ROLE OF A POLYMER MATRIX CHEMICAL STRUCTURE IN FORMING THE STRENGTH OF A LASER DYE DOPED INTO IT TO EXTERNAL FACTORS

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In this paper we present an investigation into the influence that the chemical structure of a polymer matrix and conditions of its synthesis may exhibit on the durability of a dye being doped in it to aging under the atmospheric, radiation, and other external factors. As a result of this study we have determined an optimal composition of the matrix and identified optimal conditions for its synthesizing. Thus we have found that Rhodamine dyes have better durability in copolymers of fluoroamylmethacrylate than in the copolymers of methylmethacrylate with methacrylic acid.

Insufficient durability of dyes under the action of external factors is still being a serious obstacle preventing a wide use of polymer lasing media (PLM) because of their short lifetime.[1] In this connection it seems to be an urgent task to seek such polymer matrices that would provide for high emission parameters of PLM along with good performance characteristics.

In our earlier work[2] we have shown the prospects of using, as a PLM, some copolymers of the 1,1,3-trihydroperfluoropropylmethacrylate (FA) doped with the lasing organic dyes as Rhodamine C (RC), Rhodamine 6G (R6G), and Rhodamine 4C (R4C).

The primary goal of this paper was to study how the chemical structure of a fluoroacrylate polymer matrix and, in particular, the nature of the second comonomer and conditions of the PLM synthesizing influence the photo-durability of a doping dye, as well as its durability under the action of the atmospheric, radiation and other external factors that may cause the dye aging.

The samples for experiments have been produced by the method of block radical copolymerization of the FA, when using the azodinitrile of the isooleic acid (ADN) as the initiator. The dyes were introduced into the samples during the synthesis stage by dissolving a dye in the initial monomer mixture, the dye concentration being 1.5 to $2.4 \cdot 10^{-4}$ mole/liter. In so doing we have manufactured the copolymers of FA with butylacrylate (BA), with the methacrylic acid (MAA), and with the triallilisocyanturate (TAIC) all being pigmented with Rhodamine dyes. The mass ratio in the FA–MAA and FA–BA mixtures was 95:5, while being 98:2 in the FA–TAIC mixture. Besides, we have synthesized and studied the thermoplastics from the FA–BA–MAA mixture with different proportions among the initial monomers.

To record the absorption spectra of the dyes in polymer matrices (PM), we used an SF–46 spectrophotometer. To study the dye durability in PM under the UV irradiation, we have exposed the samples to full spectrum of the emission from a DRSH–1000 mercury lamp. To measure the durability under radioactive treatment, we used an MRKH–γ–20 installation that is equipped with a ^{60}Co-based source of γ rays (State Standard 9.711–85). Samples have been irradiated by different doses of γ-radiation, from 10^6 to 10^8 R. The aging of samples under atmospheric conditions has been hastened in a climatic chamber at a temperature of 50°C and relative humidity of 80% (State Standard 11279–2–83) when irradiated by emission from a DKSTV–6000 xenon lamp. To estimate the heat and frost durability of samples, they passed a test in a special chamber at a temperature of +50°C during 35 hours and then during ten days at −50°C. The stability criterion for the optical properties of the dyes used is the ratio D/D_0 of optical thickness measured at the absorption band maximum in the end of a test, D, to that before the test, D_0.

The lasing properties of the dyes have been measured using an optical arrangement with a quasi-longitudinal pumping by a 35-ns-duration pulse of the second-harmonic radiation of a $\mathrm{Nd^{3+}}$:YAG laser (LTIPCH–5) at 532 nm wavelength. The energy density of the pump radiation used in the experiments was 0.2 to 2.5 J/cm^2. The lasing photostability has been estimated by the number of pump pulses delivered by the moment when the lasing efficiency halved.

Figure 1 presents the kinetics curves of the R6G bleaching in the PMs of different composition, including that of the copolymer of methylmethacrylate (MMA) with MAA in 90:10 proportion, the latter composition being used as a reference one. As seen from Fig. 1 the dye is most durable in the FA–TAIC copolymer, that well agrees with data from Ref. 2 where its enhanced stability, in this particular matrix, under irradiation with a cw-laser radiation was noted.

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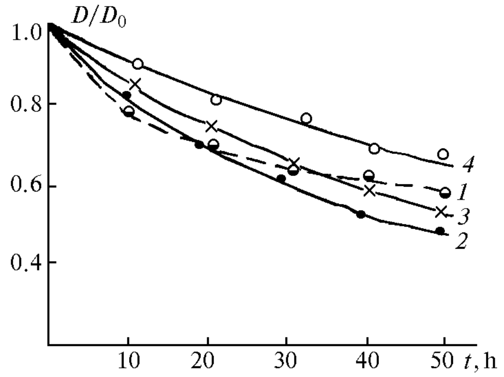

FIG. 1. Kinetics of the light-induced bleaching of Rhodamine 6G in different copolymers: MMA–MAA (1), FA–BA (2), FA–MAA (3), and FA–TAIC (4).

Analysis of the kinetic curves obtained showed that in this copolymer the bleaching kinetics of this dye may be described by a first-order equation. In the other matrices studied behavior of the bleaching process is not exponential and can be considered as a sum of kinetic processes with different rate constants. Since no direct correlation has been revealed between the photostability of the matrix and of the dye admixed the dye interaction with the macromolecules of the environment should be considered as the main factor determining the durability of the dye.

We have also found in the experiments that along with the decrease of the sample optical density within the absorption band maximum there is observed an enhancement of the absorption in the region from 280 to 420 nm (see Fig. 2) that may occur due to absorption by the photo-product produced. Most likely, the photo-product is the half-reduced form of the dye.[3]

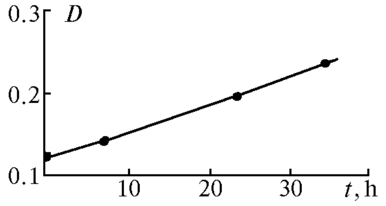

FIG. 2. Optical density of the FA–BA copolymer with the Rhodamine C dye at 400 nm *wavelength as a function of the UV-irradiation time.*

It seems to be of certain interest to study the effect that may produce the conditions of synthesizing on the photostability of a dye in a PLM, thus enabling determination of optimal conditions for the PLM manufacturing. Figure 3 presents some results of investigations into the light-induced destruction of Rhodamine C in the FA–BA–MAA (91:7:2) copolymer.

It is seen from this figure that the dye is most durable in the copolymer synthesized at 45°C polymerization temperature and 90°C temperature of final polymerization performed in the presence of ADN initiator added in the proportion of 0.1% by mass. At the same time an increase in the initiator concentration, up to 0.25% by mass, as well as the increase of the polymerization temperature, up to 65°C, leads to a fall off of the dye photostability.

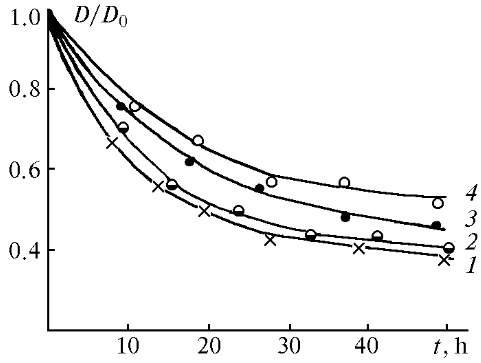

FIG. 3. Influence of the copolymerization conditions on the kinetics of light-induced bleaching of Rhodamine C in the FA–BA–MAA (91:7:2) *copolymer. Curve 1 presents the case with ADN content of* 0.25% *by mass,* $T_p = 45°C$, $T_{fp} = 80°C$; *curves 2, 3, and 4 correspond to ADN content of* 0.10% *by mass for* $T_p = 65°C$, $T_{fp} = 80°C$; $T_p = 55°C$, $T_{fp} = 80°C$; *and* $T_p = 45°C$, $T_{fp} = 90°C$.

This effect may be explained by the fact that an increase in temperature and in the amount of an initiator leads, during the reaction, to formation of shorter chains, that is to larger number of unsaturated end groups. The latter ones are less stable and yield larger amount of free radicals at a UV irradiation, which then destroy the dye molecules. At the same time, if the polymerization and final polymerization processes are complete, a smaller number of unsaturated end groups are formed and the smaller amount of residual monomer remains, what favors the dye photostability.

Some results of our investigation into the radiation stability of Rhodamine C and Rhodamine 6G dye in different copolymers are given in Table I.

It is seen from this Table that certain correlation exists between the radiation stability of a dye and that of the corresponding polyfluoroacrylate matrix, as noted earlier.[4]

Other performance characteristics of the PLM, as well as the atmospheric, heat, and frost stability of the dyes doped into the matrices from copolymers of FA and MMA are given in Table II.

As is well seen from Table II the atmospheric factors cause an essential destruction of the dyes that depend on the matrix chemical composition and purity of the initial monomer. The highest stability regarding the atmospheric factors Rhodamines 6G and C exhibit being in the copolymer FA–BA–MAA (91:7:2), provided that the initial monomers are chemically pure, that means the rectifying using an MFCN2 membrane.

TABLE I. Radiation stability of Rhodamine C and Rhodamine 6G dye in different copolymers.

Composition of the copolymer matrix	D/D_0 at a radiation dose, R					
	Rhodamine 6G			Rhodamine C		
	10^6	$6\cdot10^6$	$17\cdot10^6$	10^6	$6\cdot10^6$	$17\cdot10^6$
FA–MAA (95:5)	0.97	0.93	0.86	–	0.74	0.56
FA–TAIC (98:2)	0.92	0.89	0.78	–	–	–
FA–BA–MAA (96:3:1)	–	–	–	1.00	0.96	0.89
FA–BA–MAA (93:5:2)	–	–	–	0.97	0.87	0.79
FA–BA–MAA (91:7:2)	0.91	0.90	0.89	1.00	0.98	0.96
MMA–MAA (90:10)	0.74	0.63	0.58	0.96	0.90	0.77

TABLE II. The atmospheric, heat, and frost stability of Rhodamine 6G and Rhodamine C in the copolymers.

Composition of the copolymer matrix	D/D_0					
	Rhodamine C			Rhodamine 6G		
	DKSTV–6000	$T = 50°C$	$T = -50°C$	DKSTV–6000	$T = 50°C$	$T = -50°C$
FA–BA (95:5)	0.33	1.00	1.00	–	0.85	–
FA–MAA (95:5)	0.26	0.95	–	0.18	–	1.00
FA–BA–MAA (96:3:1)	0.13	0.90	1.00	–	–	–
FA–BA–MAA (93:5:2)	0.23	0.83	0.96	–	–	–
FA–BA–MAA (91:7:2)	0.30	0.91	1.00	0.34	–	–
MMA–MAA (90:10)	0.18	0.87	0.91	0.19	0.80	0.85

Investigation of the dyes' heat and frost stability (+50 and −50°C) has shown that in the copolymers of FA it is good enough, being higher than that in the copolymer of MMA with MAA in the majority of cases.

In these experiments we have also studied the dependence of lasing efficiency of the PLMs on the energy density of pump radiation. The data of these experiments are presented in Fig. 4. As seen from this figure there is observed maximum in the above mentioned dependence for all the dyes studied. After reaching a maximum value, the efficiency then falls off with increasing W/S ratio.

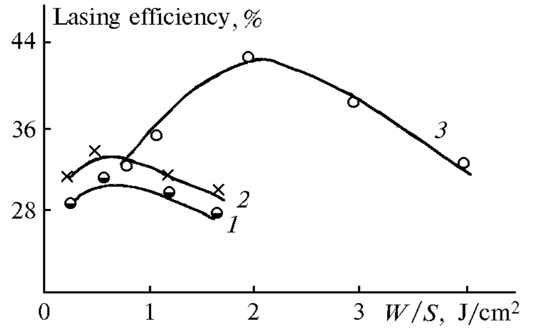

FIG. 4. The lasing efficiency of the PLMs from FA–BA copolymer with Rhodamines as a function of the pump energy density. Curve 1 is for Rhodamine C, curve 2 is for Rhodamine 6G, curve 3 is for Rhodamine 4C. The concentration of the dyes was $1.8\cdot10^{-4}$mole/liter.

It is likely that the lasing efficiency fall off observed occurs due to nonlinear scattering of radiation outside the direction of pump beam propagation as well as because of photochemical processes taking place in the active medium.[5] In this case the highest durability exhibits the R4C dye that starts to decompose only at $W/S = 2$ J/cm^2, while the Rhodamines C and 6G are being destroyed already at $W/S = 0.5$ J/cm^2. This circumstance is also confirmed by the results on the FA copolymer–based PLMs lifetime studied. In this study we experimented with the PLMs of FA–BA copolymer dyes with Rhodamines. The study conducted has shown that Rhodamine 4C endures up to 23000 pulses amounting 7.5 MJ total energy, Rhodamine C – 13500 pulses of 7MJ total energy and Rhodamine 6G – 3800 pulses of only 2 MJ total energy.

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