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Photoactivation of fluorescence of rhodamine dyes in the presence of haloalkanes

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Organic halogen derivatives, *viz.*, hexachloroethane, 2,2,2-trichloroethanol, 2,2,2-tribromoethanol, butyl trichloroacetate, 2,2,2-trichloroethyl methacrylate, can efficiently activate fluorescence of lactone forms of rhodamine dyes by UV irradiation through the UFS-1 light filter in both solutions and polymer poly(methyl methacrylate) films. This ability is also typical of the copolymer of methyl methacrylate and 2,2,2-trichloroethyl methacrylate, which is promising for the development of detecting media for archive optical data storage with fluorescent readout.

Key words: rhodamines, halogen derivatives, fluorescence, photochemical activation, date storage.

Fast development of computer and information technologies form demands in more highly productive systems capable of recording, storage, and reproduction of huge information volumes.[1—7] One of the most promising approaches to an increase in the volume of detected information on optical carriers is its recording on multilayer optical disks using the two-photon transformation of organic substances by laser irradiation with fluorescent readout.[8] This method provides basically new possibilities of information detection compared to the modern optical accumulators based on recording on one or two surfaces of an optical disk.

Single information recording and possibility of its multiple readout are performed on optical disks for archive information storage. Information is recorded due to irreversible photochemical transformations of non-fluorescent precursors (initial organic substrates) into compounds with intense fluorescence (the reversible process of fluorescence decay is possible in the course of the photochemical reaction). These phototransformations should be characterized by a high quantum yield, the photoproduct has a high fluorescence quantum yield. In addition, both the precursor and photoproduct should have a high thermal stability.[9,10]

Photosensitive derivatives of coumarins, lactones, and lactams of xanthene dyes of the rhodamine series are used, in particular, as fluorescent precursors[11—15] for archive information recording with fluorescent readout.[11,16—19] As a rule, the precursor is irradiated in the presence of a photoacid, or acid photogenerator (APG), whose role is the conversion of the precursor molecule to the fluorescing product due to the elimination of the protecting group[20,21] or opening of the lactone/lactam ring of the leucobase.[17,22,23] When working with fluorescent precursors, the deactivation of their fluorescence or shift of the emission maximum to a longer-wavelength region is attained by the protonation at their amino groups.[14,20]

The typical acid photogenerators proposed for use in detecting media for archive information recording are triarylsulfonium and triaryliodonium salts of some organic and inorganic acids,[20,24,25] sulfonic acid derivatives,[26,27] nitrobenzaldehydes and nitronaphthaldehydes.[22,23] Some halogen derivatives, in particular, carbon tetrabromide[28—32] and 2,2,2-tribromoethanol,[30—32] which was applied, for example, to fix the open form of spiropyrans, were proposed as fluorescence activators. Chlorine-substituted derivatives of alkanes have certain prospects as APGs. For instance, it has previously been shown that a CCl_4 molecule can act as an electron acceptor. Accepting an electron, this molecule gives an unstable radical anion, which very rapidly decomposes to eject the chloride ion and to form the trichloromethyl radical capable of further abstracting the hydrogen atom from the corresponding substrate; in turn, the chloride ion can act as a proton acceptor.[32,33] Examples for the photodehydrogenation of dihydropyridine and pyrazoline derivatives upon the irradiation of their solutions in CCl_4 should be mentioned.[34,35]

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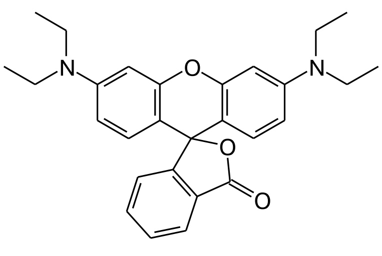
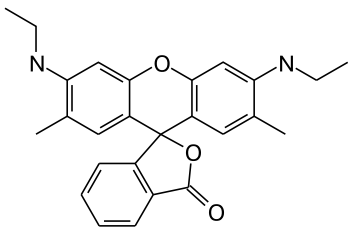
In this work, a series of organic halogen derivatives, namely, hexachloroethane (C_2Cl_6), 2,2,2-trichloroethanol (CCl_3CH_2OH), 2,2,2-tribromoethanol (CBr_3CH_2OH), butyl trichloroacetate (CCl_3COOBu), 2-chloroethanol (CH_2ClCH_2OH), 2-bromoethanol (CH_2BrCH_2OH), and 2,2,2-trichloroethyl methacrylate ($CH_2=C(Me)-COOCH_2CCl_3$), was studied as fluorescence activators of one of the most promising groups of precursors.

In addition, copolymer of 2,2,2-trichloroethyl methacrylate with methyl methacrylate (1 : 20) was synthesized, and the photoactivation of the fluorescent forms of two rhodamine dyes in the obtained copolymer was studied. Lactone forms of Rhodamine B and Rhodamine 19 were examined as precursors. In all measurements, the polymer films were irradiated through the UFS-1 light filter.



Rhodamine B



Rhodamine 19

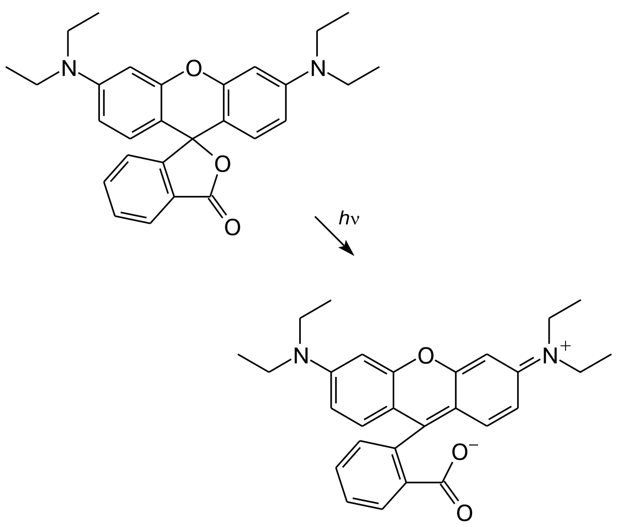
Poly(methyl methacrylate) (PMMA) was used as a polymer binding.

Results and Discussion

Lactone forms of rhodamine dyes can transform into the colored fluorescing state under UV-irradiation in the absence of any photoactivators as well (Scheme 1). As follows from Fig. 1, under UV-irradiation in the PMMA film, the lactone cycle of Rhodamine 19 is opened to form the colored fluorescent form. However, when lactone of the rhodamine dye in the polymer film is directly irradiated, the colored fluorescent form of the dye is formed and also the dye partially decomposes, which is indicated by a significant increase in the absorbance in the 400—450 nm range of the absorption spectra.

The introduction of compounds with trihalomethyl fragments into the composition of the polymer films containing lactones of Rhodamine B and Rhodamine 19 favors an efficient photoactivation of the colored fluorescent form, and this process is not accompanied by the photodecomposition of the dye formed. The spectra of the colored fluorescent forms of rhodamine dyes formed during photoactivation are identical to the spectra of these dyes in solutions. The absorption and fluorescence spectra of the PMMA films containing Rhodamine B in the presence of trichloroethanol are shown as an example in Fig. 2. It is seen that the photogeneration of the colored form of the precursor is not accompanied, under these conditions, by noticeable dye decomposition. The results of spectral measurements for the irradiation of the PMMA films containing lactones of Rhodamine B or Rhodamine 19 in the presence of various halogen derivatives are given in Table 1.

Scheme 1



We also studied butyl trichloroacetate as a photoactivator of fluorescence of rhodamine dyes, which can simultaneously act as a plasticizer of the polymer film. The irradiation of the PMMA film containing butyl

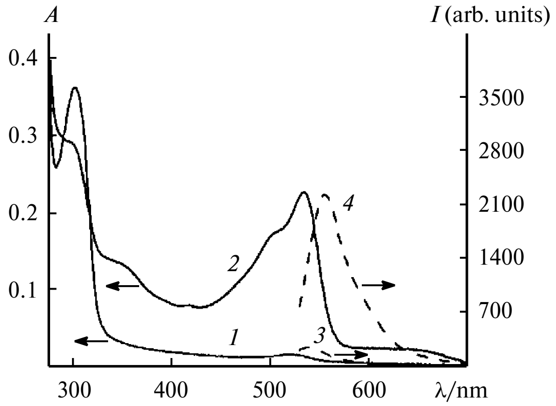


Fig. 1. Absorption (*1*, *2*) and fluorescence (*3*, *4*) spectra of the PMMA film containing lactone of Rhodamine 19 before (*1*, *3*) and after (*2*, *4*) irradiation through the UFS-1 light filter.

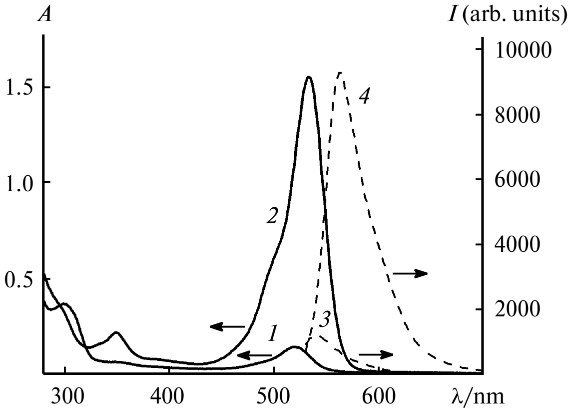


Fig. 2. Absorption (*1*, *2*) and emission (*3*, *4*) spectra of the PMMA film containing Rhodamine B and trichloroethanol before (*1*, *3*) and after (*2*, *4*) irradiation through the UFS-1 light filter.

trichloroacetate and Rhodamine B lactone results in the formation of the colored fluorescent form of Rhodamine B (Fig. 3) without noticeable properties (according to the electronic absorption spectra) of dye photodestruction. Similar results were obtained for the PMMA films containing Rhodamine 19 and butyl trichloroacetate.

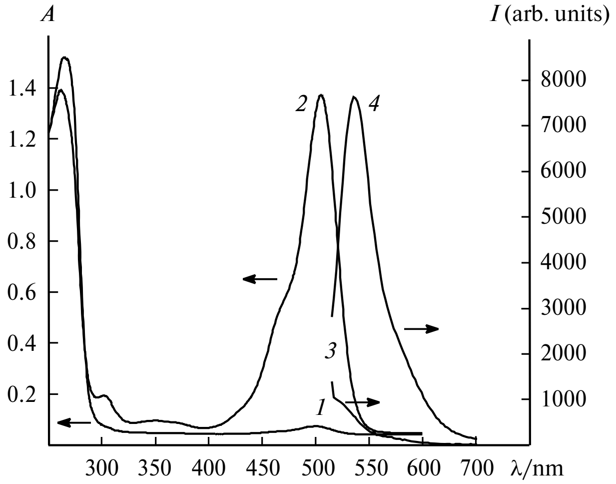


Fig. 3. Absorption (*1*, *2*) and emission (*3*, *4*) spectra of the PMMA film containing Rhodamine B and butyl trichloroacetate before (*1*, *3*) and after (*2*, *4*) irradiation through the UFS-1 light filter.

The PMMA films containing lactones of rhodamine dyes were also irradiated in the presence of ethylene chlorohydrin and ethylene bromohydrin. However, the irradiation of the corresponding samples resulted only in a weak colora-

Table 1. Compositions of the studied PMMA films and the spectral results of their irradiation

Sample	Composition	C /mmol L^{-1}	λ_{max}^{abs} /nm	ΔD^{ph}	λ_{max}^{fl} /nm	I_0	I_{act}
						arb. units	
1	Rhodamime 19	5.0	532	0.2	560	100	2220
2	Rhodamine B	6.0	560	0.3	587	80	2500
3	Rhodamine B + + hexachloroethane	5.8 130	560	1.0	587	90	5840
4	Rhodamime 19 + + hexachloroethane	1.1 180	532	0.7	563	150	6880
5	Rhodamine B + + ethylene bromohydrin	8.5 52	560	0.3	585	530	1203
6	Rhodamime 19 + + ethylene bromohydrin	2.4 620	532	0,2	560	500	1018
7	Rhodamine B + + 2,2,2-trichloroethanol	8.5 52	560	1.1	584	570	5910
8	Rhodamime 19 + + 2,2,2-trichloroethanol	2.1 52	532	0.4	562	550	4910
9	Rhodamine B + + 2,2,2-tribromoethanol	1.1 130	560	2.5	585	530	7723
10	Rhodamime 19 + + 2,2,2-tribromoethanol	1.8 180	532	1.4	563	510	9280
11	Rhodamine B + + butyl trichloroacetate	8.4 50	560	1.9	586	110	7500
12	Rhodamime 19 + + butyl trichloroacetate	8.4 52	532	1.2	560	120	5520

Note. C is concentration; λ_{max}^{abs} and λ_{max}^{fl} are the wavelengths of maximum of photoinduced absorption and fluorescence bands, respectively; ΔD^{ph} is the maximum photoinduced change in the absorbance at the absorption band maximum of the dye; I_0 and I_{act} are the fluorescence intensity at the fluorescence band maximum before and after activating irradiation in the state of photoequilibrium, respectively.

tion of the film with a low fluorescence intensity (see Table 1), which can be related to the lactone ring opening in the rhodamine dye directly under the action of UV radiation involving no halogen-containing alcohol. This is indicated, in particular, by the increase in the absorption at 400—450 nm of the electronic absorption spectrum, as in the case of sample **1** containing no halogen derivative.

Several schemes were proposed in literature to explain the activating influence of organic halogen derivatives on the photoinduced fluorescence of the precursors. In particular, the following routes of photoactivation of fluorescence of triarylmethane dyes in the presence of carbon tetrabromide are discussed[30,31]:

— reaction of the tribromomethyl radical formed upon irradiation with aromatic amine followed by the condensation of the intermediate under the action of irradiation to the triarylmethane dye;

— generation of atomic bromine followed by the formation of hydrogen bromide that converts the leucobase to the colored form;

— generation of atomic bromine acting as an oxidant of the leucobase to the colored form.

To confirm the ability of the studied halogen derivatives to act as acid photogenerators in polymer films, we prepared and irradiated through the UFS-1 light filter the PMMA films containing hexachloroethane, tribromoethanol, or trichloroethanol in the presence of the acid—base indicator Methyl Red. The change in the electronic absorption spectrum of this indicator in the film under UV irradiation in the presence of tribromoethanol is shown in Fig. 4. The initial spectrum of the indicator in the films indicates the presence of two forms: neutral (absorption band with a maximum at 410 nm) and protonated (shoulder at 490 nm). The films containing hexachloroethane, tribromoethanol, or trichloroethanol in the presence of the indicator during irradiation exhibit a decrease in the intensity of the short-wavelength absorption band of the indicator with a simultaneous increase in the long-wavelength band at 490 nm corresponding to its protonated form, indicating that the acid is accumulated in the film.

Thus, the introduction of compounds bearing trihalomethyl fragments into the composition of the polymer films containing Rhodamine B or Rhodamine 19 lactone favors the efficient photoactivation of their colored fluorescent forms, most probably, due to opening of their lactone fragments by the photogenerated acid.

The data presented in Table 1 indicate the high efficiency of trichloroethanol and tribromoethanol as acid photogenerators in the systems containing lactones of rhodamine dyes. However, free hydroxy groups in these alcohols can impede their practical use because of potentially possible lactone ring opening in the dye already in the course of film preparation. This process can increase the background color of the initial film and decrease contrast of the fluorescent centers formed.

This disadvantage of trihaloethanols can evidently be overcome by the esterification of the free hydroxy group of alcohols. In addition, the introduction of the group capable of polymerization during esterification provides the possibility to obtain a polymer containing trihalomethyl groups in its structure. The migration of the acid photogenerator in the polymer material bulk is excluded in this polymer, which should unambiguously enhance its quality when applied in devices of information recording. The transesterification of methyl methacrylate (MMA) with 2,2,2-trichloroethanol gave 2,2,2-trichloroethyl methacrylate (TCEMA), which exhibited the properties of photoacid. The combined radical polymerization of MMA and TCEMA produces their copolymer with the ratio of monomer units 20 : 1. As assumed, in films of the obtained copolymer, the photogeneration of the fluorescent form of the rhodamine dye requires no additional monomeric halogen derivative (Fig. 5, Table 2).[36]

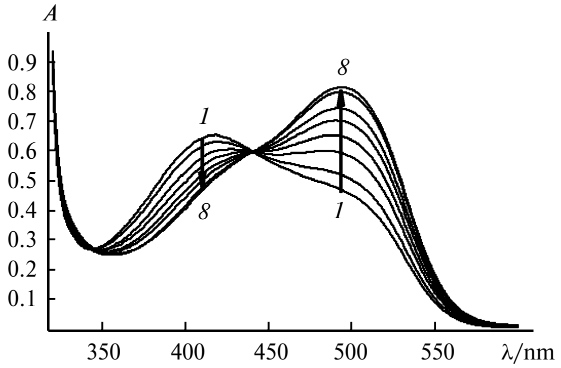


Fig. 4. Absorption spectra of the PMMA film containing tribromoethanol and acid—base indicator Methyl Red before (*1*) and after (*2—8*) irradiation through the UFS-1 light filter.

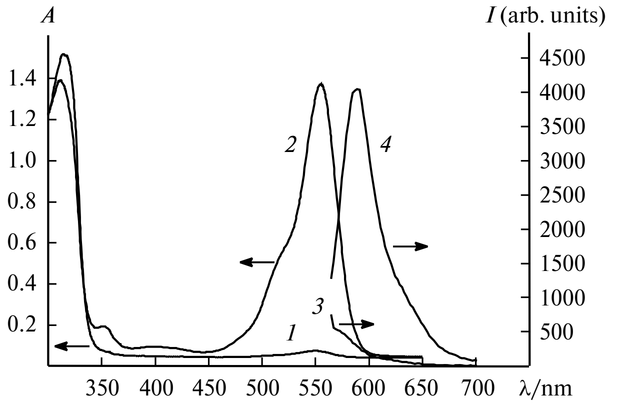


Fig. 5. Absorption spectra of the film of the copolymer of TCEMA (*1*, *2*) and MMA (*3*, *4*) containing Rhodamine B before (*1*, *3*) and after (*2*, *4*) irradiation through the UFS-1 light filter.

Comparing the data presented in Tables 1 and 2, we may assert that the use of copolymers acting simultaneous-

Table 2. Composition of the studied polymer films based on TCEMA and the spectral results of their irradiation

Sample	Film composition	C /mmol L^{-1}	$\lambda_{max}{}^{abs}$ /nm	ΔD^{ph}	$\lambda_{max}{}^{fl}$ /nm	I_0	I_{act}
						arb. units	
13	Rhodamine B + copolymer TCEMA with MMA (1 : 20)	1.1 475	560	0.7	585	100	4100
14	Rhodamine 19 + copolymer TCEMA with MMA (1 : 20)	2.0 475	532	0.5	562	110	3020

ly as polymer bindings and acid photogenerators provides high spectral characteristics required for their successful work as media for archive information recording.[36]

Thus, it was shown that a series of halogen derivatives, *viz*., hexachloroethane, 2,2,2-trichloroethanol, 2,2,2-tribromoethanol, butyl trichloroacetate, and 2,2,2-trichloroethyl methacrylate, are capable of efficient activating the fluorescence of lactone forms of rhodamine dyes upon UV irradiation through the UFS-1 light filter in both solutions and polymer PMMA films. The copolymer of MMA and TCEMA also manifests this ability, which is promising for the development of detecting media in archive recording of optical information with fluorescent readout.

Experimental

Spectrophotometric measurements (photostationary spectra) and investigation of the kinetics of photocoloration of the photoinduced form of the studied compounds in the polymer were carried out using a Cary 50 bio spectrophotometer (Varian). The spectra and kinetics of changes in fluorescence were measured using a Cary Eclipse spectrofluorimeter (Varian).

Irradiation was conducted with the filtered light from an LC-4 lamp (Hamamatsu). The UFS-1 light filter was used for photocoloration. The fluorescence intensity was measured upon excitation with the visible light through the ZhS-10 light filter, *i.e.*, at the absorption band of the photoproduct (the formed dye).

Ethylene chlorohydrin, ethylene bromohydrin, hexachloroethane, 2,2,2-trichloroethanol (TCE), and 2,2,2-tribromoethanol (TBE) (all Aldrich) and butyl trichloroacetate were used as organic halogen derivatives.

Butyl trichloroacetate. A mixture of trichloroacetic acid (13.5 g), concentrated sulfuric acid (2 mL), and butyl alcohol (55 mL) was refluxed for 4—4.5 h. Then the flask was cooled to ~20 °C, water (40 mL) was added to the content of the flask, and butyl trichloroacetate was extracted with diethyl ether. The ethereal extracts were washed with a 10% solution of sodium carbonate and dried with anhydrous magnesium sulfate, and diethyl ether was distilled off. This final product was purified by distillation. B.p. 202—203 °C (*cf*. Ref. 37: b.p. 204 °C). The yield was 13.8 g (76%). ^{1}H NMR (DMSO-d$_6$), δ: 0.97 (t, 3 H, Me, J = 6.3 Hz); 1.46, 1.74 (both m, 2 H each, CH$_2$); 4.38 (t, 2 H, OCH$_2$, J = 7.8 Hz).

2,2,2-Trichloroethyl methacrylate. A mixture of methyl methacrylate (75.1 g, 0.75 mol), 2,2,2-trichloroethanol (89.0 g, 0.60 mol), hydroquinone (2.5 g), and *p*-toluenesulfonic acid (0.75 g) was placed in a two-necked flask with a connected glass rectification column. The solution was heated to boiling in an oil bath until the temperature of the upper part of the column reached 63—64 °C corresponding to the boiling point of a methanol—MMA azeotropic mixture. As the azeotrope was formed, it was distilled off. After methanol stopped to form (~8 h), unreacted MMA was removed. 2,2,2-Trichloroethyl methacrylate was purified by distillation, b.p. 85 °C (10 Torr) (*cf*. Ref. 38: b.p. 48 °C (1.5 Torr)). ^{1}H NMR (CDCl$_3$), δ: 1.95 (s, 3 H, Me); 4.74 (s, 2 H, COCH$_2$); 5.67, 7.23 (both m, 1 H each, =CH$_2$).

Copolymer of MMA and 2,2,2-trichloroethyl methacrylate. A mixture containing MMA (5 mL), 2,2,2-trichloroethyl methacrylate (0.3 mL) *n*-dodecylmercaptane (60 μL), and azobisisobutyric acid dinitrile (5 mg) was placed in a glass ampule. Oxygen was removed by freezing—defreezing, and the ampule was sealed off. Polymerization was conducted in the temperature range 50—70 °C for 24 h and then at 110—115 °C for 2 h. After cooling, the ampule was broken and solid copolymer was taken out. The copolymer was dried by triple reprecipitation from ethyl acetate to ethanol. The copolymer was dried to a constant weight *in vacuo* ($5\cdot10^{-2}$ Torr) at 80 °C. The molecular weight was 93 kDa. The purity of the obtained copolymer was confirmed by ^{1}H NMR. ^{1}H NMR (CDCl$_3$), δ: 0.70—1.15 (m, 3 H, Me); 1.70—2.20 (m, 2 H, CH$_2$); 3.51 (s, 3 H, OMe); 4.53 (s, 0.09 H, CH$_2$CCl$_3$).

Film preparation. The films were prepared by the method of pouring the solution containing PMMA, lactone of rhodamine dye, and halogen derivative in a toluene—ethyl acetate mixture of solvents on a horizontally mounted glass Petri dish followed by solvent removal by drying. Prior to irradiation, the films were taken from the support. The films of the MMA copolymer with 2,2,2-trichloroethyl methacrylate and lactone of Rhodamine B or Rhodamine 19 but containing no monomeric halogen derivatives were prepared similarly. The film thickness was 90—100 μm.

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