant dyes to activate these media [1–8]. Much attention is paid to the development of techniques for fabricating laser active elements of necessary configuration; studying their optical, spectral, and luminescence properties; and analysing the energy, spectral, and resource characteristics of the active elements under different excitation conditions. It should be emphasised that specifically excitation conditions, which depend on the width, energy, and spectrum of pump pulses, determine to a large extent the requirements for the thermophysical and optical properties of solid matrices. In particular, to form active SSDL elements that can efficiently generate high-power microsecond pulses, one must use polymers that are, on the one hand, highly elastic and, on the other hand, appropriate for fabricating matrices of good optical quality. Previous investigations showed that polyurethane and its derivatives, for example, polyurethane acrylates [9], satisfy these requirements.

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This work continues our previous investigations, which were aimed at forming new polyurethane-based active media for high-power microsecond SSDLs [10]. The main purposes of those studies were to find the most efficient dye–polyurethane combinations, improve the techniques for preparing highly efficient laser matrices, and study their lasing characteristics. The behaviour of a particular dye in a polyurethane matrix is difficult to predict; therefore, dyes are to be chosen experimentally. Nevertheless, one can significantly narrow the field of search by testing dyes that were previously successfully used to activate other polymers. One of such dyes is rhodamine 640. Garcia-Moreno et al. [11] developed highly efficient and photostable laser matrices by incorporating this dye into appropriate polymer media. Based on these results, a similar dye was chosen as an activator of polyurethane medium, whose lasing properties are the object of our study.

2. Characteristics of the active medium and experimental technique

The active medium under study was based on the commercial transparent polyurethane resin T-809 (Italy) with incorporated dye sulforhodamine 101 (Sigma-Aldrich), which is a sulfo-derivative of rhodamine 640. During matrix preparation the resin components were carefully filtered and degassed to prevent the formation of microinclusions and bubbles in the active medium. The mixture prepared was poured into a cylindrical quartz cell with plane-parallel faces, where polymerisation occurred. To obtain the best optical quality, the process was performed at an optimal constant temperature, which was chosen experimentally.

The normalised absorption and fluorescence spectra of sulforhodamine 101 in polyurethane compound are shown in Fig. 1. Note that they are similar to the spectra of this dye in ethanol [12]; the only difference is some shift of the maxima of absorption and fluorescence bands. In both cases the spectra have a pronounced vibrational structure on the short-wavelength wing of the absorption band and in the long-wavelength part of the fluorescence spectrum. The maximum extinction coefficient of sulforhodamine 101 in polyurethane, ε_{max}, was found to be 1.31×10^5 mol^{-1} cm^{-1}, a value only slightly below the extinction coefficient of this dye in ethanol solution ($\varepsilon_{max} = 1.39 \times 10^5$ mol^{-1} cm^{-1} for ethanol solution [12]).

The active elements had a radius of 10 mm and lengths of 10 and 20 mm. Active media with dye concentrations $C = 5 \times 10^{-4}$ and 2.5×10^{-4} mol L^{-1} were introduced, respectively, into 10-mm and 20-mm matrices. The SSDL cavity was formed by planar dielectric broadband mirrors. The highly reflecting mirror had a reflectance $R \sim 99$ %, and the transmittance of the output mirror was varied. The matrices were excited trans-
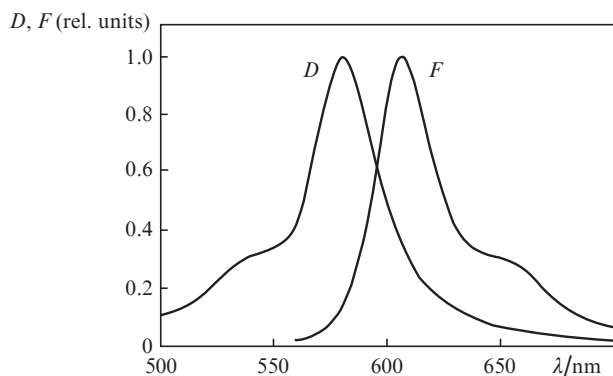
Figure 1. Normalised absorption (D) and fluorescence (F) spectra of sulforhodamine 101 in polyurethane.

versely. Two pulse-periodic lamp-pumped liquid dye lasers (LDLs) were used as excitation sources; they differed in the cell diameter. The 10- and 20-mm matrices were excited by LDLs with cell diameters of 7 and 16 mm, respectively. The active medium of the pump lasers was an ethanol solution of dye rhodamine 6G. These lasers generated pulses ~ 4 μs long (at the base level) with a wavelength close to 587 nm and energies up to 350 and 800 mJ, depending on the cell diameter. The pump beam was focused on the matrix under study using a cylindrical lens with a focal length of 60 mm. The optimal lens position with respect to the matrices was determined by the maximum SSDL energy.

In the experiment we measured the energy and spectral emission characteristics of the matrices, as well as their service life, with a change in the pump energy density and variation in the SSDL cavity parameters. The SSDL pump and lasing energies were measured by IMO-2N calorimetric energy meters. Integrated spectra were recorded by a spectrograph based on a UV-90 camera with a 1200-lines mm^{-1} diffraction grating. The evolution of the spectra was analysed using a high-speed SFR photodetector in combination with a 300-lines mm^{-1} diffraction grating.

3. Experimental results and discussion

The lasing efficiency of the active medium under study was estimated by measuring the lasing energy E_e and efficiency η for polyurethane matrices, changing the energy density and SSDL resonator Q in wide ranges. The best results for the matrices with lengths $l = 10$ and 20 mm, obtained in the single-pulse regime, are listed in Table 1. This table contains also the average pump energy densities E_p and output mirror reflectances R.

A further increase in the pump energy density led to local thermal fracture of matrices at the points where the excitation energy was maximum. The measurements showed that, depending on the pump beam divergence and degree of focusing, the maximum pump energy density on the matrix surface may exceed the average value by a factor of $1.5 - 2.5$. Hence, in the regime of single microsecond pulses this medium can withstand irradiation with an energy density not higher than 1 J cm^{-2}.

Table 1.

l/mm	R (%)	E_p/J cm^{-2}	E_e/mJ	η (%)
10	50	0.6	23.5	20
20	16	0.7	76	26

A practically important characteristic of any solid matrix is its service life. It is determined by the total effect of the radiation resistance of the polymer base and the dye photodissociation rate. Taking into account that both these factors depend on the pump energy density, we measured the dependence of the lasing energy for the matrix with the dye concentration $C = 5 \times 10^{-4}$ mol L^{-1} on the number of excitation pulses n at different pump energy densities. To reduce the effect of bulk heating of the matrix, the pulse repetition rate was limited by 0.2 Hz. Figure 2 shows the dependences of the service life for three average values of the pump energy density.
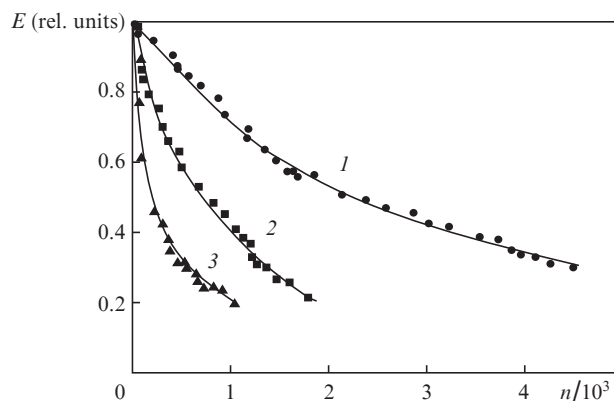

Figure 2. Normalised dependences of the lasing energy E_e on the number of pulses n at pump pulse energy densities $E_p = 0.3$ (*1*), 0.45 (*2*), and 0.55 J cm^{-2} (*3*).

These data indicate that at a pump energy density of 0.3 J cm^{-2}, which is about half of limit, the lasing energy decreases to 50% of the initial value after 2500 pulses. An increase in the excitation energy density significantly reduces the laser service life. At pump energy densities below 0.5 J cm^{-2} the only factor reducing the lasing energy is dye photobleaching, while at energies above this value the excited region in the matrix exhibits signs of thermal fracture.

Along with the energy and service life characteristics, we investigated the lasing spectra of sulforhodamine 101 in polyurethane. The main feature of these spectra was the presence of two bands. Note that similar bichromatic lasing spectra were previously observed for a series of dyes belonging to different classes but having structural luminescence spectra [10, 13, 14]. In our experiments the long- and short-wavelength bands were emitted in the ranges of 645–657 and 612–627 nm, respectively. With a change in the pump intensity and resonator Q the relative band intensity changed, but the number of bands remained the same. Only at the lowest excitation energy density and the lowest resonator Q the spectrum contained a single short-wavelength band. The time-base emission spectra, obtained by a high-speed photodetector, revealed that both bands are generated almost simultaneously and coexist throughout the entire pulse. This can be seen in the typical spectrochronogram in Fig. 3. A similar regularity in the formation of lasing spectra was observed in [13] for ethanol solutions of benzopyran dyes.

Simultaneous generation in two spectral bands in the same volume of active medium can be caused by two reasons. The first is the presence of emission centres of two types with different spectral characteristics in the active medium. Such centres can be, for example, different associated forms of dyes,
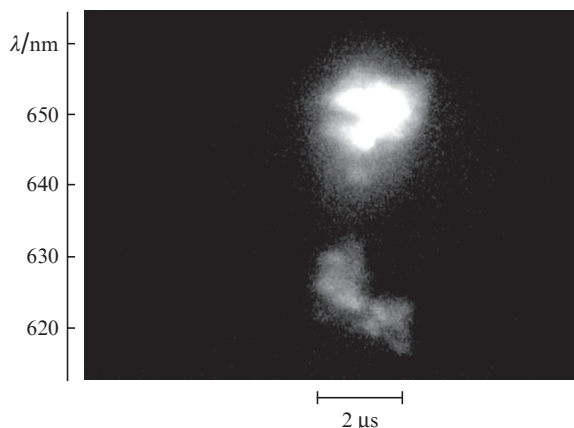
λ/nm

650

640

630

620

2 µs

Figure 3. Time scan of the lasing spectrum of sulforhodamine 101 in polyurethane.

whose interaction determines the spectral characteristics of emission. Specifically this mechanism was considered in some studies as the main to explain the effect of bichromatic emission [14].

The second reason is the existence of spaced lasing regions with different losses (and, therefore, different spectral gain profiles) in an inhomogeneously excited medium. For dye-based active media with partially overlapping structural absorption and luminescence bands these profiles have a peculiar shape, characterised by the presence of two local maxima, whose relative intensity depends on the threshold inversion in a given region [10]. Assuming that pair interactions of molecules may affect the spectral characteristics of the active medium, we nevertheless believe the second reason to be more likely.

Upon transverse laser pumping the formation of spaced lasing regions with different degrees of threshold inversion is caused by the nonuniform radiation intensity distribution both over the excitation beam cross section and along the active medium depth. The intensity is generally maximal on the beam axis and decreases to the periphery. This leads to the same nonuniform pump intensity distribution along the major axis of the focal spot of cylindrical lens. As a result the regions near the active element faces are pumped less intensively than the region near the beam axis. The pump radiation weakens when penetrating the active medium, due to which at a certain depth the pump intensity near the faces becomes lower than the threshold value, and the length of the active region decreases in this layer. Correspondingly, the loss factor increases in this region and the spectral gain profile becomes blue-shifted. The tendency to a decrease in the active-region length when penetrating the bulk of the active medium is retained up to the layers where the pump intensity cannot compensate for elevated losses. Note that this effect leads to broadening of the lasing spectra for dye active media with "structureless" spectra and to two-band lasing for dyes with a well-pronounced vibrational structure of the fluorescence spectrum.

It follows from the aforesaid that in a nonuniformly excited active medium long-wavelength radiation should be generated mainly at the periphery of the lasing region, while the short-wavelength part of the spectrum corresponds to the bulk. To confirm this suggestion, we recorded the spectra of radiation formed in different excitation regions of a 10-mm matrix with a dye concentration $C = 5 \times 10^{-4}$ mol L^{-1}. To select a certain lasing region, a mobile slit diaphragm 0.5 mm wide was placed in the SSDL cavity. This diaphragm was moved

from the external wall of the matrix to its centre using a micrometer screw. The normalised integrated lasing spectra, recorded at successive displacement of the diaphragm by a distance d into the bulk of the lasing region with a step of 0.05 mm, are shown in Fig. 4. To make the data more illustrative, the figure shows also the lasing spectrum recorded without the diaphragm.
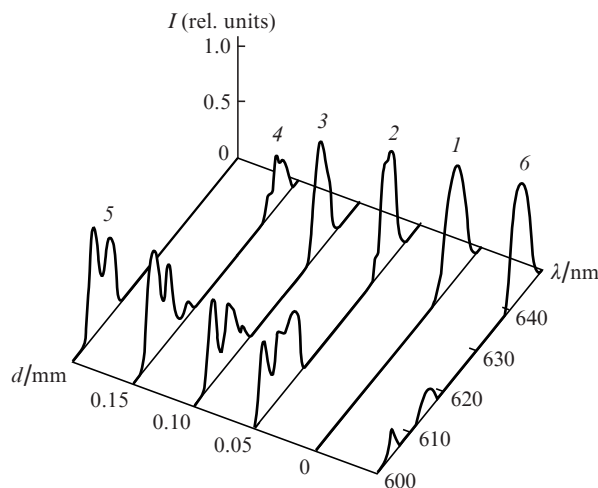

Figure 4. Integrated lasing spectra for the regions isolated by a slit at a distance d from the front wall of the matrix (1–5) and the spectrum in the absence of diaphragm (6).

The results obtained are indicative of only long-wavelength emission [spectrum (1)] near the front wall of the matrix; as penetrating the excited medium, the short-wavelength component in the lasing spectrum increases [curves (2–4)]. Finally, only short-wavelength emission [spectrum (5)] is observed in the deepest region. The shape of the spectrum from the entire volume depends on the total contribution of all emitting regions. The deeper a region is located, the smaller its energy contribution. Under our experimental conditions it is the long-wavelength component that dominates in the resulting spectrum [curve (6)]. Thus, we believe this experiment to confirm the decisive role of excitation inhomogeneity in the two-band lasing in active media based on dyes with structural fluorescence spectra.

4. Conclusions

We developed and tested a solid laser-active polyurethane medium with incorporated dye sulforhodamine 101. The energy, service life, and spectral characteristics of radiation from cylindrical solid matrices based on this medium were investigated.

Transverse laser pumping of a 20-mm long matrix by ~ 4 µs pulses made it possible to obtain a lasing energy of 76 mJ with a conversion efficiency of 26 %. The service life of the matrices was estimated for different excitation energy densities. It was found that at a pump energy density of ~ 0.3 J cm^{-2} the lasing energy decreases to 50 % of the initial level after 2500 pulses.

The specific features of the formation of two-band lasing spectra of sulforhodamine 101 in polyurethane were studied. It was shown that both spectral bands may arise almost simultaneously and coexist during the entire large pulse. It was suggested and experimentally confirmed that the two-band spectrum is

mainly caused by the presence of spaced lasing regions with different spectral gain profiles, which are formed as a result of inhomogeneous excitation of the active medium. This effect explains bichromatic lasing in any active media based on dyes of different types with partially overlapping structural absorption and fluorescence spectra.

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