

INFLUENCE OF INTERMOLECULAR INTERACTIONS ON THE LASING DURABILITY OF ACTIVE LASER MEDIA OF DYES DOPED IN POLYMER MATRICES

V.N. Serova, A.A. Vasil'ev, O.A. Cherkasova, N.A. Mukmeneva, and V.P. Arkhireev

Chemical Technological Institute, Kazan'

Received December 21, 1992

This paper presents analysis of experimental data on the influence of modifications of a copolymer of the methylmethacrylate (MMA) with methacrylic acid (MAA) on the lasing durability of a rhodamine-6G-based active media of this copolymer. The modifiers used in this study were metal salts of organic and inorganic acids and some elementoorganic (N- and P-containing) compounds. Intermolecular interactions have been investigated in the mixture of MAA+dye (modifier). This study revealed certain regularities of the influence of a dye and a modifier on copolymerization activity of MMA and MAA in the process of their block radical copolymerization. The study allowed a conclusion to be drawn on a strong dependence of lasing durability of active lasing media (ALM) of dye-doped polymers on the influence of the dye and the modifier on the kinetic and resulting parameters of the polymerization and on the intermolecular interactions occurring in the initial mixtures and in the formed polymers.

Investigations aimed at synthesizing active laser media (ALM) of dyes doped in polymer matrices that could show high photochemical resistance still have practical importance. Such media can widen applicability limits of dye lasers. From this point of view an extreme variability of polymer systems because of easy modifications of polymers that can be done physically and/or chemically is of great interest since such modifications enable one to synthesize materials with desired properties.

A possibility of increasing photochemical resistance of the ALM of dyes doped in polymethylmethacrylate by modifying the latter with alcohols and ethers was demonstrated in Refs. 1 and 2.

In this study we have used a copolymer of methylmethacrylate (MMA) with methacrylic acid (MAA), in a composition of 9 to 1 ratio of the monomers, as a polymer matrix. In order to compose active lasing media of dyes doped into this polymer which have a higher photochemical resistance we modified the polymer by adding small amounts of metal salts.

Active laser elements of this copolymer doped by rhodamine-6G (isobutyrate) dye were manufactured in the form of disks 50 mm in diameter and 8 mm thick. Experiments with these active elements were conducted using an LKI-301 laser (without scanning) hardware. Optical pumping of the active elements was performed with laser radiation at the wavelength 532 nm; the second harmonic of Nd:YAG laser radiation. Peak power of pumping pulses was about 3 MW and pulse repetition frequency was 12.5 Hz. Some lasing properties of active elements of rhodamine-6G doped into a copolymer of MMA with MAA, as a reference matrix, and into this copolymer but modified with cerium nitrate, erbium carbonate, and methacrylate of lead are given in Table I.

TABLE I. Some lasing properties of active elements of rhodamine-6G* doped into the reference and modified copolymers of MMA with MAA.

Modifier**	Lasing efficiency, %	Lifetime, pulses
Without modifier	25	1750
Ce(NO ₃) ₃	24	2900
Er ₂ (CO ₃) ₃	24	2600
Pb MAA	25	2250

* Rhodamine 6G concentration is $2 \cdot 10^{-4}$ mole/liter,

** Modifier concentration is 0.5 mass %.

We can see from this table that a modification of the copolymer enabled us to increase the lasing lifetime approximately by 1.7 times, the lifetime being defined as a number of laser pulses emitted from the beginning of lasing till moment when the pulse energy decreases twofold. The lasing efficiency is practically constant during the lifetime.

Our further investigations of this problem have shown that a greater increase of active-elements lifetime by 10 – 13 times, can be achieved by modifying the copolymer of MMA with MAA using some organic compounds like, for example, derivatives of benzylthiocyanide and amines. This is illustrated by the curve in Fig. 1. The curve presents the dependence of the active-element lifetime (N) on the content of 1-N, N-pentamethylene-3-benzylthiourea (PBTU) in the polymer matrix. In this study we also tried as modifiers the Benzon OM and Stafor II, complex aromatic ethers of phenylphosphorus acid known as photo- and thermostabilizer of many polymers,³ but no noticeable stabilization was observed.

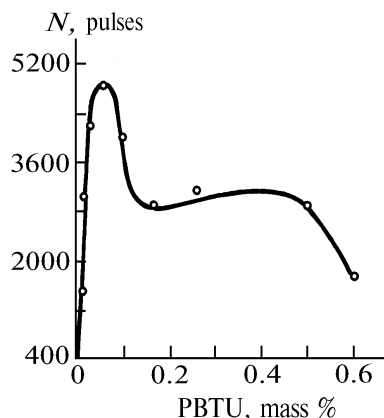


FIG. 1. The dependence of lifetime (N) of active elements of rhodamine 6G (isobutyrate) doped into the copolymer of MMA with MAA on the concentration of PBTU (concentration of the dye is $2 \cdot 10^{-4}$ mole/liter).

Analysis of the experimental data we made did not reveal any correlation between the photochemical resistance of polymer active lasing media and the optical and elastic properties of the polymer matrix. No correlation was also observed between the photochemical resistance and the abilities of N - and P -containing compounds, which are used as modifiers of polymers, to break oxidation chains due to interactions with free radicals and to decompose hydrogen peroxides without formation of radicals. At the same time we observed good correlation between the photochemical resistance of a dye doped into a polymer matrix and the photochemical resistance of the polymer matrix itself.

Thus, in Fig. 2 one can see the kinetics of photochemical bleaching of rhodamine 6G doped into a modified and the reference (nonmodified) polymer matrices in the course of their irradiation by UV light from a PRK-2 mercury-vapor lamp as well as of the viscosity of these copolymer solutions. Incidentally, the rate of the viscosity decrease seen in this figure is indicative of the number of polymeric chains broken down by light. As can be seen from these data the dye showed higher photochemical resistance in a modified (with higher photochemical resistance) polymer which is characterized by smaller number of broken macrochains.

In our study it was also found that compounds, which make an increase of photochemical resistance, contain the groups that can produce not only van der

Waals bonds but also the hydrogen and other types of intermolecular bonds.

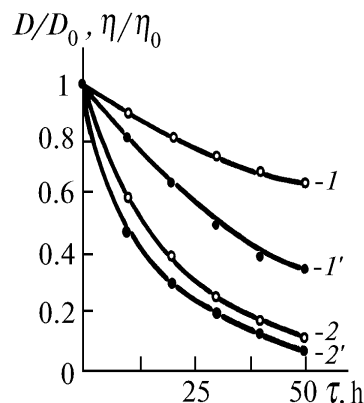
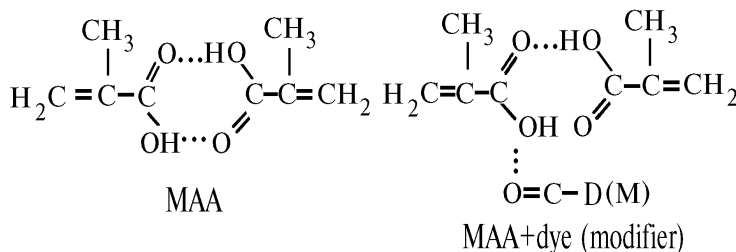


FIG. 2. Temporal behaviors of the optical depth of Rhodamine 6G and of the viscosity of a solution in a modified (curves 1 and 1') and reference (curves 2 and 2') copolymer of MMA with MAA. Concentration of the dye was $2 \cdot 10^{-4}$ mole/liter. The modifier used was PBTU (0.05 mass %), the solvent was dimethylformamide.

In this connection it was interesting to study intermolecular interactions in a complex system of a polymer, dye, and modifier. It seemed to be expedient to start this study with monomeric mixtures and, particularly, with the system of MAA + dye, since the activation by a dye, as well as a modification of a copolymer occurs during the process of its synthesis as a result of dissolution of a dye or a modifier in the initial monomers, as a rule in MAA, because their solubility in MMA is much poorer.

According to data on chemically induced shifts of spectra of paramagnetic resonance absorption of MAA (see Fig. 3) taking place when rhodamine 6G is dissolved in it the resonance signals from protons of a COOH group of MAA undergo shifts toward strong fields (diamagnetic shift). This, evidently, leads to destruction of a portion of cyclic dimers of the acid, in which form it always exists in the bulk of compound, followed by the appearance of hydrogen bonds between the proton of the COOH group of MAA and oxygen atom of a $C=O$ group of a dye. As follows from investigations, a modifier, when dissolved in MAA together with a dye, competes with the latter in creating hydrogen bonds, or bonds of different (for example, donor-acceptor) types, with the MAA molecules, see the scheme below.



Calculations of copolymerization constants of MMA and MAA made using Kelvin-Tyudosh method⁴ showed that the copolymerization activity of MAA decreases in the process of its block radical copolymerization with MMA what results in a decrease of copolymerization constant (r_2) of MAA with the growth of dye concentration in the initial mixture. At the same time the copolymerization constant

(r_1) of MMA shows no dependence on the dye concentration (see Fig. 4). This fact shows that the interaction of rhodamine 6G with MAA is stronger than that with MMA. We have also revealed from this study that many of the modifiers used showed the same effects on the copolymerization constants of monomers. This means that the number of blocks of acid in the dye-doped copolymer

increases with the growth of dye concentration while, at the same time, the number of alternating comonomer chains increases with the increase of a dye or a modifier concentration in the initial monomer mixtures.

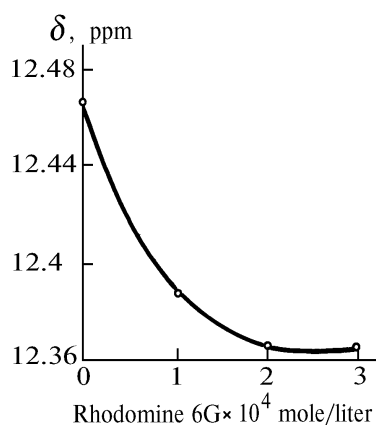


FIG. 3. Effect of rhodamine 6G on the resonance signals from protons of a COOH group of MAA.

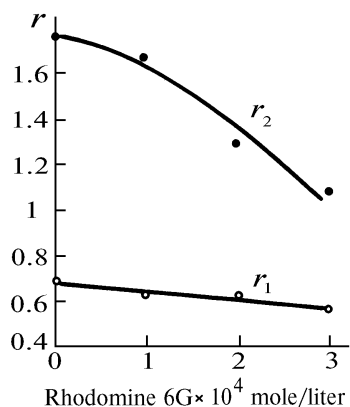


FIG. 4. Influence of rhodamine 6G dye in the copolymerization constants of MMA (r_1) and MAA (r_2).

In this connection the effect of increase of photochemical resistance of rhodamine 6G in copolymer of MMA with MAA observed with increasing content of MAA in it, or the so-called cage effect, could be related to enhanced intermolecular interaction activity both due to an increase of the number of H -type bonds and due to more regular microstructure of copolymer, since this favors intermolecular interactions. Such a cage-type interaction occurs already in monomer compositions which then keeps in the copolymer being formed.

From this point of view the observed enhancement of the photochemical resistance of rhodamine 6G dye in the copolymer of MMA with MAA modified by the above-mentioned compounds and, as a result, the increase of the lasing durability of active elements of this dye-doped copolymer can be explained not only by a stabilizing effect of modifiers on the copolymer and the dye, but also by a favorable influence of a dye and a modifier on the composition homogeneity and microstructure of the copolymer including its spatial regularity. All this makes a favorable conditions for intermolecular interactions and for formation of a more regular (defectless) supermolecular structure of a copolymer.

In conclusion it can be stated that the lifetime of active lasing elements of dye-doped polymers strongly depends on the influence of the dye and the modifier on the kinetic and final parameters of the polymerization including intermolecular interactions in the initial monomer mixtures and the polymers being formed.

REFERENCES

1. K.M. Dyumaev, A.A. Manenkov, A.P. Maslyukov, et al., *Izv. Akad. Nauk SSSR, Fiz.* **51**, No. 8, 1387–1398 (1987).
2. K.M. Dyumaev, A.P. Maslyukov, G.A. Matyushin, et al., *Dokl. Akad. Nauk SSSR* **314**, No. 5, 1154–1157 (1990).
3. I.P. Maslova, ed., *Handbook: Chemical Admixtures to Polymers* (Khimiya, Moscow, 1981), 264 pp.
4. E.P. Zil'berman and R.A. Navolokina, *Book of Problems of the Chemistry of High Molecular Compounds* (Vyshaya Shkola, Moscow, 1984).
5. F. Higuchi and J. Muto, *Phys. Lett.* **86A**, No. 1, 51–53 (1981).