

Spectral-luminescent and lasing properties of laser active media based on distyrylbenzene derivatives in various media

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Spectral-luminescent and lasing properties of distyrylbenzene (DSB) and its chlorine and methyl derivatives were investigated in the toluol and polymethylmethacrylate (PMMA) solutions. It has been shown that all compounds are well luminescing and generate laser radiation with the efficiency up to 31% in toluol and 22% in PMMA under the XeCl laser (308 nm) excitation. The photostability of these compounds in toluol and PMMA was studied as well.

Introduction

The growing interest in such compounds as distyrylbenzenes in the last decade is dictated by the promises of their use in optical communications, in photodynamic therapy and diagnostics,¹ in thin-film microelectronics and optoelectronic devices, such as light-emitting diodes and photoelectric converters,^{2–7} as well as limiters of optical radiation, etc.⁸ Dyes of this family are used as active media for frequency tunable lasers.

The lasing capabilities of various dyes in polymer matrices are now being actively studied. This is caused by the advantages of solid laser-active elements over the liquid solutions. For the red spectral region, solid active media have been created, that are highly competitive with liquid laser-active media based on xanthene and pyrromethene dyes^{9–15} in the energy conversion efficiency and photostability. For the blue region, the investigations are carried out in order to create similar media with satisfactory parameters, however only a few results have been obtained so far.^{16–18}

Since distyrylbenzene compounds efficiently generate laser radiation in nonpolar solvents, it seems to be promising to incorporate them into a polymer matrix for creation of solid laser active media in the blue spectral region and to study the effect of the

solvent on the optical properties of the initial compounds.

1. Investigation technique

1.1. Objects of the investigation

As objects of investigation, we took distyrylbenzene and its chlorine and methyl substitutes, because it is known¹⁹ that incorporation of a sterile substitute into the molecule of stilbene, which is the basis of the chosen dyes, leads to significant improvement of its luminescent properties. Of certain interest is also to study these molecules from the viewpoint of understanding the peculiarities of photophysical processes in molecules, where photoisomerization is possible upon excitation. The structure formulas of the studied molecules are shown in Fig. 1.

Polymethylmethacrylate (PMMA) was chosen as a material for the polymer matrix, because it is characterized by high optical properties (transparency, optical homogeneity, and optical damage threshold), well-developed production technology, and good performance properties (air and water resistance and others). The initial methylmethacrylate (MMA) monomer produced by Merk (Germany) was cleared from the stabilizer. As a solvent, we used a nonpolar

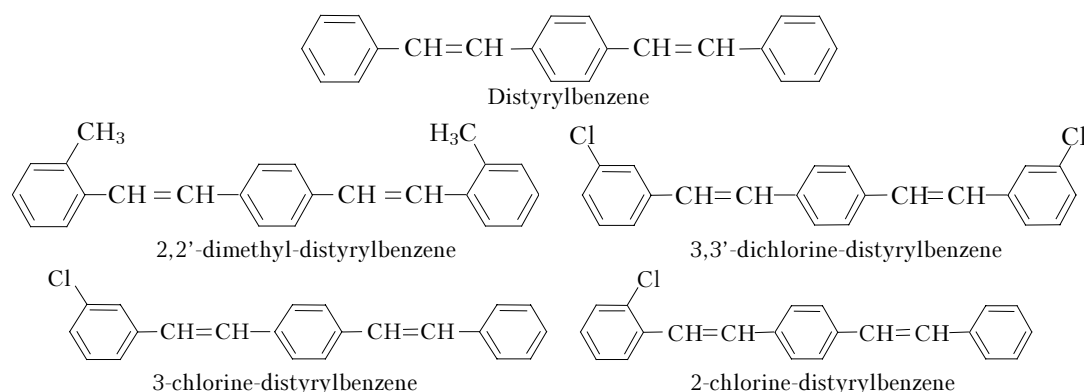


Fig. 1.

dye – spectroscopic-grade toluol. Dyes were incorporated into solutions and PMMA in the concentration optimal for lasing in the longitudinal excitation geometry, namely, 10^{-3} mol/liter.

1.2. Conditions of obtaining the polymer matrix

To obtain solid laser media based on dyes, the mixtures prepared by the method of dissolution of an organic dye in MMA were solidified through block radical polymerization. First, 0.1% thermal initiator was dissolved in the monomer. Dinitrile of azodiisobutyric acid re-crystallized by the known techniques was used as a thermal initiator. Samples were prepared from the pre-filtered solutions of the dyes and the initiator in MMA. To avoid the inhibiting effect of air, the solutions were put in glass moulds and blown with argon, after which the moulds were carefully tightened. Polymerization was carried out in dark in a thermostat at 35°C for 2 days. Then the temperature was increased up to 50°C in a 5°C step a day. Then, to decompose the rest initiator, the temperature was increased slowly up to 100°C. After that, the obtained material was gradually cooled to room temperature to avoid internal stresses and released from the moulds. As a result, we had transparent, homogeneous polymethylmethacrylate pieces, capable of luminescing and lasing in the visible spectral region. The optical treatment of the working surfaces of the elements was carried out manually.

1.3. Spectral-luminescent and lasing properties

The absorption spectra of the liquid solutions were recorded on a SPECORD M40 spectrophotometer, and the luminescence spectra

were recorded on a Hitachi 850 spectrofluorimeter. The quantum yield of fluorescence was determined by the standard procedure²⁰ with respect to distyrylbenzene (DSB) in toluol ($\phi=0.78$) (Ref. 21).

The lasing properties (photostability (lifetime) and conversion efficiency) of the dyes were studied under the excitation by the XeCl* laser radiation with the wavelength $\lambda = 308$ nm, the pulse energy $E_p = 15$ – 25 mJ, and the pulse duration $\tau_{0.5} = 12$ ns at the excitation power density $W_p = 25$ – 30 MW/cm² in the transverse excitation geometry.



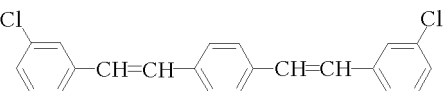
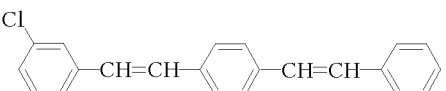
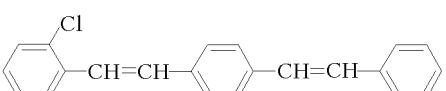
The lasing photostability of the dye ($P_{0.5}$) in solutions was taken equal to the total excitation energy pumped into the unit volume and resulting in halved lasing efficiency due to irreversible phototransformations. Since there is no volume mixing of molecules in polymer matrices and the working volume is very small, $P_{0.5}$ was taken equal to the total pump energy transmitted through the unit sample surface before the efficiency halved. The reported data on the photostability of polymer laser-active media (LAM) were obtained without scanning over the surface at excitation of the same sample area.

2. Results and discussion

2.1. Spectral-luminescent properties of DSB and its substitutes

The spectral-luminescent characteristics of the molecules studied were investigated in toluol and in the polymer PMMA matrix. Table 1 presents the absorption and fluorescence wavelengths, as well as the molar extinction coefficient and the quantum yield of the fluorescence for DSB substitutes in toluol.

Table 1. Spectral-luminescent properties of the dyes in toluol ($C = 10^{-3}$ mol/liter)

Compound	λ_{abs} , nm	ϵ , liter/(mol·cm)	λ_{fl} , nm	ϕ , rel. units	$\Delta\nu$, cm ⁻¹
	357.0	59000	392.0 413.5	0.78	3800
	347.0	58000	396.5 421.9	0.94	5100
	358.0	48000	394.0 416.0	0.78	4900
	358.4	56000	394.5 416.0	0.95	3900
	358.4	48300	398.0 421.0	0.46	4200

Note. ϵ is the molar extinction coefficient; ϕ is the quantum yield of the fluorescence; $\Delta\nu$ is the Stokes shift.

Figure 2 depicts the electronic absorption spectrum of the DSB solution in toluol. The spectroscopic studies of solutions of the distyrylbenzene-family dyes in the same solvent have shown that incorporation of chlorine as a substitute into the molecule affected neither the shape of the electronic spectrum nor the positions of the peaks of absorption bands. However, as chlorine was replaced by the *ortho*-CH₃ group, the peak of the absorption band shifted by 10 nm to the shortwave region (hypsochromic effect) with respect to the DSB solution (Table 1), and the intensity of absorption of all the DSB substitute dyes decreases. This effect is caused by the disturbance of the planar structure of the molecule.²²

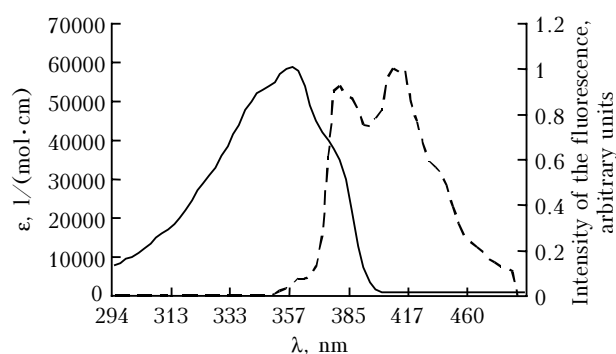


Fig. 2. Absorption (solid curve) and fluorescence (dashed curve) spectra of DSB in toluol.

The fluorescence spectra of DSB (Fig. 2) and all its substitutes have a structure character unlike the absorption spectra, which is likely indicative of the flattening of the molecules in the excited state. Upon absorption of a light quantum, the molecules with the symmetric methyl and chlorine substitutes in the *ortho*- and *meta*-forms experience deeper changes in the geometry of the molecular skeleton, as evidenced by the increase of their Stokes shift to 5100 and 4900 cm⁻¹, respectively (see Table 1). The studied

molecules in toluol are characterized by strong fluorescence, whose quantum yield for the most of the dyes studied is 78–95%. The only exclusion is the compound with chlorine in the *ortho*-form, whose emissivity is twice as low due to the spatial disturbances caused by the substitute.²²

The study of the spectral-luminescent properties of the polymer samples has shown that the substitution of toluol by PMMA was not accompanied by any significant shift of the fluorescence bands of these dyes, as would be expected, because the permittivities of toluol (~ 2.3) and PMMA (~ 6.0) have close values.

It should be noted that among all the substituted DSBs, the methylated compound undergoes the largest hypsochromic shift (~ 7 nm) upon the transition from toluol to PMMA.

2.2. Lasing properties

The lasing properties of DSB and its substitutes have been analyzed in both toluol and the polymer matrix. The lasing wavelength, efficiency, and photostability of the molecules are summarized in Table 2. The lasing spectra are insignificantly shifted with respect to the fluorescence spectra and lie in virtually the same region (414–425 nm). The efficiency of conversion of the XeCl laser radiation by these compounds is 25–30% in toluol and 14–22% in PMMA, and the lasing efficiency of 2-chlorine-DSB in the toluol and PMMA solutions is almost the same and amounts to 24 and 22%, respectively. The high lasing efficiency in PMMA is also inherent in non-substituted and 3-chlorine-substituted DSB.

The studied distyryls in toluol possess quite good lasing photostability for the compounds emitting in this spectral range. As can be seen from Table 2, the lasing photostability of non-substituted DSB and 2,2'-dimethyl DSB is about 200 J/cm³, while for other compounds it is somewhat lower.

Table 2. Lasing properties of solutions of the dyes studied ($C = 10^{-3}$ mol/liter)

Compound	Solvent	λ , nm	eff., %	$P_{0.5}$	
				J/cm ³	pulse (J/cm ²)
	toluol	414	30.0	198	
	PMMA	413	22.2		9 (2.9)
	toluol	425	31.0	175	
	PMMA	417	14.6		11 (3.3)
	toluol	418	28.0	113	
	PMMA	416	14.7		10 (3.2)
	toluol	417	25.0	70	
	PMMA	415	19.2		9 (2.9)
	toluol	420	24.0	120	
	PMMA	417	22.0		10 (3.2)

The lasing photostability of polymer LAM is about 3 J/cm^2 , which corresponds to roughly 10 "hard" pump pulses with the intensity $\sim 25\text{--}30 \text{ MW/cm}^2$. For the practical use of polymer LAM, this characteristic is not good enough and should be improved in some way. The simplest way to improve the photostability is to decrease the intensity of the pump pulse and to scan the sample surface. Such an approach can many times increase the service life of these LAM.

Conclusions

Thus, we have studied some distyryl substitutes of benzene and revealed some regularities of variation of their spectral-luminescent properties depending on the structure of the molecule and a solvent.

It has been shown that incorporation of the methyl and chlorine substitutes into the DSB molecule only slightly affects its spectral-luminescent properties.

All the studied dyes are characterized by efficient (up to 31% in the toluol solution and up to 22% in PMMA) lasing in the blue spectral region.

In addition to the high conversion efficiency, all the studied compounds have good photostability in toluol, and this makes them promising for the use as active media for tunable lasers operating in the blue region of the spectrum.

Acknowledgments

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