Photoisomerization of Triazine-stilbene Fluorescent Brighteners in Solution and in their Copolymers with Styrene

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The paper reports on the photochemical trans-cis isomerization of some new polymerizable triazine-stilbene fluorescent brighteners and their copolymers with styrene in aqueous and ethanol solutions. A dependence of trans-cis isomers in solution equilibrium and in solid polymeric films on the nature of the substituent in the triazine ring has been found.

Key words: Photoisomerization; Triazine-stilbene; Polymerizable Fluorescent Brighteners.

1. Introduction

Bleaching of polymeric materials can be achieved by blending or surface treatment with fluorescent brighteners, FBs [1]. In both cases the FB migrates with time, and the degree of whiteness decreases. The introduction of polymerizable groups into the FB makes it applicable in the copolymerization process with vinyl monomers, resulting in the formation of covalent bonds in the polymer molecule.

Fluorescent brighteners based on triazine-stilbene are well known as effective compounds for attaining high degrees of whiteness. They are substances with excellent brightening properties and are easy to produce. About 80% of the FBs produced are derived from stilbene [2]. The triazine-stilbene FBs are mainly used for whitening of cotton and polyamide textiles [3] as well as paper [4]. There exists extensive literature on FBs containing different amino and alkoxy derivatives in the triazine ring [2, 5]. The synthesis of some triazine-stilbene FBs containing different polymerizable groups is reported in [6–9], and investigation of their copolymers with acrylonitrile or styrene in [10–12]. In solution these FBs have low light resistance because they can exist in two stereoisomeric forms: *cis-* and *trans.* Exposure to light cause *trans-cis* isomerization with shift of the absorption maxima and formation of an equilibrium mixture. Isomerization to the *cis*-form results in a loss of fluorescence [13].

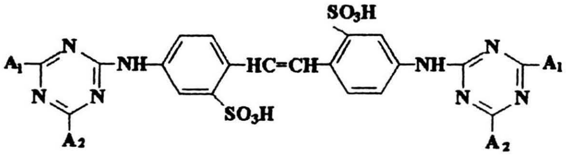
This article presents investigations on the photochemical trans-cis isomerization of triazine-stilbene fluorescence brighteners with polymerizable groups in the triazine ring in aqueous and ethanol solutions and their copolymers with styrene.

2. Experimental

2.1. Materials

(i) Triazine-stilbene fluorescent brighteners

Triazine-stilbenes with the following structure have been studied [6, 7]:



Scheme 1

FB	A_1	A_2
1	$-NHCOCH=CH_2$	$-NHC_6H_4SO_3H$ (2′)
2	$-NHCOCH=CH_2$	$-NHC_6H_4SO_3H$ (3′)
3	$-NHCOCH=CH_2$	$-NHC_6H_4SO_3H$ (4′)
4	$-NHCOCH=CH_2$	$-NHC_6H_3(SO_3H)_2$ (2′, 4′)
5	$-NHCOCH=CH_2$	$-NHCOCH=CH_2$
6	$-NHCOCH=CH_2$	–morpholino
7	$-NHCOCH=CH_2$	$-N(CH_3)_2$
8	$-NHCOCH=CH_2$	$-N(CH_2CH_3)_2$
9	$-OCOCCH_3=CH_2$	–morpholino
10	$-OCOCCH_3=CH_2$	$-N(CH_3)_2$
11	$-OCOCCH_3=CH_2$	$-N(CH_2CH_3)_2$

(i) Formation of poly(St-co-Fb) blends

The synthesis of poly(St-co-FB) is described in [12]. The concentration of FB in the copolymer was 1 wt%. The solid-state poly(St-co-FB) films were produced in the dark by slow evaporation of solutions of pure benzene by depositing 10% solutions on Petri disks with fixed diameter to control the thickness. Once the benzene was evaporated, the polymer films were removed and dried under vacuum at 40 °C for 24 hs to remove residual solvent. The polymer films, 30–40 μm thick, gave absorptions in the range of 0.8 to 1.0.

2.2. *Electron Absorption Measurements*

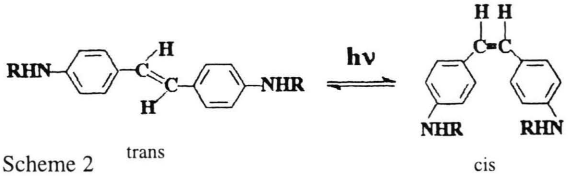
UV spectra were recorded using water and ethanol solutions at a concentration of $5 \cdot 10^{-5}$ mol · l^{-1} and solid copolymer, poly(St-co-FB), films on a Hewlet Packard 8452A spectrophotometer.

2.3. *Investigations of trans-cis Isomerization*

Photochemical trans-cis isomerization was studied in solutions at $2 \cdot 10^{-3}$ wt% FB and in a thin polymer film, after exposition to monochromatic light of 366 nm. The irradiation was carried out in an inert atmosphere to avoid photochemical breakdown. The course of isomerization was followed spectrometrically and by TLC. The reaction rate of photoisomerization and the final products in equilibrium were monitored by TLC using *n*-butanol:acetone:pyridin:25v-%NH_3 (1 : 0.25 : 1 : 1) on Silicagel plates (Fluka $F_{60}254$ 20×20; 0.2 mm). The chromatograms were developed by irradiation at 366 nm.

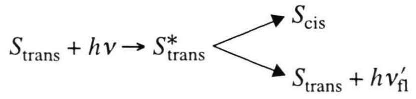
3. Results and Discussion

Triazine-stilbene fluorescent brighteners have poor photostability in solution. One of the major photoreactions causing loss of fluorescence is trans(e) → cis(z) isomerization, a reaction which involves rotation of the stilbene molecule around the central ethylene bond [14–16]. The photochemical process of trans-cis isomerization is illustrated in Scheme 2.



Scheme 2

The processes operative in the photoexcited trans-form FBs leading to a cis-conformation can be represented by Scheme 3:



$$S_{\text{trans}} + h\nu \rightarrow S^{*}_{\text{trans}} \begin{cases} \rightarrow S_{\text{cis}} \\ \rightarrow S_{\text{trans}} + h\nu'_{\text{fl}} \end{cases}$$

Scheme 3

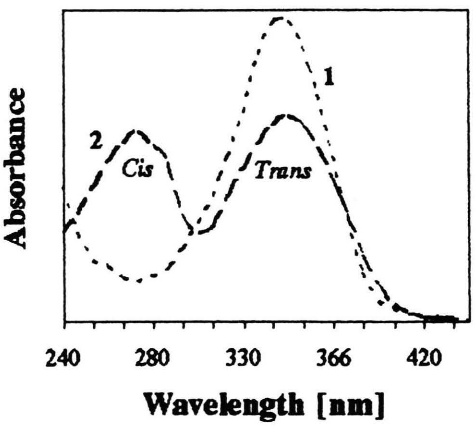


Fig. 1. Absorption spectra of FB6 in aqueous solution before, 1, and after, 2, irradiation.

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 $S_1 \rightarrow S_0$.

Figure 1 shows the absorption spectra of FB **6** in aqueous solution before and after irradiation. In the initial mixture the trans-isomer is predominantly excited. Its concentration decreases during irradiation while that of the cis-isomer increases till equilibrium is reached. The two isomeric forms have different absorption maxima. The trans-isomer absorbs at 343–238 nm in aqueous solution and 346–350 nm in ethanol, while the cis-isomer is hypsochromically shifted to 260–274 nm for both solvents (Tables 1 and 2). The absorption spectra observed for triazine-stilbene FBs are in agreement with the literature [17–20]. In daylight, the photostationary state favours the cis-isomer. This leads to disintegration of the molecular compactness. Thus the cis-isomers lose their fluorescence properties and affinity to the brightened material, and the FBs become less effective. Figure 2 shows the changes in the concentration of transsomers of FBs in aqueous solution occurring with irradiation time. As seen, the photoisomerization is a reaction of first order. The rate constants *K* of isomerization are calculated according to:

$$K = \frac{2.3}{t} \lg \frac{A_0}{A}, \tag{1}$$

where A_0 and A are the absorptions of FBs in trans from before and after irradiation for the time t. The calculated rate constants K are between $2.2 \cdot 10^{-3}$ and $7.4 \cdot 10^{-4}$ s^{-1}.

Table 1. Absorption maxima (λ_A) of cis and trans isomers, isobestic points and retention factors R_f of the fluorescent brighteners **1–11** in aqueous solution.

FB	cis λ_A (nm)	trans λ_A (nm)	trans log ε	Isobestic point (nm)	R_f cis	R_f trans
1	260	348	4.04	300	0.20	0.58
2	268	344	4.03	302	0.24	0.61
3	270	346	4.02	302	0.25	0.66
4	268	348	4.05	304	0.13	0.53
5	265	343	4.01	302	0.32	0.60
6	268	348	4.05	303	0.42	0.71
7	264	346	4.06	305	0.36	0.73
8	265	346	4.02	306	0.42	0.68
9	266	348	4.12	302	0.13	0.41
10	268	346	4.02	304	0.21	0.51
11	272	346	4.09	304	0.24	0.57

Table 2. Absorption maxima (λ_A) of cis and trans isomers and isobestic point of the fluorescent brighteners **1–11** in ethanol solution.

FB	cis λ_A (nm)	trans λ_A (nm)	trans log ε	Isobestic point (nm)
1	264	350	4.08	303
2	266	348	4.07	303
3	268	350	4.09	304
4	268	350	4.10	305
5	262	346	4.09	302
6	270	352	4.12	305
7	272	348	4.16	307
8	274	350	4.18	306
9	272	350	4.16	305
10	274	348	4.16	304
11	274	348	4.15	306

Table 3. Percentages of the trans-(C_t) and cis-(C_c) forms of the fluorescent brighteners **1–11** in aqueous and ethanol solutions.

FB	in Water C_t	in Water C_c	in Ethanol C_t	in Ethanol C_c
1	34	66	32	68
2	35	65	34	64
3	35	65	32	68
4	36	64	33	67
5	28	72	26	74
6	64	36	61	39
7	65	35	63	37
8	65	35	61	39
9	65	35	60	40
10	66	34	62	38
11	66	34	63	37

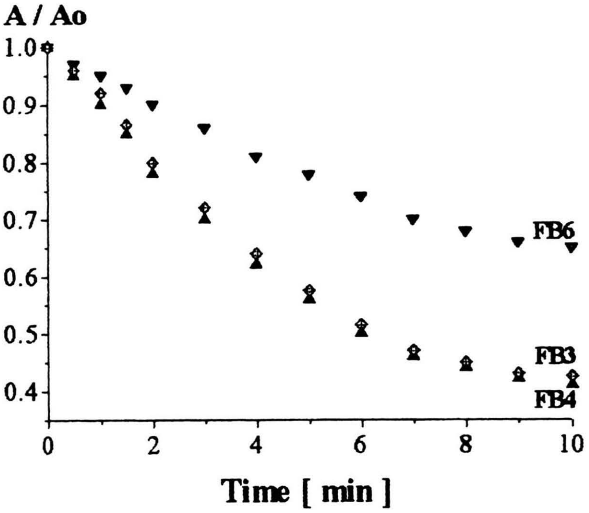


Fig. 2. Irradiation time dependence of trans isomer conversion of the FBs **3**, **4** and **6** in aqueous solution.

At the isobestic points the FBs when the concentration does not depend on the composition of trans- and cis-isomers in the solution, can be used for quantitative measurements. The wavelength λ_A at the isobestic point in aqueous solution is 300–306 nm (Table 1), and in ethanol solution it is in the region 303–307 nm (Table 2).

The obtained percent content of the isomers of FBs studied in solution after exposition to light was estimated according to [21]

$$C_t = \frac{A_t(A_c' - A_c)}{A_c' A_t - A_c A_t'} 100\% \qquad (2)$$

and

$$C_c = (100 - C_t)\ \%,$$

where A_t and A_c are the absorptions of the trans- and cis-isomers before exposing the solution. A_t' and A_c' are the respective absorptions after exposure. C_t and C_c are the percentage concentrations of the trans- and cis-isomers in the solution.

Table 3 presents the resulting C_t and C_c for the two isomers of the FBs **1–11**. At equilibrium in water the concentration of trans-isomers prevails (C_c is 64–66%) for the FBs **6–11** containing as substituents A_1 aliphatic residues, whereas the aromatic residues (FBs 1–5) increase the cis-isomers (C_c is 66–72%). In ethanol solution the dependence is similar to that in aqueous

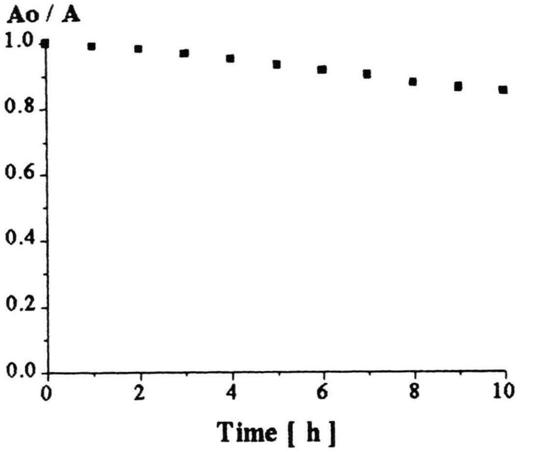


Fig. 3. Irradiation time dependence of the relative trans isomer absorption of FB **9** in a poly(St-co-FB**9**) solid film.

solution. The results achieved show that the nature of the substituent A_2 affects significantly the contents of trans and cis isomers in equilibrium. Aromatic substituents (FBs **1–5**) favour the trans → cis isomerization to a greater degree.

Figure 3 shows the change with time of the trans isomer of poly(St-co-FB**9**) as an example for copolymers. As seen, in solid poly(St-co-FB**9**) film the trans-cis isomerizations negligible, which is due to the chemical bonding of FBs to the polymer chain. On the other hand it is due to the firm fixation the FBs in the solid polymeric matrix. Thus there is little possibility for conformational changes in the chromophoric system of the FBs. The intensity blue fluorescence at UV irradiation confirms the latter fact [12].

It is well know that the triazine-stilbene FBs show two values for the retention factor R_f from TLC, characteristic for the two stereoisomeric forms [22, 23]. Table 1 selects data of the retention factor R_f for the trans- and cis-isomers of the triazine-stilbene FBs **1–11** obtained from the trans-cis isomeric mixtures. It is seen that the two isomers of the FBs studied have different retention factors R_f, which is an indication of the different absorbencies. The cis form is due to the disturbed coplanarity of the molecule and to the weaker substantiality and lower R_f values.

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