Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 74 (2007) 187–194
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Novel polymerizable light emitting dyes – combination of a hindered amine with a 9-phenylxanthene fluorophore. Synthesis and photophysical investigations

Vladimir B. Bojinov [a,*], Ionka P. Panova [a], Ivo K. Grabchev [b]

[a] Department of Organic Synthesis, University of Chemical Technology and Metallurgy, 8 Kl. Ohridsky street, 1756 Sofia, Bulgaria
[b] Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Received 9 December 2005; received in revised form 26 January 2006; accepted 27 January 2006
Available online 29 March 2006

Abstract

The synthesis of new 9-phenylxanthene dyes, containing hindered amine stabilizer fragment is reported. Two polymerizable dyes, a combination of Fluorescein or Eosin with 2,2,6,6-tetramethylpiperidine, as well as two 9-phenylxanthene intermediates were synthesized in good yields under variable reaction conditions. Their light absorption and fluorescence properties in solution have been determined and discussed. Photooxidative stability of the new fluorophores has been studied and compared to other similar fluorescent dyes, not containing hindered amine fragment in their molecules. It was shown that the presence of a HALS (hindered amine light stabilizer) fragment in the dyes' molecules improved their photostability. The ability of the dyes to co-polymerize with vinyl monomers such as methyl methacrylate was demonstrated.

Keywords: Fluorescein; Eosin; 4-Amino-2,2,6,6-tetramethylpiperidine, Polymerizable fluorescent dyes; Phase transfer catalysis; Photostability; Co-polymerization

1. Introduction

The 9-phenylxanthene derivatives due to their good spectral properties have been the most common fluorescent reagents in a number of areas including laser active media [1], potential photosensitive biologically units and fluorescent markers in biology [2], ion probes [3], light emitting diodes, photo-induced electron transfer fluorescent sensors and switchers [4]. Unfortunately, Fluorescein-based dyes have several drawbacks, including a relatively high rate of photobleaching and pH-sensitive fluorescence that is significantly reduced below pH 7. The photobleaching and pH sensitivity of the Fluorescein and its derivatives make quantitative measurements with these fluorophores problematic. Furthermore, Fluorescein's relatively high photobleaching rate limits the sensitivity that can be obtained, a significant disadvantage for applications requiring ultrasensitive detection, such as DNA sequencing, fluorescence in situ hybridization and localization of low-abundance receptors [5]. These limitations have encouraged the development of alternative fluorophores.

Incorporation of dyes in a polymer matrix gives the opportunity for increasing their light-fastness [6]. The introduction of a polymerizable allyl group into the 9-phenylxanthene molecule could provide the dyes' capability of covalent bonding to the polymer chain. During the last years some polymerizable 9-phenylxanthene derivatives have been synthesized and investigated for their ability to co-polymerize with different monomers [7]. The advantage of using polymerizable dyes over conventional dyes is that the dye becomes chemically bonded to the polymer. The dye, therefore, cannot be extracted from the polymer. The solvent-fastness of a polymer colored with a polymerizable dye is, as a consequence, much greater than a polymer colored with conventional dyes [8]. On the other hand, the use of side-chain polymers provides ecologically more tolerant application of these dyes for coloring the foodstuffs and cosmetics.

---

* Corresponding author. Tel.: +359 281 632 06.
E-mail address: vlbojin@uctm.edu (V.B. Bojinov).

0143-7208/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2006.01.034

Photostability of the polymers is one of their most important properties. To solve the problem of polymer stabilization, a number of different stabilizers have been applied successfully [9]. Among them, hindered amines such as 2,2,6,6-tetramethylpiperidine derivatives are of a great interest due to their high photostabilizing efficiency [10]. They inhibit the process of autoxidation by transformation of the parent amines to *N*-oxyl radicals, either by reaction with peroxyl radicals or occasionally by reaction with singlet oxygen, which stop oxidative degradation by the coupling of alkyl radicals [11].

A combination of 2,2,6,6-tetramethylpiperidine stabilizer and unsaturated allyl group through a 9-phenylxanthene unit in one molecule could result in new type of fluorescent dyes with both increased light-fastness and decreased pH fluorescence sensitivity, capable of simultaneous chemically dyeing and photostabilizing the polymer materials.

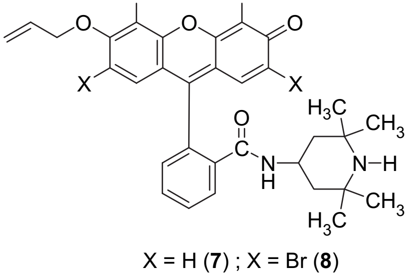
In previous papers we demonstrated the possibility for ‘‘one-step’’ coloration and stabilization of different polymers, where a fluorescent 1,8-naphthalimide or benzanthrone dye and a stabilizer were combined in one molecule [12]. In this paper, the synthesis of new fluorescent 9-phenylxanthenes, containing both an allyl group and a hindered amine fragment, and the ability of the dyes to co-polymerize with methyl methacrylate (MMA) in bulk is reported (Scheme 1). The basic photophysical characteristics and the photostability of the monomeric fluorescent dyes have been studied. Among 9-phenylxanthene derivatives, Fluorescein and Eosin are the most recognized, and for this reason, we used them as model compounds.

2. Results and discussion

The aim of the present study was to synthesize Fluorescein-based fluorescent dyes, containing both a 2,2,6,6-tetramethylpiperidine stabilizer fragment and a polymerizable allyl group, as combined agents for ‘‘one-step’’ chemically dyeing and stabilization of polymers.

2.1. Synthesis of dyes

The synthesis of combined polymerizable hindered amine – 9-phenylxanthene dyes **7** and **8** was carried out in just two steps as outlined in Schemes 2 and 3.



X = H (**7**) ; X = Br (**8**)

Scheme 1.

First, the intermediate dyes 2-(3-hydroxy-6-oxo-6*H*-xanthen-9-yl)-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide **4** and 2-(2,4,5,7-tetrabromo-3-hydroxy-6-oxo-6*H*-xanthen-9-yl)-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide **5** were prepared by condensation of the commercially available 2,2,6,6-tetramethylpiperidine-4-ylamine **3** with Fluorescein **1** or Eosin **2**, respectively. Reactions were conducted in dry chlorobenzene in the presence of aluminum(III) chloride at 100 °C (Scheme 2).

In order to obtain polymerizable fluorescent dyes **7** and **8**, functionalized with polymerizable allyl group, based on our previous experience, the intermediate dyes **4** and **5** were reacted with allylbromide **6** under phase transfer catalysis (PTC) conditions [7a]. By selection of the favorable reaction conditions, in a solid–liquid two-phase system in the presence of 18-crown-6 as a phase transfer catalyst, the desired compounds **7** and **8** were obtained in high yields (Scheme 3).

All of the synthesized compounds were characterized by their melting points and TLC R_f values (Table 1) and identified by elemental analysis data, FT-IR and ^{1}H NMR spectra. Dyes **7** and **8** were additionally characterized by absorption (Table 2) and fluorescence spectra (Table 3).

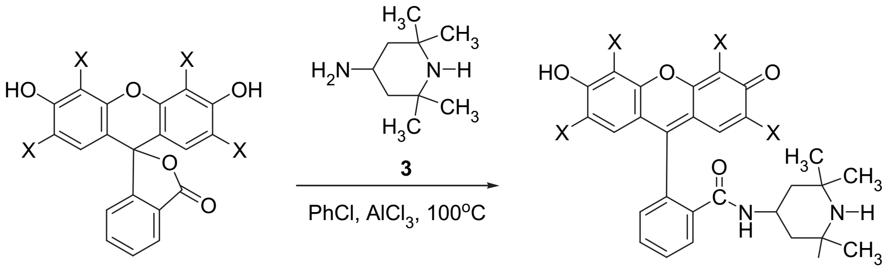
2.2. Photophysical characterization of the dyes

2.2.1. Light absorption properties

The light absorption properties of the dyes under study are basically related to the polarization of the 9-phenylxanthene molecule on irradiation, resulting from the electron donor–acceptor interaction between the substituents at C-3 position and the carbonyl group at C-6 position of the chromophoric system, and may be influenced by the environmental effect of the media upon this interaction. Absorption spectra of the dyes **7** and **8** were recorded in solvents of different polarity. The data are presented in Table 2, where they are compared with those for commercially available Fluorescein **1** and Eosin **2**.

The absorption maximum of the Eosin **2** in ethanol is bathochromically shifted with respect to Fluorescein **1** in the same solvent, which is related to the enhanced electron donor–acceptor interaction in the chromophoric system of the Eosin. The picture is kept the same in the case of combined Eosin–HALS dye **8** and Fluorescein–HALS dye **7** (Fig. 1).

A comparison of the absorption spectra reveals the strong influence of the polarization of the molecule upon the spectral properties. As can be seen from the data presented in Table 2, the absorption maxima of the dyes in polar protic solvents, such as MeOH and EtOH, are hypsochromically shifted in comparison with the absorption maxima of the dyes in the aprotic chloroform and *N*,*N*-dimethylformamide. Such behavior can be satisfactorily explained by the intermolecular H-bonds formation between the dyes and solvents. The proton-donating solvents form H-bonds with the carbonyl group of the dyes thus decreasing the electron donor–acceptor interaction in the chromophoric system. This effect is enhanced in the molecules of Eosin **2** and Eosin derivative **8**, where the



Scheme 2.

protic solvents additionally form intermolecular H-bonds with the bromine atoms of the dyes.

Data presented in Table 2 and the graphics plotted in Fig. 2 show that the incorporation of a HALS fragment in the dye molecule has a small effect on the 9-phenylxanthene absorption properties in comparison with the absorption properties of the dyes, not containing a hindered amine moiety. It was observed that a small bathochromic shift, was better pronounced in the spectrum of Eosin–HALS dye **8** in protic solvents.

2.2.2. Fluorescence properties

Basic fluorescent characteristics of the combined dyes **7** and **8** such as fluorescence (λ_F) maxima, Stokes shift ($\nu_A - \nu_F$), oscillator strength (f), fluorescent both quantum (Φ_F) and energy (E_F) yields were measured in ethanol solution and compared with those for Fluorescein **1** and Eosin **2** (Table 3).

In ethanol solution dyes under study displayed intense fluorescence with well pronounced maxima (λ_F) at 517–560 nm. Figs. 2 and 3 display absorption and fluorescence spectra of Fluorescein **1** and Eosin **2**. The fluorescence curves are approximately a mirror image of the absorption curves, which indicate that the molecular structure of the dyes is retained in the excited state and that the fluorescence prevails [13].

The absorption and fluorescence spectra of the combined molecules **7** and **8** in ethanol showed similar trends (Figs. 4 and 5). The fluorescence maxima of dyes **7** and **8** are 8–11 nm bathochromically shifted in comparison with the maxima of the corresponding Fluorescein **1** and Eosin **2** (Table 3), which is well correlated to the light absorption behavior of the dyes.

Data presented in Table 3 and Figs. 2–5 show that the HALS fragments have a small effect on both the absorption and the fluorescence maxima of final dyes **7** and **8**.

The Stokes shift ($\nu_A - \nu_F$) and oscillator strength (f) are important characteristics for the fluorescent compounds. The Stokes shift is a parameter that indicates the differences in the properties and structure of the fluorophores between the ground state S_0 and the first excited state S_1. The Stokes shifts (cm^{-1}) were calculated by Eq. (1).

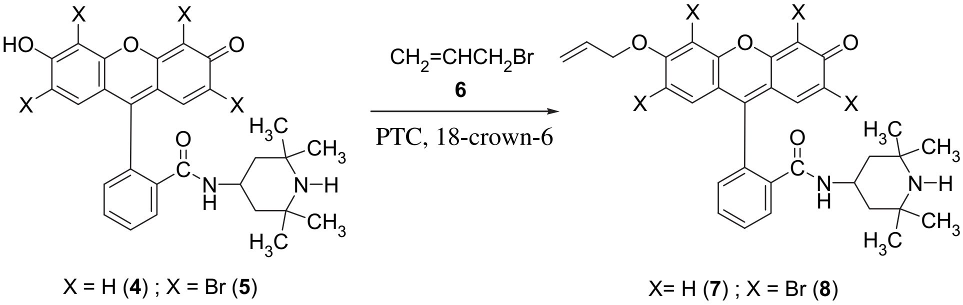
$$(\nu_A - \nu_F) = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F}\right) \times 10^7 \qquad (1)$$

The Stokes shift values of the dyes under study in ethanol were relatively small, as is common for the xanthene dyes [14]. It is interesting to note that the Stokes shift values of the Fluorescein-based dyes **1** and **7** in ethanol solution, 1405 cm^{-1} and 1529 cm^{-1}, respectively, are almost doubled with respect to the Eosin dyes **2** and **8** values (833 cm^{-1} and 800 cm^{-1}, Table 3).

The oscillator strength (f) shows the effective number of electrons whose transition from ground to excited state gives the absorption area in the electron spectrum. Values of the oscillator strength were calculated using Eq. (2) where $\Delta\nu_{1/2}$ is the width of the absorption band (cm^{-1}) at 1/2 (ε_{max}) [15].

$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2}\varepsilon_{max} \qquad (2)$$

As expected the values of the oscillator strength for the Fluorescein-based dyes **1** and **7** were sufficiently higher (0.618 and 0.481, respectively) than those of the Eosin-based analogues **2** and **8** (0.284 and 0.150, respectively), which can be related to narrowing the absorption bands of the latter.



Scheme 3.

Table 1
Yields, melting points and TLC R_f values for 9-phenylxanthenes **4**, **5**, **7** and **8**

Compound	Yield (%)	M.p. (°C)	R_f[a]
4	77	218–220	0.25
5	68	>260	0.37
7	95	117–119	0.20
8	93	136–138	0.33

[a] TLC solvent system *n*-heptane/acetone (1:1).

On the other hand, the oscillator strength values (f) for combined dyes **7** and **8** were relatively smaller than those of Fluorescein **1** and Eosin **2** in accordance with some decrease in their extinction coefficient ε.

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield (Φ_F). The quantum yields of fluorescence were calculated using Rhodamine 6G ($\Phi_{ref} = 0.95$) as a standard according to Eq. (3) [16], where A_{ref}, S_{ref}, n_{ref} and A_{sample} S_{sample}, n_{sample} represent the absorbance at the excited wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively.

$$\Phi_F = \Phi_{ref}\left(\frac{S_{sample}}{S_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n^2_{sample}}{n^2_{ref}}\right) \tag{3}$$

The energy yield of fluorescence E_F (Table 2) calculated by Eq. (4) could also be used instead of Φ_F

$$E_F = \Phi_F \frac{\lambda_A}{\lambda_F} \tag{4}$$

Comparing the fluorescence quantum yields of Fluorescein **1** ($\Phi_F = 0.79$) and Eosin **2** ($\Phi_F = 0.67$), not containing hindered amine fragments, with those of 2-(3-allyloxy-6-oxo-6*H*-xanthen-9-yl)-*N*-(2,2,6,6-tetramethylpiperidin-4-yl) benzamide **7** ($\Phi_F = 0.77$) and 2-(3-allyloxy-2,4,5,7-tetrabromo-6-oxo-6*H*-xanthen-9-yl)-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide **8** ($\Phi_F = 0.64$), a combination of 9-phenylxanthene with a 2,2,6,6-tetramethylpiperidine in one molecule, clearly shows (the values are approximately the same) that the combination of the two different structural units does not result in their interaction as an intramolecular quenching due to an electronic energy transfer.

2.3. Photooxidative stability of the dyes

The fluorescent dyes' photostability is a very important characteristic with regard to their practical usage. To study the influence of 2,2,6,6-tetramethylpiperidine fragment on the photostability of the target dyes **7** and **8**, DMF solutions of the dyes were subjected to irradiation with UV light in a SUNTEST equipment. In order to receive a more complete comparative picture of this influence, Fluorescein **1** and Eosin **2**, not containing a hindered amine moiety in their molecules were involved in the present study and investigated under the same conditions.

Table 2
Absorption maxima (nm) of 9-phenylxanthene dyes **1**, **2**, **7** and **8**

Compound	Chloroform	EtOH	MeOH	DMF
1	486	482	484	488
2	536	525	520	538
7	490	486	486	490
8	544	535	532	544

Table 3
Photophysical characteristics of 9-phenylxanthene dyes **1**, **2**, **7** and **8** in ethanol solution

Compound	λ_A (nm)	log ε ($l\,mol^{-1}\,cm^{-1}$)	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	f	Φ_F	E_F
1	482	4.595	517	1405	0.618	0.79	0.74
2	525	4.743	549	833	0.284	0.67	0.64
7	486	4.426	525	1529	0.481	0.77	0.71
8	536	4.544	560	800	0.150	0.64	0.61

The kinetics of the dyes' photodegradation was monitored colorimetrically. The correlation between the dye concentration and the time of irradiation was monitored using the method of the standard calibration curve (Fig. 6).

As seen, the photostability of the target dyes **7** and **8**, containing hindered amine fragments, was higher than those of Fluorescein **1** and Eosin **2**, not containing stabilizer fragments in their molecules. The photodegradation of the latter was much faster when compared to that of dyes **7** and **8**. Within half an hour the dyes solutions **1** and **2** lost their absorption maxima as a result of photodegradation of the dye chromophoric system. The study also showed that the presence of the bromine atoms in the dyes' molecule slightly increased the dyes' photostability (Fig. 6).

2.4. Co-polymerization of the dyes with methyl methacrylate

The applicability of the new fluorescent compounds **7** and **8** for simultaneously coloring and stabilization of polymers was examined on the basis of their ability to co-polymerize with MMA. The co-polymerization process was conducted in bulk at 70 °C under conditions used other similar 9-phenylxanthene derivatives [7]. Solid transparent co-polymers with an intense fluorescence have been obtained. They were

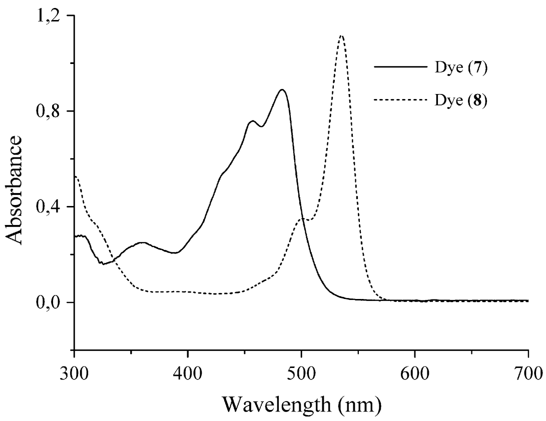


Fig. 1. Comparison of the absorption maxima of combined 9-phenylxanthene–HALS dyes **7** and **8**.

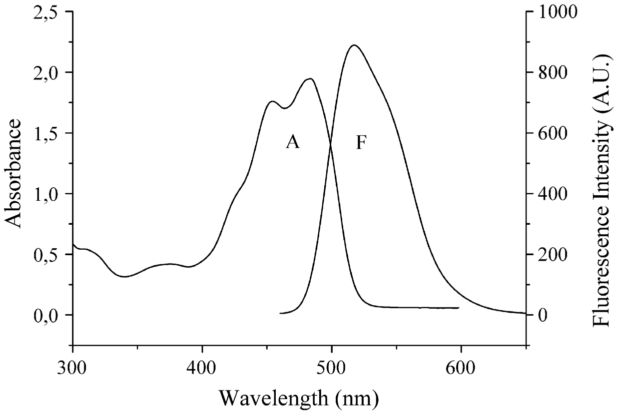


Fig. 2. Absorption and fluorescence spectra of Fluorescein **1**.

several-fold re-precipitated to remove the unreacted monomers. Polymers thus treated retained their color and fluorescence, which indicated that the dyes were chemically bonded to the polymer. UV/vis spectroscopic and TLC techniques proved the presence of a covalent bond between the monomeric dye units and the polymer chain.

The UV/vis absorption spectra of the re-precipitated polymers had similar absorption maxima as the monomeric dyes, showing that the basic dyes' chromophore did change, neither during the polymerization nor as a result of its bonding to the polymer chain. That is why the percentage of the chemically bonded dyes in the polymer chain was determined spectrophotometrically using the method of the standard calibration curve. It was estimated that 65–70% of the initial amount of monomeric dyes **7** and **8** was incorporated into the macromolecule. These values are satisfactory for the production of intensively colored polymers. More detailed investigations on the polymerization process and on the co-polymers' photostability will be the object of our future investigations.

3. Experimental

3.1. Materials

The starting Fluorescein **1**, Eosin **2**, 2,2,6,6-tetramethylpiperidine-4-ylamine **3** and allylbromide **6** (Fluka products), p.a. grade, was used without purification. Commercial methyl methacrylate (MMA, Merck) was distilled under reduced pressure in nitrogen atmosphere before use. Dibenzoylperoxide (DBP, Fluka, 99.6%) re-crystallized from chloroform was used as an initiator of the free radical co-polymerization. All solvents were of p.a. or analytical grade.

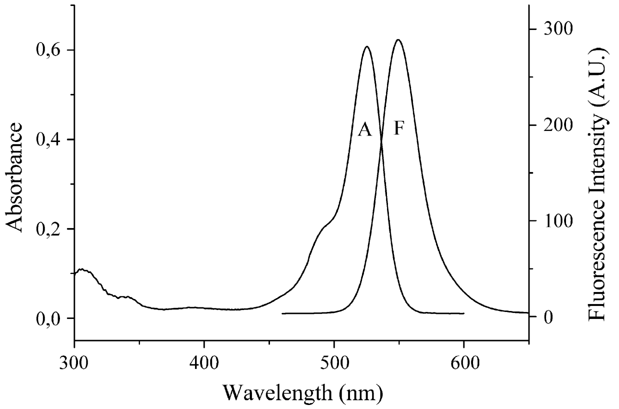


Fig. 3. Absorption and fluorescence spectra of Eosin **2**.

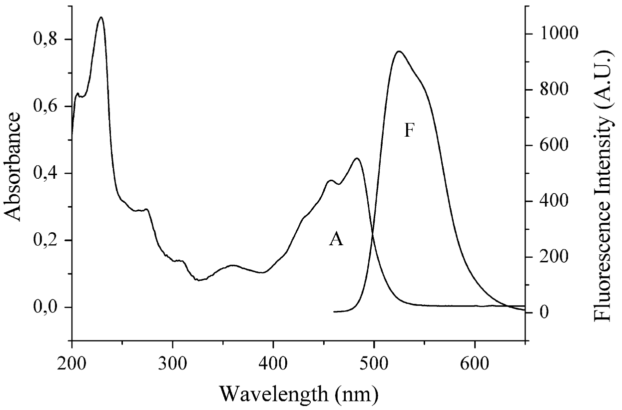


Fig. 4. Absorption and fluorescence spectra of combined Fluorescein–HALS dye **7**.

3.2. Methods

FT-IR spectra were recorded on a Bruker IFS-113 spectrometer at 2 cm^{-1} resolution using KBr discs. The ^{1}H NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz. The UV/vis spectra were recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution at room temperature. The fluorescence spectra were taken on an SFM 25 spectrophotometer (KONTRON instruments). Fluorescence quantum yields were determined on the basis of the absorption and fluorescence spectra. Rhodamine 6G was used as standard ($\Phi_{\text{ref}} = 0.95$). TLC was performed on silica gel, Fluka F60 254, 20 × 20, 0.2 mm, using an eluant solvent systems *n*-heptane/acetone (1:1). The melting points were determined by means of a Kofler melting point microscope.

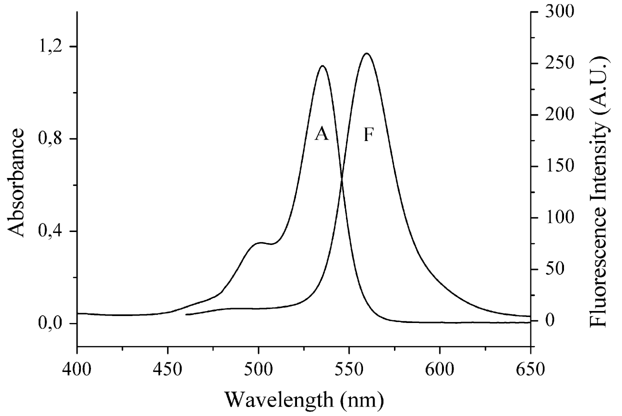


Fig. 5. Absorption and fluorescence spectra of combined Eosin–HALS dye **8**.

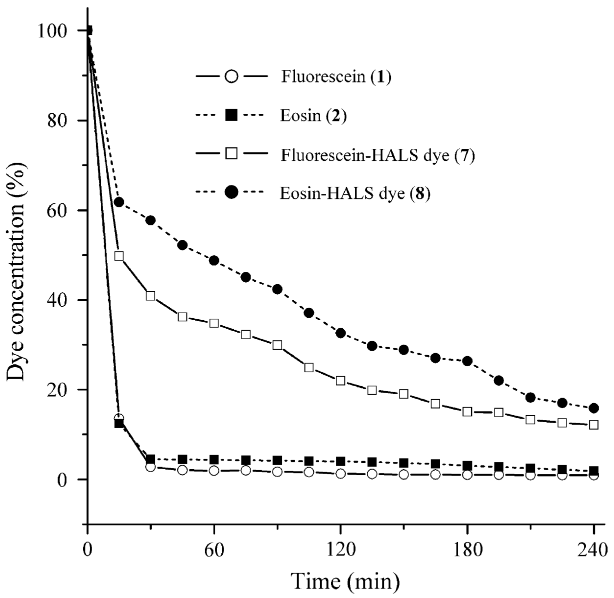


Fig. 6. Photodegradation of dyes **1**, **2** and **7**, **8** in DMF solution.

3.3. Synthesis of dyes

*3.3.1. General preparation procedure for combined hindered amine — 9-phenylxanthene intermediate dyes **4** and **5***

To a solution of Fluorescein **1** (1.0 g, 3 mmol) or Eosin **2** (1.94 g, 3 mmol) and aluminum(III) chloride (0.4 g, 3 mmol for compound **4** and 2.0 g, 15 mmol for compound **5**) in 20 ml of dry chlorobenzene, 0.47 g of 2,2,6,6-tetramethylpiperidine-4-ylamine **3** ($d = 0.91$, 30 mmol) was added dropwise under stirring at ambient temperature over a period of 30 min. The resulting mixture was stirred at 100 °C for 6 h (TLC control in a solvent systems *n*-heptane/acetone = 1:1). The heating was discontinued and the reaction mixture was allowed to cool to room temperature. Ice-cold aqueous hydrochloric acid solution (2%) was added with stirring to break the aluminum complex. A yellow-orange precipitate was formed. The reaction mixture was filtered, washed with water and dried to give 1.09 g (77%) of 2-(3-hydroxy-6-oxo-6*H*-xanthen-9-yl)-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide **4** or 1.60 g (68%) of 2-(2,4,5,7-tetrabromo-3-hydroxy-6-oxo-6*H*-xanthen-9-yl)-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide **5**.

*3.3.1.1. 2-(3-Hydroxy-6-oxo-6H-xanthen-9-yl)-N-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide (**4**).* FT-IR (KBr) cm^{-1}: 3420 (νOH); 3350 (νNH); 3058 (νCH=); 2880 (νCH_3); 1760 (νC=O); 1650 (νCONH).

^1H NMR (DMSO-d_6, 250 MHz) ppm: 9.46 (br s, 1H, OH); 7.97 (dd, 1H, $J = 7.5$, 1.4 Hz, Ph 6-H); 7.73 (m, 2H, Ph 4-H and Ph 5-H); 7,24 (d, 1H, $J = 7.4$ Hz, Ph 3-H); 6.71 (d, 2H, $J = 2.4$ Hz, 4-H and 5-H); 6.53 (m, 4H, 1-H, 2-H, 7-H and 8-H); 4.12 (m, 1H, piperidine CH); 3.38 (br s, 2H, NH and piperidine NH); 1.79 (dd, 1H, $J = 13.2$, 3.5 Hz, piperidine CH_2); 1.49 (t, 2H, $J = 13.2$ Hz, piperidine CH_2); 1.40 (s, 12H, piperidine $4 \times CH_3$).

*3.3.1.2. 2-(2,4,5,7-Tetrabromo-3-hydroxy-6-oxo-6H-xanthen-9-yl)-N-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide (**5**).* FT-IR (KBr) cm^{-1}: 3390 (νNH); 3070 (νCH=); 2876 (νCH_3); 1752 (νC=O); 1620 (νCONH); 1594 (νC=C).

^1H NMR (DMSO-d_6, 250 MHz) ppm: 8.20 (dd, 1H, $J = 7.6$ Hz, $J = 1.1$ Hz, Ph 6-H); 7.72 (m, 2H, Ph 4-H and Ph 5-H); 7,23 (d, 1H, $J = 7.5$ Hz, Ph 3-H); 6.70 (d, 2H, $J = 2.2$ Hz, 4-H and 5-H); 6.53 (m, 4H, $J = 8.9$ Hz, 1-H, 2-H, 7-H and 8-H); 6.15 (m, 1H, allyl CH=); 5.40 (d, 1H, $J_{trans} = 17.1$ Hz, allyl=C*H*H); 5.29 (d, 1H, $J_{cis} = 10.4$ Hz, allyl =CH*H*); 4.59 (d, 2H, $J = 5.2$ Hz, allyl OCH_2); 4.16 (m, 1H, piperidine CH); 3.40 (br s, 2H, NH and piperidine NH); 1.82 (dd, 2H, $J = 12.9$, 3.6 Hz, piperidine CH_2); 1.48 (t, 2H, $J = 12.9$ Hz, piperidine CH_2); 1.39 (s, 12H, piperidine $4 \times CH_3$).

*3.3.2. General preparation procedure for combined polymerizable hindered amine — 9-phenylxanthene dyes **7** and **8***

To a mixture of intermediate **4** or **5** (2 mmol) in 30 ml of DMF, 0.032 g of 18-crown-6 (0.12 mmol, 6 mol% to the intermediate) and 0.33 g (2.4 mmol) of finely ground potassium carbonate, 0.36 g of allylbromide ($d = 1.398$, 3 mmol) was added dropwise under vigorous stirring at ambient temperature over a period of 10 min. The resulting mixture was stirred under the same conditions for 6 h (TLC control in a solvent systems *n*-heptane/acetone = 1:1), then cooled to room temperature. The resulting solution was poured into 100 ml of water. The precipitate was filtered off, washed with water and dried to give 0.98 g (95%) of 2-(3-allyloxy-6-oxo-6*H*-xanthen-9-yl)-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide **7** or 1.54 g (93%) of 2-(3-allyloxy-2,4,5,7-tetrabromo-6-oxo-6*H*-xanthen-9-yl)-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide **8**.

*3.3.2.1. 2-(3-Allyloxy-6-oxo-6H-xanthen-9-yl)-N-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide (**7**).* FT-IR (KBr) cm^{-1}: 3410 (νOH); 3345 (νNH); 3064 (νCH=); 2896 (νCH_3); 1730 (νC=O); 1648 (νCONH).

^1H NMR (DMSO-d_6, 250 MHz) ppm: 9.52 (br s, 1H, OH); 8.11 (s, 1H, 1-H); 8.04 (dd, 1H, $J = 7.4$, 1.5 Hz, Ph 6-H); 7.56 (m, 2H, Ph 4-H and Ph 5-H); 7.09 (dd, 1H, $J = 7.6$, 1.5 Hz, Ph 3-H); 6.85 (s, 1H, 8-H); 4.12 (m, 1H, piperidine CH); 3.84 (br s, 1H, NH); 2.13 (t, 2H, $J = 12.2$ Hz, piperidine CH_2); 1.72 (br s, 1H, piperidine NH); 1.42 (d, 2H, $J = 12.2$ Hz, piperidine CH_2); 1.18 (s, 6H, piperidine $2 \times CH_3$); 0.97 (s, 6H, piperidine $2 \times CH_3$).

Elemental analysis: Calculated for $C_{32}H_{34}N_2O_4$ (MW 510.62) C 75.27, H 6.71, N 5.49%; Found C 75.62, H 6.63, N 5.58%.

*3.3.2.2. 2-(3-Allyloxy-2,4,5,7-tetrabromo-6-oxo-6H-xanthen-9-yl)-N-(2,2,6,6-tetramethylpiperidin-4-yl)benzamide (**8**).* FT-IR (KBr) cm^{-1}: 3395 (νNH); 3060 (νCH=); 2890 (νCH_3); 1726 (νC=O); 1614 (νCONH); 1598 (vC=C).

^1H NMR (DMSO-d_6, 250 MHz) ppm: 8.02 (s, 1H, 1-H); 7.98 (dd, 1H, $J = 7.4$, 1.5 Hz, Ph 6-H); 7.63 (m, 2H, Ph 4-H and Ph 5-H); 7,11 (dd, 1H, $J = 7.6$, 1.5 Hz, Ph 3-H); 6.84 (s, 1H, 8-H); 6.18 (m, 1H, allyl CH=); 5.47 (dd, 1H, $J_{trans} = 17.0$, 1.3 Hz, allyl=C*H*H); 5.33 (d, 1H, $J_{cis} = 10.3$ Hz allyl=CH*H*); 4.65 (br s, 1H, NH); 4.60 (d, 2H, $J = 3.8$ Hz, allyl OCH_2); 4.10 (m, 1H, piperidine CH); 2.09 (t, 2H, $J = 12.2$ Hz, piperidine CH_2); 1.99 (br s, 1H, piperidine NH); 1.34 (d, 2H, $J = 12.2$ Hz, piperidine CH_2); 1.00 (s, 6H, piperidine 2 × CH_3); 0.88 (s, 6H, piperidine 2 × CH_3).

Elemental analysis: Calculated for $C_{32}H_{30}Br_4N_2O_4$ (MW 826.21) C 46.52, H 3.66, N 3.39%; Found C 46.25, H 3.71, N 3.46%.

3.4. Photodegradation of dyes

The studies on the photodegradation of the fluorescent dyes were performed in a solar simulator SUNTEST CPS equipment (Heraeus, Germany), supplied with an air-cooled Xenon lamp (Hanau, 1.1 kW, 765 W m^{-2}). The photodestruction of the dyes was monitored spectrophotometrically using the method of a standard calibration curve.

3.5. Synthesis of fluorescent co-polymers

The radical co-polymerization of dyes **7** and **8** with MMA was carried out in ampoules, previously purged with dry and pure nitrogen. The process of co-polymerization was conducted at 70 °C for 8 h in the presence of 0.1 wt.% of the monomeric compounds **7** and **8** and 0.5 wt.% of DBP with respect to the MMA monomer. The transparent side-chain co-polymers thus obtained were several-fold re-precipitated with ethanol from toluene until the filtrate was colorless. The precipitated co-polymers were repeatedly washed with ethanol, recovered by filtration and dried in vacuum to constant weight.

4. Conclusions

Novel Fluorescein-based **7** and Eosin-based **8** dyes, a combination of 2,2,6,6-tetramethylpiperidine and a polymerizable group through the molecule of 9-phenylxanthene were successfully synthesized. The basic photophysical properties of the new dyes in solution have been determined and discussed. Photodegradation of the new fluorophores have been studied and compared to those of Fluorescein and Eosin, not containing a hindered amine fragment in their molecules. The presence of a HALS fragment in the dyes' molecules did not affect the ordinary absorption and fluorescent properties of the 9-phenylxanthene dyes but improved their photostability. The new compounds were suitable for preparing fluorescent PMMA-based co-polymers and represent the possibility of "one-step" coloration and stabilization of polymers.

Acknowledgements

We thank the Science Foundation at the University of Chemical Technology and Metallurgy for the financial support of these investigations.

References

[1] Johnson S, Wells I. Fluorescent labels for confocal microscopy. In: Stevens J, Mills L, Trogadis J, editors. Three-dimensional confocal microscopy. Hardbound: Academic Press; 1994. p. 101.

[2] (a) Cong R, Turksen S, Russo P. Macromolecules 2004;37:4731;
(b) Peng XY, Li PCH. Anal Chem 2004;76:5282;
(c) Crovetto L, Orte A, Talavera E, Alvarez-Pez J, Cotlet M, Thielemans J, et al. J Phys Chem B 2004;108:6082;
(d) Wang S, Gaylord B, Bazan G. J Am Chem Soc 2004;126:5446;
(e) Öberg C, Carlsson S, Fillion E, Leffler H, Nilsson U. Bioconjugate Chem 2003;14:1289;
(f) Metallo S, Kane R, Holmlin R, Whitesides G. J Am Chem Soc 2003;125:4534;
(g) Disney M, Zheng J, Swager T, Seeberger P. J Am Chem Soc 2004;126:13343;
(h) Tahtaoui C, Parrot I, Klotz P, Guillier F, Galzi J-L, Hibert M, et al. J Med Chem 2004;47:4300;
(i) Ternon M, Dias-Mochon J, Belsom A, Bradley M. Tetrahedron 2004;60:8721;
(j) Nguyen T, Francis M. Org Lett 2003;5:3245.

[3] (a) Clark MA, Duffy K, Tibrewala J, Lippard SJ. Org Lett 2003;5:2051;
(b) Gee K, Zhou Z-L, Qian W, Kennedy R. J Am Chem Soc 2002;124:776;
(c) Qian W, Gee K, Kennedy R. Anal Chem 2003;75:3136;
(d) Yin H, Sensi S, Ogoshi F, Weiss J. J Neurosci 2002;22:1273;
(e) Sumner J, Aylott J, Monson E, Kopelman R. Analyst 2002;127:11;
(f) Hebbink G, Grave L, Woldering L, Reinhoudt D, van Veggel F. J Phys Chem A 2003;107:2483;
(g) Hirano T, Kikuchi K, Urano Y, Nagano T. J Am Chem Soc 2002;124:6555.

[4] (a) Nolan E, Burdette S, Harvey J, Hilderbrand S, Lippard S. Inorg Chem 2004;43:2624;
(b) Qu D-H, Wang Q-C, Ren J, Tian H. Org Lett 2004;6:2085;
(c) Jing B, Zhu D. Tetrahedron Lett 2004;45:221;
(d) Hattori S, Hasobe T, Ohkubo K, Urano Y, Umezawa N, Nagano T, et al. J Phys Chem B 2004;108:15200;
(e) Miura T, Urano Y, Tanaka K, Nagano T, Ohkubo K, Fukuzumi S. J Am Chem Soc 2003;125:8666;
(f) Ramakrishna G, Das A, Ghosh H. Langmuir 2004;20:1430;
(g) Guo X, Zhang D, Zhou Y, Zhu D. J Org Chem 2003;68:5681;
(h) Clark M, Hilderbrand S, Lippard S. Tetrahedron Lett 2004;45:7129;
(i) Sparano B, Shahi S, Koide K. Org Lett 2004;6:1947;
(j) Guo X, Zhang D, Tao H, Zhu D. Org Lett 2004;6:2491.

[5] Molecular probes – handbook of fluorescent probes and research products. 9th ed. Web version, <http://www.probes.com/handbook/>; October 2004.

[6] Marechal E. Prog Org Coat 1982;10:251.

[7] (a) Bojinov V, Konstantinova T. Dyes Pigments 1998;39:69;
(b) Konstantinova T, Kirkova G, Becheva R. Dyes Pigments 1998;38:11;
(c) Meallier P, Guittonneau S, Emmelin C, Konstantinova T. Dyes Pigments 1999;40:95;
(d) Konstantinova T, Cheshmedjieva-Kirkova G, Konstantinov H. Polym Degrad Stab 1999;65:249;
(e) Konstantinova T, Cheshmedjieva-Kirkova G. Polym Degrad Stab 2000;70:77;
(f) Cheshmedjieva-Kirkova G, Konstantinova T. J Univ Chem Technol Metall 2002;37:71.

[8] (a) Marechal E. Pure Appl Chem 1990;52:1923;
(b) Oda H. Dyes Pigments 2001;48:233.

[9] Ranby B, Rabek J. Photodegradation, photo-oxidation and photostabilization of polymers. London: Wiley; 1975.

[10] (a) Chirinos-Padron AJ. J Photochem Photobiol A Chem 1989;49:1;
(b) Bojinov V, Grabchev I. J Photochem Photobiol A Chem 2002;150:223;
(c) Bojinov V, Grabchev I. Polym Degrad Stab 2001;74:543;
(d) Bojinov V. Photochem Photobiol Sci 2002;1:340.

[11] (a) Allen NS. Chem Soc Rev 1986;15:373;
(b) Kamiya Y, Niki E. Aspects of degradation and stabilization of polymers. In: Jellinek HH, editor. Amsterdam: Elsevier; 1978. p. 103.
[12] (a) Bojinov V, Konstantinova T. Polym Degrad Stab 2000;68:295;
(b) Bojinov V, Konstantinova T. Dyes Pigments 2002;54:239;
(c) Konstantinova T, Lazarova R, Bojinov V. Polym Degrad Stab 2003;82:115;
(d) Bojinov V, Grabchev I. Dyes Pigments 2003;59:277;
(e) Bojinov V. J Photochem Photobiol A Chem 2004;162:207;
(f) Bojinov V, Ivanova G, Simeonov D. Macromol Chem Phys 2004;205:1259.
[13] Krasovitskii B, Bolotin B. Organic luminophores. Moskow: Chimia; 1984 [in Russian].
[14] Griffiths J, Lee WJ. Dyes Pigments 2003;57:107.
[15] Gordon P, Gregory P. Organic chemistry in colour. Berlin: Springer-Verlag; 1983.
[16] (a) Du H, Fuh RA, Li J, Corkan A, Lindsey JS. Photochem Photobiol 1998;68:41;
(b) Kubin RF, Fletcher AN. J Lumin 1982;27:455.