

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.



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 J/cm².

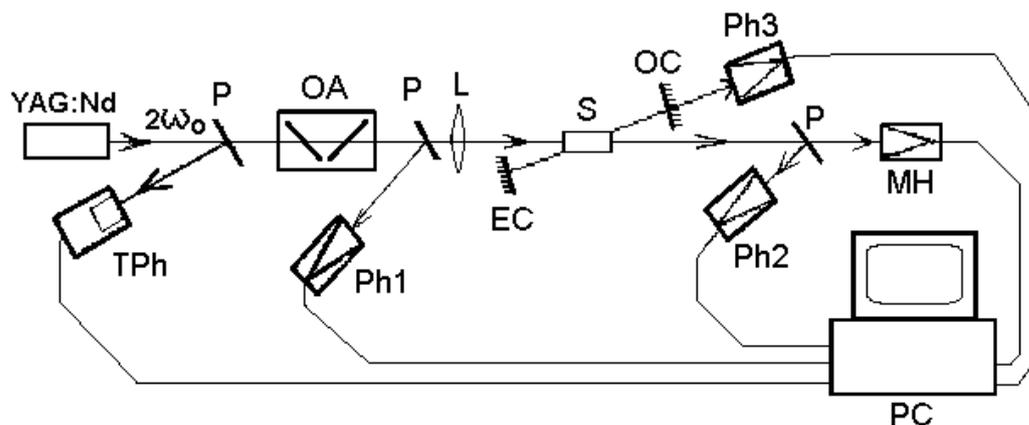


Figure 2. The scheme of experimental setup arrangement for sample oscillation study. YAG:Nd laser; P – flat-parallel plates; OA – optical attenuator; L – lens; S-sample; EC – end coupler; OC – output coupler; TPh – photo receiver for starting measurement process; Ph1-Ph3 photo diodes; MH – measurement 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 $\lambda = 530\text{-}650$ nm, which is characteristic of the rhodamine 6G dye. Bands observed in the shortwave region of the spectrum - in the range of $\lambda = 350\text{-}475$ nm, apparently correspond to the intrinsic fluorescence of the polymer matrix.

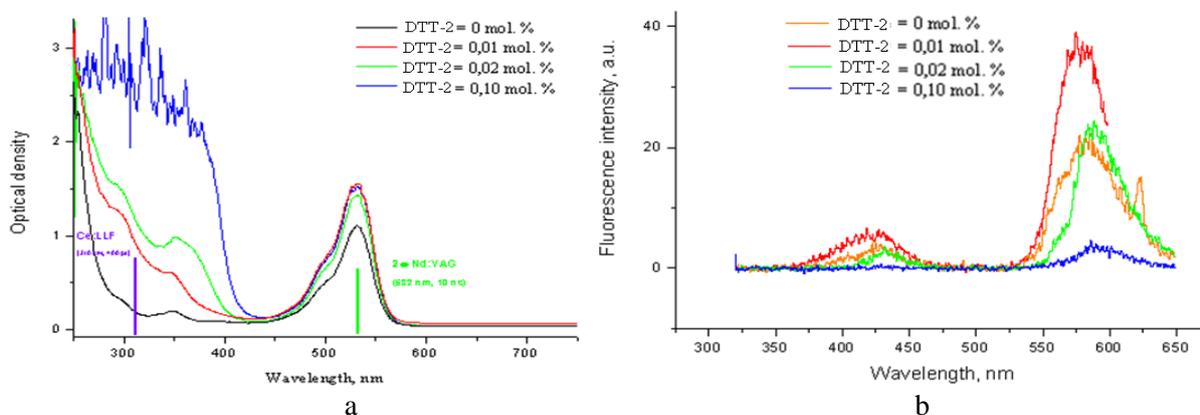


Figure 3. Absorption (a) and fluorescence (b) spectra of the polymer samples, doped with Rhodamine 6G and modified by DTT-2

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.

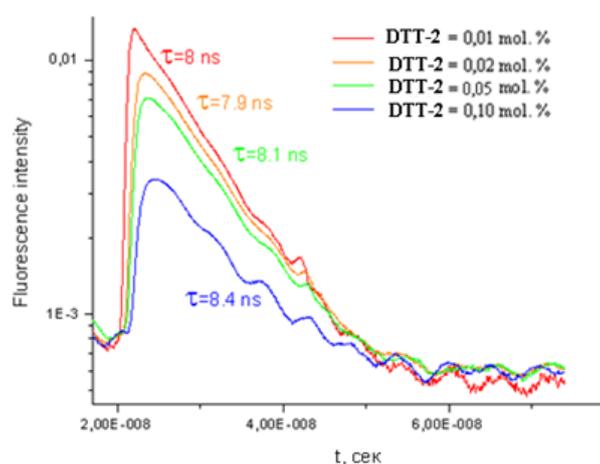


Figure 4. Fluorescence kinetic of the polymer samples doped with Rhodamine 6G and modified by DTT-2.

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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