

Photochemistry of some polymerizable fluorescent brighteners

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Abstract

The study presents investigations on the basic photophysical characteristics of seven polymerizable triazine–stilbene fluorescent brighteners in aqueous and ethanol solutions and their photochemical *trans–cis* isomerisation. It was established that the type of substituents in triazine ring does not affect significantly the absorption–fluorescence assignments. The concentration of *trans*- and *cis*-isomers depends on the nature of the substituents. It was found that the nature of the solvents influences the quantum yield of fluorescence. The absorption and fluorescence properties of the copolymers with styrene in solid film have been discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Triazine–stilbene fluorescent brighteners; *trans–cis* isomers

1. Introduction

The fluorescent brighteners (FBs) are essentially colourless, fluorescent dyes used for whitening textiles [1], paper [2] and synthetic polymer materials [3]. Materials treated with FBs obtain a high degree of whiteness which cannot be achieved by the common bleaching methods. Fluorescent brighteners absorb light in the near ultraviolet region of the spectrum (about 340–380 nm) and re-emit the light as violet-blue fluorescence in the visible region. An important class of fluorescent brighteners are based on triazine–stilbene, containing different amino and alkoxy derivatives in the triazine ring [4]. In solution these FBs have low photo resistance determined of their being able to isomerize and exist in two isomeric forms [5]. It is due to the fact than the double ethylene bond in stilbene molecule favours *trans–cis* isomerization of FBs. The active component of this FBs is the *trans* isomer (the (E)-stilben), which is fluorescent, whereas the *cis* isomers (the (Z)-stilben), are not.

Bleaching of polymeric materials is achieved by blending the fluorescent brighteners with the polymer or surface treatment of the materials. In both cases the FBs migrate with time, and the degree of whiteness decreases. The introduction of unsaturated polymerizable groups into their structure makes them applicable in the copolymerization process with vinyl monomers, resulting in the formation of covalent bonds in the polymer molecule, obtaining structural bleached and

fluorescent polymers with resistance to wet treatment and solvents. We have previously reported on the synthesis of some triazine–stilbene FBs, containing different polymerizable groups [6–8] and on the investigation of their copolymers with acrylonitrile or styrene [9–11].

In this article, we present basic photophysical characteristics and photochemical *trans–cis* photoisomerization of triazine–stilbene fluorescent brighteners with unsaturated polymerizable allyloxy groups in the triazine ring and their copolymers with styrene.

2. Experimental

2.1. Materials and methods

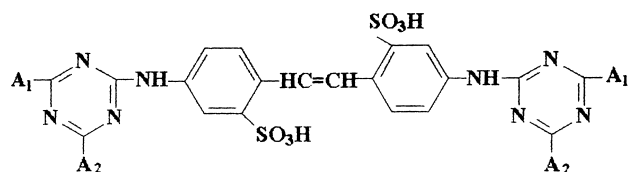
Derivatives of triazine–stilbene fluorescent brighteners with the structure presented in Scheme 1 were studied.

The substituents A_1 and A_2 are as shown.

1	–OCH ₂ CH=CH ₂	–NHC ₆ H ₅
2	–OCH ₂ CH=CH ₂	–NHC ₆ H ₄ SO ₃ H(4')
3	–OCH ₂ CH=CH ₂	–NHC ₆ H ₄ SO ₃ H(3')
4	–OCH ₂ CH=CH ₂	–Morpholino
5	–OCH ₂ CH=CH ₂	–N(CH ₃) ₂
6	–OCH ₂ CH=CH ₂	–N(CH ₂ CH ₃) ₂
7	–OCH ₂ CH=CH ₂	–OCH ₂ CH=CH ₂

The details from their synthesis are described in [8,12]. The details from the synthesis of poly(St-co-FB) are described elsewhere [10].

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Scheme 1.

2.2. Electronic absorption measurements

UV spectra were recorded using aqueous and ethanol solutions at a $5 \times 10^{-5} \text{ mol l}^{-1}$ concentration and in solid copolymer films on a Hewlett-Packard 8452A spectrophotometer. The concentration of FBs in the copolymer was 1 wt.%. The thickness of 45–50 μm was optimised to give films with absorption in the range 0.8–1.0.

2.3. Emission measurements

Fluorescence measurements of FBs in aqueous and ethanol solutions at a concentration of $10^{-6} \text{ mol l}^{-1}$ and a thin polymer film of poly(St-co-FB) were recorded on a Perkin-Elmer MPF 44 spectrophotometer at room temperature. Fluorescence quantum yields were calculated by comparing corrected fluorescence spectra of the FBs with the spectrum of the sodium salicylate ($\Phi_0=0.55$) [13]. Phosphorescence measurements of FBs were recorded in ethanol solution in 77 K.

2.4. Investigations of trans–cis isomerization

Photochemical *trans*–*cis* isomerization was studied in solution at 2.10^{-3} wt.% concentration of the FBs and exposition of the solution to monochromatic light at 366 nm. The irradiation was carried out in an inert atmosphere to avoid photochemical breakdown. The course of isomerization was followed spectrometrically and by thin layer chromatography (TLC).

The rate of reaction of photoisomerization and final products in the equilibrium was monitored by TLC using *n*-butanol:pyridin:25 vol.% NH_3 (1:1:1) on silicagel

Table 2

Absorption of *cis* and *trans* isomers and basic photophysical characteristics of the fluorescent brighteners 1–7 in ethanol solution (see text)

FBs	<i>Trans</i>		Isobestic point (nm)	λ_F (nm)	$\Delta\nu$ (cm^{-3})	Φ_F	E_F	
	<i>Cis</i>	<i>Trans</i>						
	λ_A (nm)	λ_A (nm)	$\log \epsilon$					
1	260	347	4.71	304	439	6039	0.51	0.40
2	279	349	4.48	309	448	6332	0.43	0.33
3	279	348	4.37	310	443	6162	0.39	0.30
4	280	354	4.64	306	439	5469	0.42	0.34
5	277	351	4.59	308	435	5501	0.50	0.41
6	276	354	4.72	310	440	5521	0.48	0.38
7	271	355	4.53	307	438	5338	0.49	0.40

plates. The chromatograms were developed by irradiation at 366 nm.

3. Results and discussion

3.1. Spectral characteristics of monomeric FBs

Tables 1 and 2 show the basic photophysical characteristics of FBs 1–7, obtained from the measurement of the FBs dissolved in aqueous solution and ethanol. In this tables the values of the ground state position of the absorption maxima (λ_A) for *trans* forms and the extinction coefficient (ϵ) of the FBs are presented. The values of fluorescent maxima (λ_F), Stokes shift ($\Delta\nu$), quantum yield of fluorescence (Φ_F) and the energy yield (E_F) are also presented.

The absorption and fluorescence spectra for the FB1 in aqueous solution are shown in Fig. 1 as an example. The absorption and fluorescence spectra of all the compounds have similar curve profiles. Only their intensity changes with respect to those of FB1. In aqueous solution all the FBs absorbed in the UV region ($\lambda_A=344$ – 351 nm). On light absorption FBs pass from the ground singlet state S_0 to the first excited state S_1 . Fluorescence emission was observed in the region 375–510 nm with a well pronounced maxima at 432–444 nm. In ethanol the absorption maxima are at 347–355 nm and respective fluorescent maxima are at 438–448 nm. As seen from the data listed in Tables 1 and 2

Table 1

Absorption of *cis* and *trans* isomers and basic photophysical characteristics of the fluorescent brighteners in aqueous solution (see text)

FBs	<i>Trans</i>		Isobestic point (nm)	λ_F (nm)	$\Delta\nu$ (cm^{-1})	Φ_F	E_F	
	<i>Cis</i>	<i>Trans</i>						
	λ_A (nm)	λ_A (nm)	$\log \epsilon$					
1	258	344	4.69	301	434	6028	0.34	0.27
2	277	346	4.52	306	444	6379	0.27	0.21
3	275	346	4.48	307	439	6122	0.24	0.19
4	274	351	4.66	305	434	5448	0.30	0.24
5	275	348	4.59	305	432	5587	0.32	0.26
6	273	351	4.72	306	441	5814	0.31	0.24
7	269	351	4.61	304	436	5554	0.32	0.26

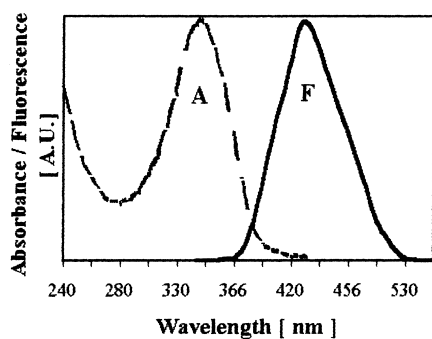


Fig. 1. Absorption (A) and fluorescence (F) spectra of FB1 in aqueous solution.

the changes in the solvents have only a small effect upon the positions of the absorption and fluorescence maxima of the FBs 1–7. An important parameter characterising the FBs is the energy of the excited state E_{S_1} . The energy of the excited state E_{S_1} and the corresponding λ_{S_1} were determined by the interaction of the fluorescence and absorption spectra. The energy of the excited state E_{S_1} in water is 298–311 kJ mol⁻¹ and 300–314 kJ mol⁻¹ in ethanol. The FBs studied do not phosphoresce in ethanol solution either at room temperature nor at 77 K. This indicates that being in the excited state the FBs are in the singlet state S_1 . The FBs molecules are deactivated on fluorescence light emission and pass from the S_1 to the ground S_0 state.

The Stokes shift is a parameter which indicates the differences in properties and structure of the FBs between the ground state S_0 and the first excited state S_1 . The Stokes shift was found by Eq. (1):

$$\Delta\nu = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F} \right) \times 10^7 \quad (\text{cm}^{-1}) \quad (1)$$

The calculated values of Stokes shift in aqueous solution are between 5448–6379 cm⁻¹ and 5338–6332 cm⁻¹ in ethanol. The significant Stokes shift is due to the energy losses during the transition into excited state. This is an evidence of notable steric changes which the molecules undergo during the transition from basic to excited state. The Stokes shift for FBs 1–3 having aromatic substituents in the triazine ring is greater. The effect is enhanced with the introduction of sulpho groups into these substituents.

The ability of the molecules to emit the absorbed light energy is characterised quantitatively by the quantum fluorescent yield Φ_F . It was determined on the basis of the absorption and fluorescence spectra of the FBs dissolved in water and in ethanol. The results for Φ_F are in the region 0.24–0.34 (aqueous solution) and 0.39–0.51 (ethanol). It shows that the fluorescence involves non-emission deactivation of the S_1 state in aqueous solution.

Besides Φ_F the energy yield of fluorescence E_F can also be used [14] (Eq. (2)):

$$E_F = \frac{\Phi_F \lambda_A}{\lambda_F} \quad (2)$$

Table 3

Retention factor R_f on *trans*- and *cis*- forms of the fluorescent brighteners and their concentrations (C_T , C_C) in aqueous and ethanol solutions

FBs	R_f		In water			In ethanol		
	<i>Cis</i>	<i>Trans</i>	C_T	C_C	C_T/C_C	C_T	C_C	C_T/C_C
1	0.24	0.61	47.5	52.5	0.91	43.5	56.5	0.77
2	0.38	0.50	40.5	59.5	0.67	38.5	61.5	0.63
3	0.38	0.50	34.8	65.2	0.53	32.5	67.5	0.48
4	0.17	0.44	66.4	33.6	1.97	61.9	38.1	1.62
5	0.48	0.69	65.3	34.7	1.88	64.5	35.5	1.81
6	0.52	0.77	68.1	31.9	2.13	67.3	32.7	2.06
7	0.43	0.61	61.9	38.1	1.62	59.3	40.7	1.45

The data from $\Delta\nu$, Φ_F and E_F reveal the domination of non-radiate deactivation processes during the transition $S_1 \rightarrow S_0$ which are parted by isomerization in non-fluorescence *cis*-form.

3.2. Spectral characteristics of polymeric FBs

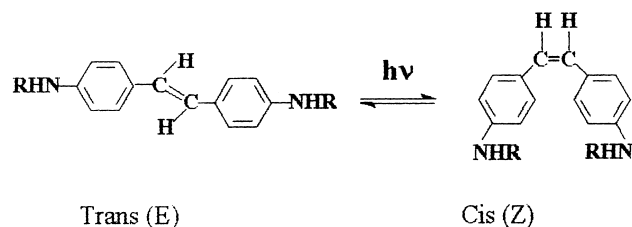
The spectral characteristics of the structurally modified polystyrene are also interesting to study. Table 3 presents data estimated from the absorption and fluorescence spectra of poly(St-co-FBs) in the isotropic state. An absorption maxima was observed at 338–344 nm as well as a well pronounced fluorescence maximum at 418–422 nm. It is remarkable that absorption and fluorescent spectra of the solid polymer films differ significantly from those in aqueous solution. There is a slight hypsochromic shift of about 4–9 nm of the absorption maxima and a more significant one of the fluorescence maxima of 14–20 nm. The phenomena might be explained by the fact that the chromophore system is better fixed in the polymer chain hence there are less possibilities for changes. The Stokes shift values are between 5430–5715 cm⁻¹. The energy of the excited state E_{S_1} was determined and it was 309–310 kJ mol⁻¹.

3.3. *Trans*–*cis* isomerization in solutions

It is well known that triazine–stilbene fluorescent brighteners are light sensitive products. They have very poor photostability in aqueous solution and one of the major photoreactions causing loss of fluorescence is *trans*(E)→*cis*(Z) isomerisation, a reaction which involves rotation of the stilbene molecule around the central ethylene bond [15–17]. The photochemical processes of *trans*–*cis* isomerization is illustrated in Scheme 2.

The mechanism of the emissionless deactivation of the singlet state FBs is in fact a conformation transition of a singlet excited state of the *trans* isomer being in the *cis* form accompanied by a well pronounced non-radiative emission $S_1 \rightarrow S_0$.

Table 4 collects the data of retention factor R_f for *trans*- and *cis*-isomers. As seen the two isomers for the FBs studied have different retention factor R_f values which is an indica-



Scheme 2.

Table 4
Photophysical characteristics of poly(St-co-FB) in solid polymer films

Copolymers	λ_A (nm)	λ_F (nm)	$\Delta\nu$ (cm^{-1})	E_{S1} (kJ mol^{-1})
poly(St-co-FB1)	340	422	5715	310.2
poly(St-co-FB4)	338	420	5430	308.6
poly(St-co-FB5)	342	420	5602	308.9
poly(St-co-FB6)	344	418	5662	309.6

tion of the different absorbencies. The *cis* form is due to a disturbed co-planarity of the molecule hence it has a weaker substantiality and lower R_f values.

In Fig. 2 shows the absorption spectra of FB1 before and after irradiation in aqueous solution. It is seen that the absorption spectrum after irradiation showed two bands characteristic for *trans*- and *cis*-isomers. In the initial mixtures *trans*-isomer is predominantly excited and its concentration decreases with irradiation time while this of *cis*-isomer increases till its photo equilibrium is reached. The two isomeric forms have different absorption maxima in the UV region. The *trans*-isomers absorb at 344–351 nm in aqueous solution and 347–355 nm in ethanol while the *cis*-isomers are hypsochromically shifted to 258–279 nm region for both solvents (Tables 1 and 2). In daylight, the photo equilibrium state favours the *cis*-isomer. This leads to disintegration of the molecular compactness. Thus *cis*-isomers lose their fluorescence properties and affinity to the brightened material and the FBs become less effective.

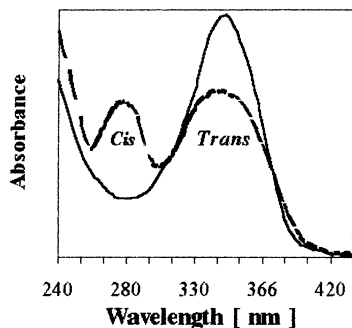


Fig. 2. Absorption spectra of FB1 in aqueous solution before (—) and after (---) irradiation.

The obtained percent content of the isomers of FBs studied in solution after exposure to light was estimated according to Eqs. (3) and (4) [18]:

$$C_T = \frac{A_T(A'_C - A_C)}{A'_C A_T - A_C A'_T} 100\% \quad (3)$$

$$C_C = (100 - C_T)\% \quad (4)$$

where A_T and A_C are the absorption of the *trans*- and *cis*-isomers before exposing the solution. A'_T and A'_C are the respective absorption after exposure. C_T and C_C are the percent concentrations of the *trans*- and *cis*-isomers in the solution.

Table 4 presents the results for C_T and C_C of the two isomers for the FBs 1–7. In equilibrium in aqueous solution the concentration of *trans*- isomers prevails (C_T is 62–68%) for FBs 4–7 containing aliphatic residues as substituents whereas the aromatic residues (FBs 1–3) increase the *cis*-isomers (C_C is 52–65%). In ethanol solution the dependence is similar to this in aqueous solution.

In the isosbestic points the FBs concentration does not depend on the composition of *trans*- and *cis*-isomers in the solution, and can be used for quantitative measurements. The wavelength at isobestic points in aqueous solution λ_A is 301–307 nm (Table 1), while in ethanol solution it is in the region 304–310 nm (Table 2).

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