SOME ASPECTS OF PURPOSEFUL PREPARATION OF ACTIVE LASER DYE MEDIA IN POLYMER MOULDS

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We present here some results of the research of photostability and spectral and lasing properties of active laser media based on organic dyes like rhodamine 6G and coumarin 7 in the methylmethacrylate with methacrylic acid copolymer, modified by a number of urea derivatives. The photostabilizing effect of these compounds revealed as well as its impact on the kinetic and resulting characteristics of the copolymerization process were studied.

Active laser media based on dyes in hard polymeric solutions attract much attention in the laser optics due to their operational, technological, and ecological advantages as compared with liquid ones.[1–6] At the same time, an increase in their resource characteristics connected with the necessity for higher photochemical stability of polymeric active laser media (PALM) is one of the main problems in facilitating wide application of lasers with polymeric active elements.

As shown in Refs. 4 and 6, the photostability of PALM as well as their spectral lasing characteristics is determined not only by the properties of an organic dye but also by the nature of a polymeric mould and modifying additions doped in it. Earlier we have shown[7–10] the possibility of improving the photostability of PALM based on rhodamine 6G in a methylmethacrylate (MMA) and methacrylic acid (MAA) copolymer due to small amounts of metal salts or some organoelemental compounds what enables an increase in the resource of a tunable LKI–301 laser[5,11] when these PALM are used as its working substance.

This paper continues investigation of photostability and spectral lasing properties of PALM based on rhodamine 6G (isobutyrate) and coumarin 7 in the MMA–MAA copolymer with some modifying additions and the influence of the latter on the main kinetic and resulting MMA–MAA copolymerization parameters aimed at looking for a possibility of constructing the copolymer structure and, consequently, the control over synthesis of PALM possessing higher photostability and other performance characteristics.

A number of urea derivatives, namely, *N, N'*-diphenylurea (DPU), *N, N'*-diphenylthiourea (DPTU), hexamethylene-*N, N'*-double (tetrahydroxyethylurea) (HMDU), and *N, N'*-pentamethylene-benzoylthiourea (PBTU), were studied as modifying additions. The choice of the above compounds is caused by the fact[12] that organic compounds containing amino groups are able to inhibit chain (photo) oxidation processes by interaction with peroxyradicals; and sulfur containing organic compounds can inhibit the processes by destruction of hydroperoxides without forming radicals.

The characteristics of the initial substances, conditions of PALM synthesis, and methods of determining the kinetic parameters of the copolymerization process are similar to those described earlier in Ref. 13. The concentration of the dopants varied from 0.002 mole % to 0.120 mole % depending on their solvability in the initial monomers. The concentration of dyes corresponded to $2\cdot10^{-4}$ mole/liter and mass ratio MMA:MAA was 9:1 what is optimal in order to obtain PALM with given optical and physico-mechanical properties.[5]

The absorption spectra of dyed samples and the spectral phototransmission coefficient of colorless ones were recorded with SF–18 and SF–46 spectrophotometers. To investigate the photostability, samples of 1 mm thickness were subjected to the irradiation by full light from a PRK–2 mercury lamp. In the investigations of lasing properties of PALM we used a quasi-longitudinal scheme of pumping with radiation of the second harmonic of a Nd:YAG laser (λ = 532 nm) for PALM based on rhodamine 6G in a copolymer and the third harmonic of this laser (λ = 355 nm) for PALM based on coumarin 7 in a copolymer; t_p = 12 ns at a pulse repetition frequency of 1 Hz and energy of 4.5 mJ. The samples were placed to a resonator of 12.5 cm length with two flat mirrors with $R_1 \sim 99\%$ and $R_2 = 20\%$. The lifetime was determined by the pulse number until the generation energy decreases two times. The radiation of this laser also excited the luminescence of the samples. The laser operated in a monopulse regime. The laser radiant flux density was 1 mJ/cm^2. Luminescence spectra have been recorded by an automated spectroscopic complex.

To investigate laser stability of the samples, radiation of the second harmonic of the laser with t_p = 10 ns and pulse repetition frequency 12.5 Hz was

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used. The optical scheme of the device for investigation of the laser stability can be found in Ref. 9. The number N of pulses endured by the sample until its destruction under the constant output density of 0.5 and 0.63 J/cm^2 was taken as a criterion of laser durability.

IR spectra of the initial mixtures and of the copolymer were recorded with a "Specord-75IR" spectrophotometer.

The investigation of spectral-luminescent properties did not reveal any essential influence of modifying dopants on the absorption and luminescence spectra of the dyes in a copolymer. Here $\lambda_{\max}^{\text{abs}}$ = 532–533 nm, $\lambda_{\max}^{\text{lum}}$ = 551–552 nm in the case of rhodamine 6G and $\lambda_{\max}^{\text{abs}}$ = 450–451 nm, $\lambda_{\max}^{\text{lum}}$ = 495–497 in coumarin 7. The value of the molar extinction coefficient ε of the dyes in a modified copolymer, differing slightly from ε in a reference one, corresponded to the data from Ref. 5.

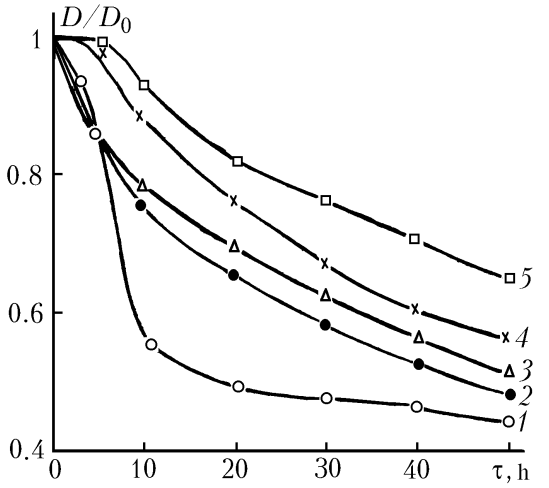

FIG. 1. Kinetic decolorization curves of rhodamine 6G in the MMA–MAA copolymer with modifying dopants: without dopants (1), with HMDU (2), DPU (3), DPTU (4), and PBTU (5). Dopant concentration is 0.004 mole %.

The influence of dopants on photodecolorization kinetics of rhodamine 6G in a copolymer is demonstrated in Fig. 1 as functions of the relative change D/D_0 of optical density in the absorption band maximum of the dyed samples on the period of their irradiation (D_0 and D are optical densities before and after the irradiation). Kinetic curves demonstrate that one can observe photostabilizating action of dopants on rhodamine 6G in a copolymer; the action increases in accordance with the sequence HMDU < DPU < DPTU < PBTU. Most strong photostabilization effect has been observed from DPTU and PBTU dopants from first hours of the irradiation. For instance, a decrease in D value of a dye in a reference copolymer amounted to 45% after 10 hours of irradiation, and that of the copolymer with dopants PBTU and DPTU amounts to 5% and 10%, respectively.

According to experimental data, the chosen modifiers cause similar photostabilization effect on both coumarin 7 in a copolymer and a colorless copolymer. The photostability of a copolymer can be judged from the relative change in viscosity of its solutions in dimethylformamide, i.e., the ratio η/η_0 from which one can determine the number of macrochain gaps under irradiation and also from relative change of phototransmission coefficient of a colorless copolymer K/K_0 at the wavelength λ = 300 nm at which a decrease in the value K during the irradiation of samples was more considerable.

Figure 2 shows the ratios η/η_0 and D/D_0 for a dyed copolymer and K/K_0 for a colorless one found after 20 hours of irradiation as functions of DPTU concentration. The increase of the value D/D_0 shows that the photostability increases in both dyes in a copolymer take place with an increase of DPTU concentration. The photostability of a copolymer increases too; namely, the value of η/η_0 increases, i.e., the number of gaps in copolymer chains decreases under the irradiation. The growth of DPTU contents implies a lower change in the coefficient K of a colorless copolymer during the same period of irradiation. The view of the presented functions close to cymbate is indicative of the fact that higher photostability of dyes observed in a modified copolymer is a consequence of the photostability increase of a colorless copolymer caused by modification of the copolymer as a polymer mould in which the dye is doped.

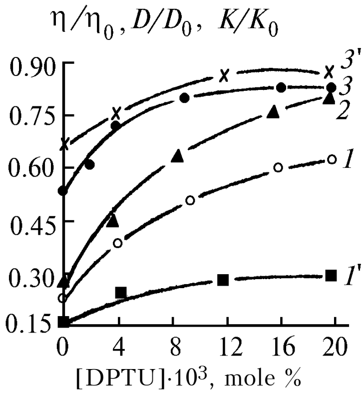

FIG. 2. Functions of relative viscosity change η/η_0 *of colored MMA–MAA copolymer solutions (1, 1'), phototransmission coefficient* K/K_0 *of a colorless copolymer (2), and optical density of dyes* D/D_0 *in a copolymer (3, 3') after* 20 *hours of radiation on the DPTU concentration in copolymer: rhodamine* 6G *(1, 3); coumarin 7 (1', 3').*

TABLE I. The influence of modifying dopants on the laser stability of the MMA-MAA copolymer.

Dopant concentration $\times$□10^3, mole %	N/N_r			
	DPU*	DPTU**	PBTU**	HMDU*
1.0	1.7	8.3	1.0	1.0
4.0	1.2	13.8	3.3	1.0
10.0	1.0	19.6	4.0	1.2
16.0	1.0	58.5	21.8	9.8
40.0	–	–	62.6	2.8
120.0	–	–	10.8	–

* Output density of 0.5 J/cm^2.

** Output density of 0.63 J/cm^2.

The influence of the additives on the laser stability of a copolymer is demonstrated in Table I, where the ratio N/N_r (N_r and N are numbers of pulses endured by the sample of the reference and modified copolymer respectively until its destruction) is presented. According to the obtained data, a considerable increase in the laser stability of a copolymer (~60 times) is observed only after inclusion of DPTU and PBTU with the amount 0.004–0.016 mole % and 0.016–0.120 mole %, respectively.

In order to explain the results of our investigations, we have made a comparison of the IR spectra of the copolymer and modifying dopants. Portions of these spectra are presented in Fig. 3. Characteristic absorption bands of the valent vibrations of the C=O group of MMA and MAA are observed at 1720 and 1680 cm^{-1}, respectively. The absorption band $\nu_{C=O}$ in the IR spectrum of DPU as well as in that of PBTU is at 1650 cm^{-1}. As to the HMDU, it is a wide absorption band at 1530–1575 cm^{-1}. The absorption band $\nu_{C=S}$ in the DPTU spectrum is observed at 1550 cm^{-1}.

According to the photostabilization mechanism proposed in Ref. 4, higher photostabilizating effect should be observed from the PBTU and DPU dopants. It is caused by vibrational cross-relaxation between copolymer and dopant macromolecules and, consequently, by energy transfer because the absorption bands of the C=O group in the IR spectra of these compounds are close to that of $\nu_{C=O}$ of the MAA copolymer bonds. However, as judged from the experimental data, the photostabilizating influence of DPU is less considerable than that of DPTU and PBTU. So a more expressed photostabilizating action of DPTU and PBTU can be explained by a greater ability of these compounds to inhibit chain photooxidizing processes by interaction with peroxyradicals and destruction of hydroperoxides[12] because they are amine derivatives and sulfur-containing organic compounds at the same time. Moreover, the highest photostabilizating action of PBTU dopants is apparently due to both inhibiting and quenching exited states in the energy transfer mechanism.

FIG. 3. Portions of IR spectra: HMDU (1), PBTU (2), DPTU (3), DPU (4), MMA–MAA copolymer (5).

One could assume that the presence of a larger, than in other modifiers, number of active functional groups in PBTU should also result in the influence of PBTU on copolymerization kinetics including the intermolecular interaction in the initial monomer mixtures. The results of spectroscopic investigations are indicative of the immediate participation of PBTU molecules in the intermolecular interactions already at the stage of preparation of the initial mixtures. For instance, a new and absent in spectra of individual compounds absorption band at 1545 cm^{-1} related to a valent vibration of ν_{COO} was observed in the IR spectrum of PBTU–MAA mixtures. This can be explained by formation of hydrogen bonds between the proton of the MAA COOH-group and the MAA carbonyl oxygen in a PBTU molecule and also between the proton of PBTU NH-group and the carbonyl oxygen in a MAA molecule. As kinetic investigation shows that this circumstance can explain copolymerization activity of monomers and, consequently, its influence on the structure of the copolymer obtained.

TABLE II. The influence of PBTU on copolymerization constants of MMA (r_1) and MAA(r_2).

Dopant	r_1	r_2	$r_1 \cdot r_2$
Without a dopant	0.70±0.03	1.77±0.36	1.24
PBTU	0.54±0.03	1.95±0.49	1.05

PBTU concentration is 0.02 mole %.

The influence of PBTU on MMA and MAA copolymerization constants is shown in Table II. The decrease of the product of copolymerization constants $r_1 \cdot r_2$ is observed if PBTU is doped into the copolymerized system. As known[14] this fact is indicative of the increasing tendency to alternation of the ether and acid links in the copolymer formed, i.e., most favorable conditions are created for intermolecular contacts with a participation of active copolymer and a modifier and, consequently, for a more efficient energy transfer from the copolymer macrochains to the dopant molecules what likely explains more efficient photostability of a polymer mould and, correspondingly, that of the dye doped in it. So the efficiency of PALM photostability is determined not only by special properties of modifiers but also by their influence on the kinetic PALM synthesis parameters determining the regularity of the formed copolymer structure.

The investigations of generation properties performed for PALM based on rhodamine 6G in the MMA–MAA copolymer demonstrate that the lifetime of PALM increases due to copolymer modification by PBTU by more than 13 times. At the same time no improvement of the resource characteristics is observed if such a traditional photostabilizer as benzone OM is used.

REFERENCES

1. T.F. Ivanova, M.P. Votinov, A.V. Dokumino, et al., Izv. Akad. Nauk SSSR, Ser. Fiz. **45**, No. 4, 662–665 (1981).
2. V.I. Bezrodnyi, O.V. Przhonskaya, E.A. Tikhonov, et. al., Kvant. Elektron. **9**, No. 12, 2455–2466 (1982).
3. V.S. Burakov, N.N. Vasil'ev, A.Ya. Gorelenko, and A.P. Shkadarevich, Dokl. Akad. Nauk BSSR **26**, No. 12, 1085–1087 (1982).
4. K.M. Dyumaev, A.A. Manenkov, A.P. Maslyukov, et al., Izv. Akad. Nauk SSSR, Ser. Fiz. **51**, No. 8, 1387–1398 (1987).
5. L.K. Denisov, A.I. D'yachkov, V.N. Kristaleva, et al., Plast. Massy, No. 12, 22–23 (1987).
6. N.N. Barashkov, V.T. Yaroslavtsev, T.M. Murav'eva, et al., Zh. Prikl. Spektrosk. **58**, No. 3, 386–393 (1993).
7. V.N. Serova, A.A. Vasil'ev, M.A. Dubinskii, et al., Kvantovaya Elektronika (Naukova Dumka, Kiev), No. 43, 45–49 (1992).
8. V.N. Serova, A.A. Vasil'ev, O.A. Cherkasova, et al., Atmos. Oceanic Opt. **6**, No. 3, 168–170 (1993).
9. V.N. Serova, A.A. Vasil'ev, M.A. Dubinskii, et al., Atmos. Oceanic Opt. **6**, No. 6, 424–426 (1993).
10. V.N. Serova, A.A. Vasil'ev, E.L. Koryagina, et al., in: *Advances Solid-State Lasers and Compact Blue-Green Lasers. Technical Digest* (OSA, Washington, 1993), Vol. 2, pp. 173–175.
11. V.I. Zhil'tsov, A.G. Klimanshina, V.E. Mnuskin, et al., Zh. Prikl. Spektrosk. **45**, No. 1, 35–39 (1986).
12. Yu.A. Shlyapnikov, S.T. Kiryushkin, and A.P. Mar'in, *Anti-Oxidizing Stabilization of Polymers* (Khimiya, Moscow, 1986), 256 pp.
13. V.N. Serova, A.A. Vasil'ev, L.N. Shmotova, et al., Zh. Prikl. Khim. **10**, 2371–2374 (1993).
14. G.E. Ham, ed., *Copolymerization* [Russian translation] (Khimiya, Moscow, 1971), 609 pp.