Generation of microsecond laser pulses in polyurethane matrices doped with dyes

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

Abstract. **Active laser elements based on polyurethane matrices doped with rhodamine 6G and oxazine 17 dyes are fabricated and tested. Lasing in the yellow – green and red spectral regions is obtained upon excitation of these matrices by a dye laser at 532 nm. The spectral and spatial – angular parameters of emission are studied. It is shown that these parameters are similar for polymer and liquid dye lasers. It is confirmed that pump radiation causes strong thermal distortions of active polymer media and the degree of influence of these distortions on lasing is demonstrated in experiments. The tuning of a laser based on a rhodamine 6G-doped polymer matrix is demonstrated in the range between 579 and 601 nm.**

Efficient lasers tunable in the visible range are required for solving many scientific and applied problems. Dye lasers satisfy these requirements. They offer wide possibilities because can operate both in the pulsed and cw regimes and can generate high-power broadband and narrowband tunable radiation [1 – 5]. The active medium of dye lasers is traditionally liquid solutions of organic dyes. The prospects for using liquid active media was first associated with their high optical quality and the possibility to change rapidly the active liquid in a laser cell and select arbitrarily the cell size and design [6 – 8]. However, what was good at the stage of laboratory experiments proved to be rather inconvenient in the development of dye lasers intended for applications. The presence of systems for active liquid circulation inevitably makes the laser design cumbersome and often hazardous in operation. It is this circumstance that prevents considerably wider technological applications of dye lasers.

The obvious solution of this problem is the development of a dye laser with a solid active element which would combine the operation properties of solid-state lasers with the spectral parameters of dyes. The investigations in this field have been underway already for over thirty years [9 – 14]. Various materials for fabricating solid matrices activated by dyes have been tested, and their spectroscopic, photochemical, and optical properties have been studied. As a result, it was found that three groups of materials are most promising for these purposes: polymers (polymethyl methacrylate, epoxy and polyurethane resins), a sodium-borosilicate porous glass, and sol – gel compositions. Each of these materials has its own specific features related to its chemical, thermal, and mechanical properties. Thus, the chemical properties of a matrix determine the possibility of its doping with dyes of one or other classes and their photostability upon pumping. The thermal and mechanical properties of a material determine the radiation resistance and optical quality of active laser elements made of it [15].

By now polymethyl methacrylate (PMMA) and its derivatives were most successfully used for fabrication of polymer matrices from organic glasses. This is explained by a relative simplicity of manufacturing active elements from PMMA, which is, however, inherent in all polymers, and by a good optical quality of matrices. The main disadvantage of PMMA is its low radiation resistance and hard polymerisation conditions resulting in the decomposition of dyes. Nevertheless, the selection of dyes withstanding such conditions and the introduction of various plasticizers enhancing the radiation resistance make it possible to produce quite efficient active elements. A number of companies, in particular, in Russia produce commercially such elements, which are used as efficient converters of radiation from lasers of other types.

Note that in most studies devoted to the development of dye lasers based on polymer matrices pumping was performed by pulsed lasers. The length of the active region was from a few tens of microns in films to several centimetres in bulky matrices, while the pump pulse duration did not exceed, as a rule, several nanoseconds. Only in [11] lasing of dyes in epoxy-polymer matrices pumped by microsecond pulses was reported. However, no information about the energy efficiency of such matrices was presented.

Attempts to use flashlamps for pumping PMMA-based active elements were unsuccessful [16, 17]. This is explained by the above-mentioned disadvantages of polymer matrices such as a low optical quality of polymers and a low resistance of polymers and dyes to the UV radiation of flashlamps. In addition, upon pumping by long flashlamp pulses of duration from microseconds to few tens of microseconds, the role of triplet – triplet absorption in dyes increases due to an increase in the triplet-state lifetime

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of dyes in solid matrices [18]. Also, the damage threshold of polymers decreases with increasing the pump pulse duration [19].

Unlike organic glasses, elastomers such as polyurethane and its derivatives have a high radiation resistance. The disadvantage of polyurethane matrices is their lower transparency compared to PMMA and higher thermoelastic distortions caused by pump radiation. To overcome these difficulties, polyurethane matrices were often fabricated in the form of multilayer structures consisting of thin polymer layers placed between glass substrates [15, 20]. It is obvious that such active elements are suitable only for laser pumping and cannot be used instead of other polymer matrices successfully operating under the same conditions. However, polyurethanes are highly resistant to UV radiation, although they strongly absorb in the UV region. An advantage of polyurethanes is also 'soft' polymerisation conditions, which make it possible not only to dope them with dyes of many classes but also provides their good photostability during pumping [15].

To use the advantages of polyurethane in full measure, it is necessary to study the properties of polyurethane matrices under conditions close to flashlamp pumping in order to determine the prospects for the development of flashlamp-pumped dye lasers based on elastomer matrices. This is the aim of our paper.

Active elements intended for flashlamp pumping should, first, have the size corresponding to the discharge gap of flashlamps. Second, they should withstand without damage the radiation power densities produced by flashlamps and, third, they should produce efficient lasing upon excitation by microsecond pulses. The fulfilment of the first two requirements depends on the properties of the polymer and on the manufacturing technology of matrices. At the same time, it is safe to say that, whatever the manufacturing technology is used, the fabrication of monolithic matrices with a long active layer will be always limited by the optical properties of polyurethane. Therefore, it was reasonable to restrict at once the problem to the manufacturing of matrices of the acceptable length, i.e. the length at which losses caused by scattering by inhomogeneities do not yet prevent the development of lasing. This does not contradict to the solution of the problem as a whole because such matrices could be used as individual modules in long composite active elements [21]. In our opinion, most important is the question about the ability of dyes doped into polyurethane to produce lasing upon microsecond pumping, which was the main subject of our study.

We fabricated a number of polyurethane matrices with the active layer of length $1-2$ cm. The matrices were quartz cylinders with the inner diameter of 7 mm restricted by plane–parallel ends and filled with polyurethane doped with a dye. Thus, their shape resembled that of a dye cell in a standard liquid dye laser. Experiments were performed with rhodamine 6G and oxazine 17 dyes, which could be easily doped into polyurethane and were not decomposed during polymerisation. The components of a polymer compound were carefully degassed before mixing and the mixture was poured into quartz cells where polymerisation occurred. The polymerisation time of the entire volume depended on the temperature regime and was from a few days to a few weeks. Concentrations of rhodamine 6G in samples were 0.025, 0.05, and 0.1 mg cm^{-3}, and of oxazine 17 – 0.02, 0.04, and 0.0 mg cm^{-3}.

Figure 1 shows the normalised absorption spectra $D/D_{\max}$ of rhodamine 6G and oxazine 17 in polyurethane (solid curves) recorded with a SF-8 spectrophotometer. For comparison, the absorption spectra of these dyes in ethanol are also presented (dashed curves). One can see that the absorption spectra of these dyes in polyurethane do not differ considerably from those in ethanol, although the absorption band of rhodamine 6G is shifted to the red by 6 nm, while the absorption band of oxazine 17 is shifted to the blue by 10 nm.
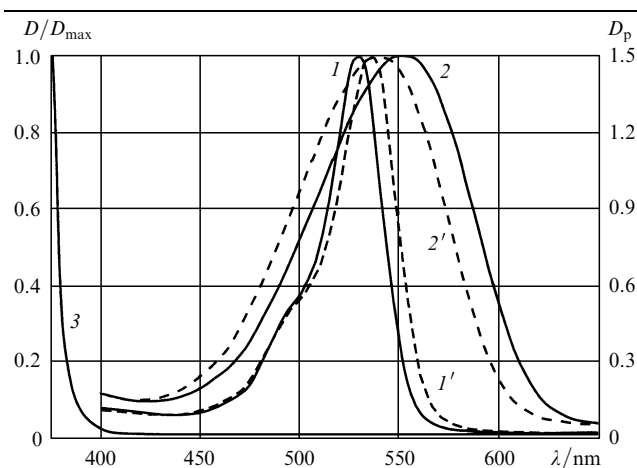

Figure 1. Normalised absorption spectra $D/D_{\max}$ of rhodamine 6G ($1, 1'$) and oxazine 17 ($2, 2'$) in polyurethane ($1, 2$) and ethanol ($1', 2'$) and the absorption spectrum D_{p} of pure polyurethane (3) of thickness 2 mm.

An important characteristic of a matrix is its absorption spectrum. Curve (3) in Fig. 1 shows the spectral dependence of the optical density D_{p} of a 2-mm thick pure polyurethane sample. One can see that polyurethane strongly absorbs in the wavelength region shorter than 400 nm, i.e., this region is unsuitable for excitation of dyes in polyurethane. In the region above 420 nm, polyurethane is virtually transparent and does not absorb pump radiation.

It follows from the absorption spectra of rhodamine 6G and oxazine 17 that these dyes should be pumped in the green spectral region between 500 and 550 nm. We performed pumping by a coumarin 289 dye laser at 530 nm. Coumarin 289 was pumped by a 13/150A coaxial flashlamp. The dye-cell length and diameter were 150 and 13 mm, respectively. This laser generated 3-μs, 800-mJ pulses.

Figure 2 shows the scheme of the experimental setup. We used transverse pumping of a matrix with a dye, which is the only variant possible for pumping ~ 2-cm long matrices. Radiation from pump laser (1) was focused with cylindrical lens (2) to matrix (3). The resonator of the dye laser was formed by highly reflecting mirror (7) with the reflectance ~ 0.99 and output mirror (8) with the variable reflectance. An intracavity dispersion element [interference–polarisation filter (4)] was used to narrow down the laser linewidth and to tune lasing. The output energy was measured with an IMO-2M calorimeter and emission spectra were recorded with a UF-90 camera on photographic plates.

We obtained stable lasing in all tested matrices a broadband resonator of length 10 cm. Depending on the pump intensity, the laser pulse duration was $1.5-2$ μs. Note
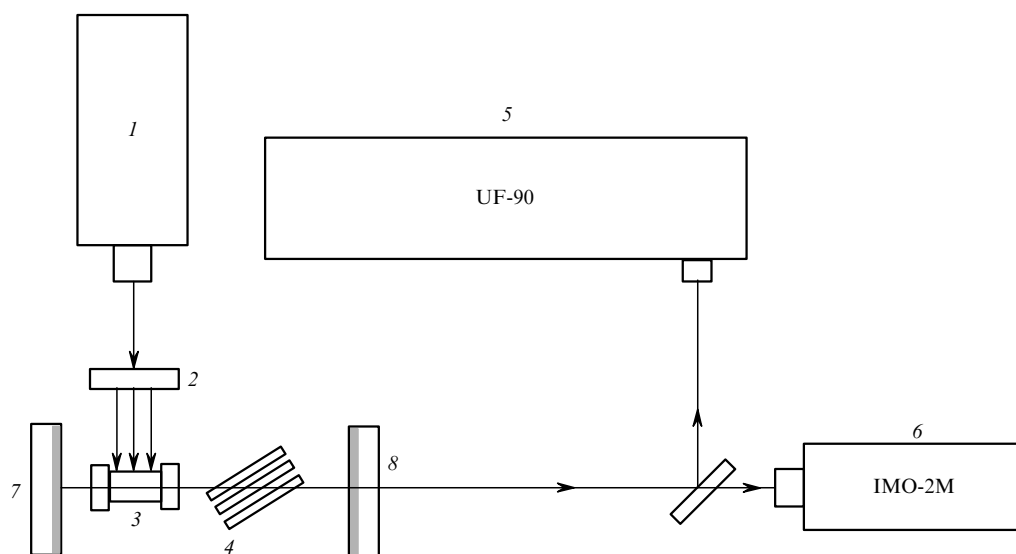
Figure 2. Scheme of the experimental setup: (*1*) pump laser; (*2*) cylindrical lens; (*3*) polyurethane matrix; (*4*) interference – polarisation filter; (*5*) UF-90 camera; (*6*) IMO-2M power meter; (*7, 8*) resonator mirrors.

that polyurethane matrices were not damaged upon exposure to radiation energy densities up to 1 J cm^{-2}. Above this pump energy density, point damage regions appeared around microinclusions in some samples. However, such high pump energies were not necessary because, for example, at pump energy densities from 0.6 to 1 J cm^{-2}, 1.5–2-cm long matrices doped with rhodamine at concentrations from 0.05 to 0.1 mg cm^{-3} produced efficient lasing even when the matrix end served as the output mirror. The maximum output energy of 12 mJ for rhodamine 6G was obtained in this regime in a matrix of length 2 cm at the dye concentration 0.1 mg cm^{-3}. The pump energy conversion coefficient was $\sim$ 6 %. Such a low conversion coefficient can be explained by the fact that the entire system was not optimised as a whole.

The increase of the pump radiation conversion coefficient in polyurethane matrices pumped by microsecond pulses will be the subject of further studies. These studies can be based on the results obtained in paper [15] where the conversion coefficient $\sim$ 30 % was obtained in a polyurethane matrix doped with rhodamine 6G. However, lasing was obtained upon quasi-longitudinal pumping of a 2-mm thick matrix by the 18-ns second-harmonic pulses of a Nd^{3+} : YAG laser. Nevertheless, we hope that the conversion coefficient can be increased upon pumping by microsecond pulses as well by improving the optical quality of matrices and optimising the system as a whole.

Matrices doped with oxazine 17 generated somewhat lower output powers. Thus, the output power generated in a matrix of length 1.6 cm at the oxazine 17 concentration of 0.08 mg cm^{-3} was 8 mJ. In this case, the reflectance of output mirror (*8*) was 0.35.

The emission spectra recorded under the above conditions are shown in Fig. 3 where the reference mercury lines are also presented. One can see that the rhodamine 6G and oxazine 17 lasers emit in the 579-nm and 625-nm regions, respectively. Note that the width and position of broadband laser emission spectra of dyes in polyurethane matrices depend on the dye concentration, transmission of the resonator mirrors, and pump intensity. In this respect,
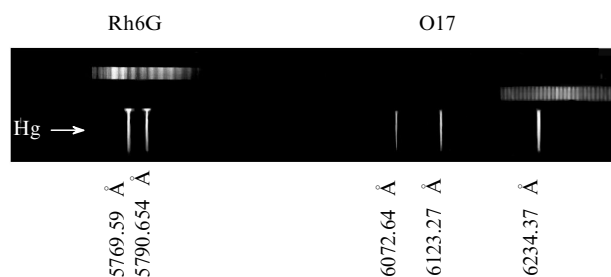

Figure 3. Laser emission spectra of rhodamine 6G and oxazine 17 in a broadband resonator.

lasers based on polymer matrices are completely identical to liquid dye lasers.

The similarity between liquid and polymer dye lasers was also revealed in the study of spatial–angular characteristics of their radiation. Our experiments showed that the radiation of lasers based on polyurethane matrices has a high angular divergence. Figure 4 shows the typical far-field radiation intensity distribution. The distribution has a central spot to which laser beams with the lowest divergence are focused, and many rings formed by the groups of beams propagating at large angles to the resonator axis. Let us estimate the beam propagation angles from the far-field pattern in Fig. 4. The divergence within the central spot was $\sim$ 5 mrad, within the first broad ring – $\sim$ 18 mrad, within the second ring – $\sim$ 29 mrad, and for the next rings it was $\sim$ 36, $\sim$ 42, $\sim$ 47, etc., up to the $\sim$ 70 mrad.

Similar far-field radiation intensity distributions were observed for liquid dye lasers. The specific features of these distributions were explained by thermooptic distortions in the active medium of lasers caused by the pumped radiation [22]. It is likely that similar distortions also take place in the active medium of polymer lasers. The influence of thermal distortions of a polyurethane active element was especially distinct in experiments with repetitively pulsed pumping. When the pump pulse repetition rate was increased up to 6–10 Hz, lasing in a polymer matrix disappeared after
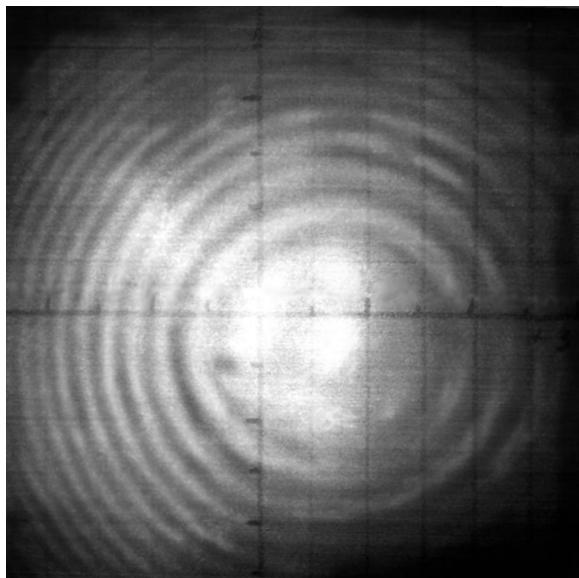
Figure 4. Far-field radiation pattern of a laser based on a polyurethane matrix doped with rhodamine 6G.

Figure 5. Output tuning curve $E_e(\lambda)$ of a laser based on a polyurethane matrix doped with rhodamine 6G.

15 – 20 pulses, and could be excited again within a few minutes after termination of pumping. This suggests that at such a pulse repetition rate, thermal stresses in the matrix increase, having no time to relax, and distort the resonator so that lasing is quenched. After cooling of the active element, its optical properties are recovered and lasing can be observed again. Thus, our experiments confirmed that polymer matrices are subject to considerable thermal distortions which can strongly influence lasing. Therefore, thermooptic distortions in polymer matrices should be minimised by selecting proper excitation conditions and using efficient cooling.

The main advantage of dye lasers is that they can be continuously tuned. We performed tuning experiments with the most efficient polyurethane matrix doped with rhodamine 6G by using an intracavity interference – polarisation filter as a dispersion element consisting of three 1-mm thick quartz plates. The background transmission of the filter was ~ 0.57, the transmission bandwidth was ~ 1.87 nm, and the free spectral range was ~ 40.6 nm. The filter was placed at the Brewster angle to the resonator axis. The resonator length was 36 cm and the reflectance of the output mirror was 0.55. Under such conditions, we performed tuning of the laser between 579 and 601 nm.

Figure 5 shows the output tuning curve of the laser. Note that the extension of the tuning range, especially, to the short-wavelength region was prevented by broadband lasing appearing in a 'parasitic' short resonator formed by the highly reflecting mirror and the matrix end, whose Q factor became higher than that of a main long resonator tuned to the slope of the output curve. This can be avoided by using matrices with skewed ends, as is usually done in tunable dye lasers.

Thus, we have fabricated cylindrical active polyurethane elements doped with rhodamine 6G and oxazine 17 dyes and tested them upon pumping by microsecond pulses. We have obtained pulsed lasing in the yellow – green and red spectral regions with the pulse duration of up to 2 μs. The integrated emission spectra of lasers and far-field radiation distribu-
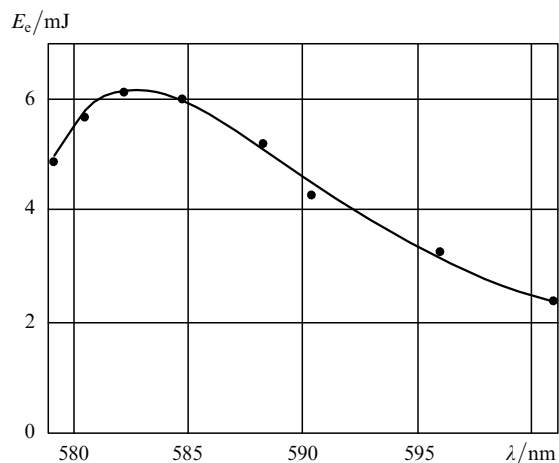
tions obtained in our experiments are similar to those of liquid dye lasers, which suggests the spectral and spatial – angular characteristics of solid-state polymer and liquid dye lasers are formed similarly. Our experiments have confirmed that an active polymer medium experiences strong thermal distortions upon pumping and have demonstrated the influence of these distortions on lasing. The tuning of the laser based on a polymer matrix doped with rhodamine 6G has been demonstrated in the range from 579 to 601 nm. Our study has shown that polyurethane can be used for the development of solid-state microsecond dye lasers.

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