

The development of polymer laser-active media with improved performances

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Abstract. The influence of modification of organic glass by additives new derivatives of thiazole and thiourea on the spectral-fluorescent and lasing characteristics of the Rhodamine 6G laser dye has been investigated. For the sample modified by additive - N-(4-carbomethoxy-5-phenyl-thiazol-2-yl)-N'-phenylthiourea taken in amounts of 0.01 mol% the maximum rise of the absorption and fluorescence intensity to compare with the unmodified sample 1.3 and 2.3 times, respectively, was detected. The 8.3 times more lasing energy, and the 7.3 times higher laser photostability has been achieved.

1. Introduction

Optically transparent polymers and organic glasses based on methacrylates doped with laser dyes represent a new class of solid-state laser-active media (LAM). Research results of their properties are described in [1-3] and in other papers. The polymeric LAM successfully replaces liquid LAM - solutions of laser dyes. However, in order to broaden an area of practical application of laser devices with polymeric LAM it is necessary to improve their performances. It is well known that during the synthesis and subsequent treatment of the polymeric LAM the polymer matrix and incorporated dye undergo irreversible changes caused by free radical chain processes. As it is known [4,5], these processes lay in the basis of photochemical ageing and degradation of polymers. Therefore it is necessary to investigate new highly effective stabilizers.

In this paper new derivatives of thiazole and thiourea (DTT) were studied as modifying compounds (potential photostabilizers) synthesized in Institute of Organic and Physical Chemistry named after A.E. Arbuzov, Kazan scientific center of Russian Academy of Sciences. Namely these compounds are: N - (thiazol-2-yl)-N'-phenylthiourea (DTT-1) and N-(4-carbomethoxy-5-phenyl-thiazol-2-yl)-N'-phenylthiourea (DTT-2). In order to provide the comparison the commercially available N, N'-diphenylthiourea (DPTU) was also investigated as reference specimen. Structural formulas of all additives are shown in Figure 1.



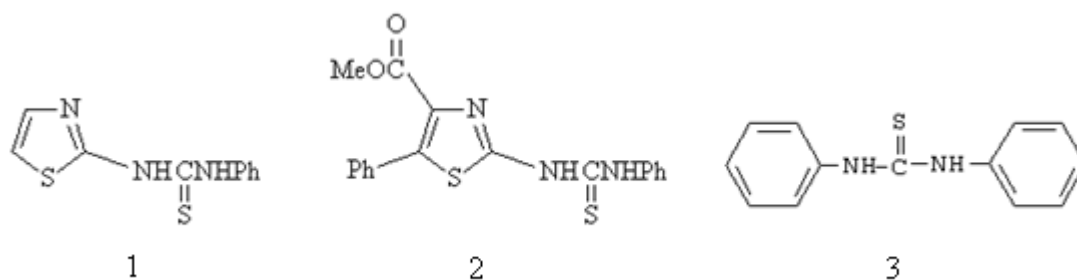


Figure 1. Structural formulas of modifying compounds: 1 is N - (thiazol-2-yl)-N'-phenylthiourea (DTT-1), 2 - N-(4-carbomethoxy-5-phenyl-thiazol-2-yl)-N'-phenylthiourea (DTT-2), 3 - N, N'-diphenylthiourea (DPTU)

Here we tested the modification of DTT, because of previously we have been established the ability of these compounds to inhibit (suppress) free-radical chain processes [6].

This work was aimed at the study of fluorescence spectral properties and laser characteristics of samples of organic glasses doped with Rhodamine 6G and DTT, and to elucidate the possibility of using them as LAM with improved performances.

2. Experimental

The objects of our research were prepared in the form of plates of organic glass doped with classical Rhodamine 6G laser dye -. The concentration of Rhodamine 6G in the initial mixture was $2 \cdot 10^{-4}$ mol·L⁻¹ for the study of spectral-fluorescent properties and $4,57 \cdot 10^{-4}$ mol·L⁻¹ for laser tests. The thickness of the synthesized samples was 0.5 mm and 1.5 mm, respectively. Modifiers concentration have been varied between 0.01 - 0.10 mol. %.

In the work methylmethacrylate (MMA) and methacrylic acid (MAA) purified by vacuum distillation were used. Here are some physical properties of the compounds: MMA - refractive index 1.4130, density $0.943 \text{ g} \cdot \text{cm}^{-3}$, MAA - refractive index 1.4314, density $1.0153 \text{ g} \cdot \text{cm}^{-3}$.

DTT and Rhodamine 6G were dissolved in a mixture of MMA and MAA, and then their block radical-free copolymerization was carried out. The weight ratio MMA:MAA was equal to 90:10. Azobisisobutyronitrile (0.1 wt.%) as the initiator of reaction was used.

Registration of absorption spectra was carried out on a dual-beam scanning spectrophotometer «Lambda 35» (Perkin-Elmer, USA). To excite fluorescence in the samples UV solid-state Ce:LLF picosecond laser (Ultraviolet Solution LLC) was used. It provided single 400 ps laser pulses with pulse repetition rate 10 Hz at the wavelength $\lambda = 310 \text{ nm}$. The fluorescence spectra were studied by Stellarnet spectrometer and fluorescence kinetics were registered by Alphalas UPD photodiodes with 50 ps rise time and 3.5 GHz bandwidth Tektronix DPO 7354 digital oscilloscope. The CW fluorescence spectra were also registered using a spectrofluorimeter Cary Eclipse (Varian, USA).

The scheme of experimental setup which used for study of the sample performances is presented on Fig.2. To achieve the laser oscillation from investigated samples and to study it photostability the second harmonic radiation of the Nd:YAG laser was applied. The study of the laser properties was realized in the flat-parallel cavity which formed by EC and OC couplers with quasilongitudinal scheme of lasing excitation. The resonator length was 70 mm, the angle between cavity axis and pump beam was about 7° . Measurement of every pulse falling energy, not absorbed energy and oscillation energy of a sample were carried out with photodiodes with have peak-detectors, Ph1 – Ph3 respectively. The parts of energy beam from every point of measurements were branched off to every photodiode with help of flat-parallel plates P. Measurement head MH allow of absolute energy measuring and it is used for calibration of photodiode Ph1-Ph3. For starting of measuring processes of the setup from every pulse of pumping was used the triggering photodiode TPh. Energy values from all of point measurements of the setup were drawn on the computer's monitor PC. Energy density of pumping sample was being changed by changing energy with using optical attenuator OA.

Degradation of laser oscillation in polymer active media were carried out in the cavity with highly reflecting coupler - EC (99,9 % reflection in the range 500 nm – 650 nm) and output coupler - OC with 0,6 % reflection around 600 nm. Energy density of the pump radiation was kept at the level about $0,142 \text{ J/cm}^2$.

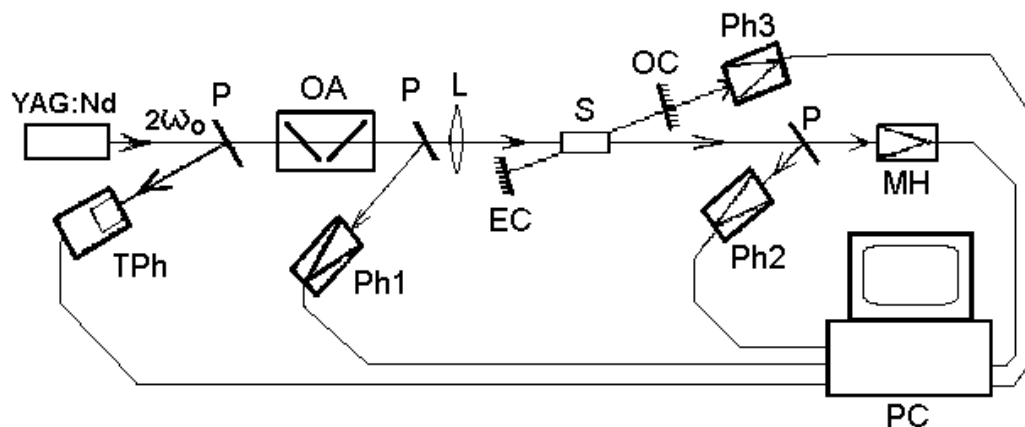


Figure 2. The scheme of experimental setup arrangement for sample oscillation study. YAG:Nd laser; P – flat-parallel plates; OA – optical attenuator; L – lens; S – sample; EC – end coupler; OC – output coupler; TPh – photo receiver for starting measurement process; Ph1-Ph3 photo diodes; MH – measurement head for absolute measurement energy value; PC – personal system.

3. Results and discussions

Figure 3 illustrates the influence of concentration of the modifying compound DTT-2 in the polymer matrix doped with laser dye on the fluorescence and absorption characteristics. Figure 3 shows that both absorption coefficient and fluorescence intensity of rhodamine 6G are increased in the modified polymer matrix at concentration of DTT-2 of 0.01 mol%. It is explained by an increasing of molecular stability of the dye in copolymerized system. That is, the introduction of a modifier has ensured safety of higher amount of optically active molecular centers of rhodamine 6G during synthesis process. However, with increasing concentration of DTT-2 in the polymer matrix the decreasing of fluorescence intensity of the dye (particularly at 0.10 mol %) is observed. It can be explained by reabsorption of fluorescence of rhodamine 6G by the modifying additive. Fluorescence of the dye occurs in the region $\lambda = 530\text{--}650 \text{ nm}$, which is characteristic of the rhodamine 6G dye. Bands observed in the shortwave region of the spectrum - in the range of $\lambda = 350\text{--}475 \text{ nm}$, apparently correspond to the intrinsic fluorescence of the polymer matrix.

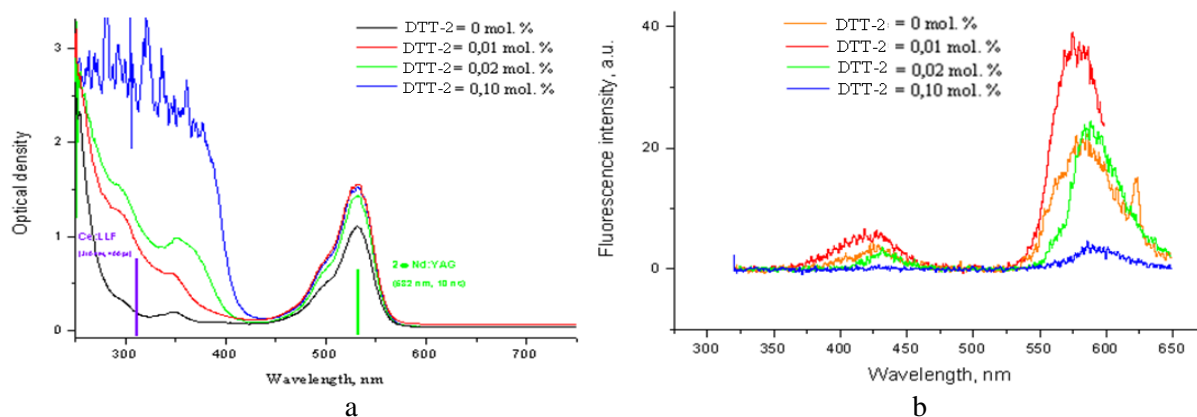


Figure 3. Absorption (a) and fluorescence (b) spectra of the polymer samples, doped with Rhodamine 6G and modified by DTT-2

Results of the study of spectral-fluorescence properties of the check (unmodified) sample, and the samples modified by additives DTT presented in Table 1. The table contains data characterizing the position of the maximum fluorescence (λ_{fl}) and fluorescence intensity values (I). The results of laser tests of doped polymer samples are also presented. These are presented as relative change in energy of generation – E_m/E and laser photostability of dye in a polymer matrix – N_m/N (E_m and E – output energy of laser radiation of the sample with the additive of the modifier and check one, respectively; N_m and N – number of pumping radiation pulses, that lead to half the height dropping of the output energy of laser action. In Table 1 the corresponding characteristics are also given for the sample modified by diphenylthiourea (DPTU), which was previously investigated as stabilizer polymer matrix and incorporated therein a laser dye [7]. The level of concentration of the modifying compounds in all cases was the same.

As the table shows, there is a small shift of the position of the fluorescence maximum λ_{fl} in modified samples relative to the check sample. The fluorescence intensity (I) considerably increases at the same time. The maximum value of intensity was detected for the sample of the modified by DTT-2 additive.

In the case of modifying samples with additives DTT, the energy of laser action and lasing photostability of the dye in the polymer matrix increased significantly. At the same time output energy E exceeds the value of corresponding indicator for the polymer matrix modified by DPTU additive.

Table 1. Results of the study of spectral-fluorescent properties and laser test of the samples

Modifying additive*	λ_{fl} , nm	I, a.u.	E_m/E	N_m/N
Without additives	549	1460	-	-
DTT-I	551	2281	8,4	7,3
DTT- 2	553	3385	5,0	4,6
DPTU	550	1892	3,4	4,6

As shown in Fig. 4, the decay time of the fluorescence intensity of the dye in the polymer matrix is approximately the same at all concentrations of the modifying additive – DTT-2. Therefore this type additive does not lead to Rhodamine 6G fluorescence quantum yield dropping in modified polymer matrix.

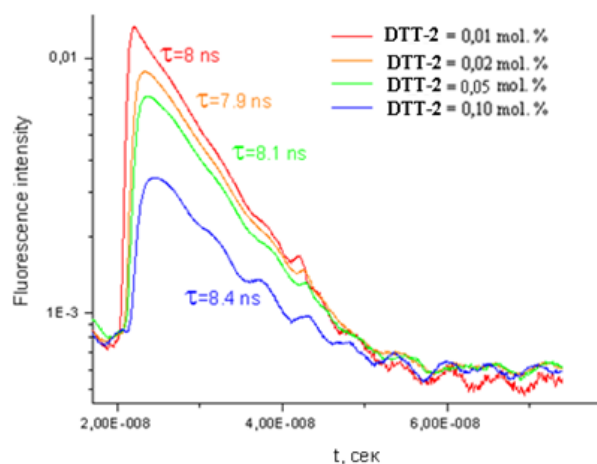


Figure 4. Fluorescence kinetic of the polymer samples doped with Rhodamine 6G and modified by DTT-2.

Conclusion

Therefore, spectral-fluorescent and lasing characteristics of samples of organic glasses, modified by the addition of DTT and doped laser rhodamine 6G dye were studied. There is a tendency to reabsorb the dye fluorescence by studied additives with increasing of their concentration in a polymer matrix. So, it means that necessary to choose the optimal concentration of modifying additives. It is shown that the modification by DTT leads to a considerable increasing in optical density, fluorescence, energy of laser action and the laser photostability of rhodamine 6G dye doped polymer samples, and it may be promising for obtain polymer LAM with improved performances

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