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The Synthesis and Properties of some Triazene–Stilbene Fluorescent Brighteners

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ABSTRACT

Some triazene–stilbene fluorescent brighteners containing methacrylic groups have been synthesised. Their fluorescence and absorption characteristics in solution in water, methanol, ethanol and dioxane are reported, and studies made on their copolymerisation with styrene and on their bleaching effect on cotton.

1 INTRODUCTION

Triazene–stilbene fluorescent brighteners (FBs) are widely used in the textile and paper industry. A large number of FBs of this class, containing different amino and alkoxy derivatives in the triazene ring is known.[1] The introduction of unsaturated polymerisable groups into their structure enables them to be used in copolymerisation processes with vinyl monomers, resulting in the formation of covalent bonds in the polymer molecule. We have previously reported the synthesis of a group of triazene–stilbene FBs containing allyl groups in the triazene ring[2] and also concluded that, during the polymerisation of acrylonitrile in the presence of these FBs, a covalent bond was formed in the polymer molecule.[3] When used for the whitening of textile materials[4] and paper[5] they provide a high degree of brightness and have good light stability. We now report the synthesis of some triazene–stilbene FBs, containing methacrylic groups and a study of their properties and application.

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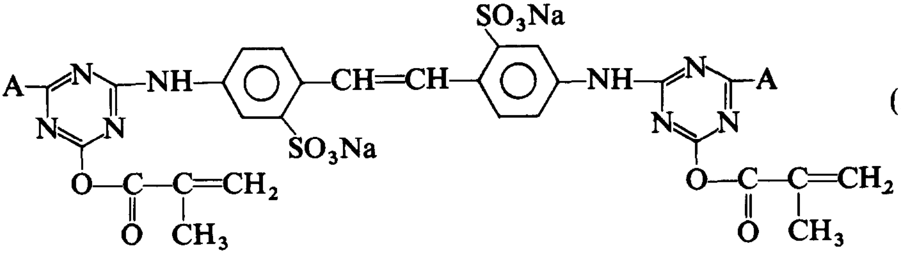
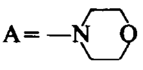
2 RESULTS AND DISCUSSION

2.1 Synthesis of FBs

The FBs prepared have the general formula (1):



(1)



1a; $-N(CH_3)_2$ 1b; $-N(C_2H_5)_2$ 1c

Compounds **1a**–**1c** were obtained by conventional methods. Thus, 2 mol of cyanuric chloride was reacted with 1 mol of 4,4'-diaminostilbene-2,2'-disulphonic acid in water–acetone (1 : 1) at 0–5°C for 2 h, maintaining a pH of 6 by addition of 10% aqueous sodium hydroxide. When the first condensation stage was complete, the temperature was increased to 25–30°C and 2 mol of the corresponding amine AH added at pH 7. After 3 h the temperature was increased to 80°C, 2 mol of sodium methacrylate were added and reaction was continued at 80°C for 5 h. After cooling to ambient temperature the product was isolated by addition of sodium chloride. The FBs thus obtained were very soluble in water, alcohols, dioxane and dimethylformamide (DMF) and showed an intense blue fluorescence in solution. Characterisation data are shown in Tables 1 and 2.

2.2 Spectral data

The absorption and fluorescence characteristics in water, methanol, ethanol and DMF solutions are presented in Table 2. The compounds absorbed in the UV region (λ_{max} 346–350 nm) in water, methanol and ethanol; in DMF a bathochromic shift of 24–26 nm was observed. FBs pass from the basic singlet S_0 to the first excited state S_1 on light absorption. The energy of the excited state E_{s_1} and the corresponding λ_{s_1} were determined. The energy of the excited state E_{s_1} in water, methanol or ethanol is 72 kcal mol^{-1}, while in DMF solution it is 70 kcal mol^{-1}. The FB molecule is deactivated on fluorescence light emission, and passes

TABLE 1
Characterisation Data for FB of Formula (1)

FB	*Yield (%)*	*Elemental analysis N (%)*	*FT-IR (KBr) (cm^{-1})*	*^{1}H-NMR: δ (ppm) (DMSO)*
1a	81	Calc.: 15·38 Found: 15·29	3243 [ν(—NH)] 1755 [ν(—C=O)] 1636 [ν(=CH_2)] 1590 [ν(C=N)] 1235 [ν(SO_2)] 1061 [ν(C—O—C)] 771 [δ(CH—Ar)]	10·3 (s, 2H, NH) 7·4–8·2 (m, 8H) 4·3–5·2 (m, 4H, =CH_2) 3·1–3·4 (t, 16H, —CH_2—) 1·2–1·4 (t, 6H, —CH_3)
1b	84	Calc.: 16·94 Found: 16·80	3238 [ν(—NH)] 1740 [ν(—C=O)] 1639 [ν(=CH_2)] 1586 [ν(C=N)] 1354 [δ(—CH_3)] 1241 [ν(SO_2)] 770 [δ(CH—Ar)]	10·8 (s, 2H, NH) 7·1–8·1 (m, 8H) 4·4–5·2 (m, 4H, =CH_2) 2·0 (s, 6H, —CH_3) 1·1 (s, 12H, —CH_3)
1c	82	Calc.: 15·89 Found: 15·60	3219 [ν(—NH)] 1742 [ν(—C=O)] 1640 [ν(=CH_2)] 1587 [ν(C=N)] 1351 [δ(—CH_3)] 1238 [ν(SO_2)] 771 [δ(CH—Ar)]	10·6 (s, 2H, NH) 7·3–8·2 (m, 8H) 4·4–5·1 (m, 4H, =CH_2) 3·4–3·6 (q, 8H, $\underline{CH_2}CH_3$) 1·4–1·7 (t, 12H, $CH_2\underline{CH_3}$) 1·1 (s, 6H, —CH_3)

from the S_1 to the basic S_0 state. The lifetime in the excited state is given by the expression:[6]

$$\tau_L^0 = \frac{3{\cdot}33 \times 10^8}{\bar{\nu}_{max}^2 \int_{\bar{\nu}_1}^{\bar{\nu}_2} \varepsilon \, . \, d\bar{\nu}}$$

The values of τ_L^0 determined indicate that the lifetime is within the range 3–10 × 10^{-8} s.

The FBs emitted in the blue region at λ_{max} 434–444 nm. The Stoke's shifts in water, ethanol or methanol solution was 88–90 nm, while in DMF it was 68–70 nm. In the IR spectra, intense bands at 1740–1755 cm^{-1} are typical for the vibration of the C=O group and the bands recorded at 1636–1640 cm^{-1} are due to the presence of the =CH_2 bond, showing that metacrylic groups are present. This is additionally confirmed by ^{1}H-NMR spectral data, where a complex multiplet,

TABLE 2
Absorption and Fluorescence Characteristics of FBs in Various Solvents

	Water			*Methanol*			*Ethanol*			*DMF*		
	1a	*1b*	*1c*	*1a*	*1b*	*1c*	*1a*	*1b*	*1c*	*1a*	*1b*	*1c*
λ_{abs} (nm)	348	346	346	350	348	348.	350	348	348	374	370	372
log ε	4·12	4·08	4·09	4·16	4·12	4·12	4·16	4·16	4·15	4·24	4·22	4·21
λ_{fl} (nm)	438	434	436	406	404	404	406	404	404	406	403	403
				440	436	438	440	436	438	444	440	440
λ_{S_1} (nm)	386	390	388	390	386	386	390	388	386	409	410	408
E_{S_1} (kcal mol^{-1})	72	72	72	72	72	72	72	72	72	70	70	70
Stokes shift (nm)	90	88	90	90	88	90	90	90	90	70	70	68
τ_L^0 (10^{-8} s)	5	4	4	3	5	6	4	4	5	9	10	10

characteristic for the protons of the $=CH_2$ group is observed in the range 4·3–5·2 ppm. Full data are shown in Table 1.

2.3 Bleaching of cotton

Compounds **1a**–**1c** were applied at an initial concentration of 0·6 wt %, to cotton using the procedure previously described.[4] The degree of whiteness and the CIE-coordinates were determined using the D_{65} light source. The results obtained are presented in Table 3. It is apparent that the compounds impart a high degree of whiteness with a very weak red–violet nuance (R1) and a good resistance to light.

2.4 Copolymerisation with styrene

The polymerisation was carried out for 8 h in an inert atmosphere[7] at 80°C in the presence of 0·2 wt % of FB and of 0·1 wt % of dibenzoyl

TABLE 3
Degree of Whiteness and Colour Data for 100% Cotton Treated with FBs

FB	*Whiteness*		*Tint value for classment*		*Coordinates*			*Light-fastness*
	Berger	*CIE*			*x*	*y*	*Y*	
1a	149·7	148·0	−0·6	R1	0·294	0·302	80·876	4
1b	160·0	154·8	−1·1	R1	0·291	0·299	82·334	4
1c	159·9	152·8	−1·3	R1	0·292	0·301	83·452	4

TABLE 4
Molecular Masses and Polydispersity of Homopolystyrene and Corresponding Copolymers with FBs

FB	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	M_w/M_n
1a	1·19	4·25	2·80
1b	1·31	5·28	2·48
1c	1·24	4·75	2·61
—	1·58	7·49	2·11

peroxide, an initiator. Transparent polymers having a blue fluorescence were obtained. The intense fluorescence was retained after three- to four-fold precipitation of the polymers from toluene and ethanol, thus indicating the presence of a covalent bond between the FB and the polymer molecule. It was found that the polymer contained over 90% of the FB introduced, as determined spectrophotometrically. The molecular mass and the polydispersity of the polymers were also determined and the values obtained were not essentially affected by the presence of the FB (Table 4).

3 EXPERIMENTAL

IR spectra (KBr) were recorded on a Perkin-Elmer 1600 FT–IR, UV–Vis spectra were recorded (using water, methanol, ethanol and DMF solutions of a concentration of $2 \cdot 10^{-5}$ mol litre^{-1}) on a Hewlett Packard 8452A and fluorescence spectra on a Perkin-Elmer MPF 44. The colour coordinates of the textiles were determined using a Texflach ACS/DATA COLOR spectrophotometer. Molecular masses of the polymers were determined using a TOSO HLC-802 UR gel permeation chromatograph with a TSK-GEL H-type column, in tetrahydrofuran, using styrene as standard.

3.1 General method for preparation of FBs

Cyanuric chlorides were (0·02 mol) dissolved in 50 ml of acetone and the solution was added to a 50 ml cold aqueous solution of 0·01 mol 4,4'-diaminostilbene-2.2'-disulphonic acid. After stirring for 2 h at 0–5°C, keeping a pH of 6 through addition of 10% aqueous sodium hydroxide, the temperature was raised to 30°C and 0·02 mol morpholine, dimethylamine or diethylamine were added. The mixture was then stirred for 3 h at pH 7 and the temperature was increased to 80°C prior to addition of 0·02 mol sodium methacrylate. After a further 3 h the mixture was cooled to ambient temperature. Sodium chloride was added and the precipitate obtained was filtered and dried under vacuum at 40°C.

3.2 Copolymerisation with styrene

Styrene (10 g), 0·02 g of FB (**1a**, **1b** or **1c**) and 0·01 g dibenzoyl peroxide were placed in a glass ampoule, and the system was purged with N_2. The sealed ampoule was heated in a thermostat for 8 h at 80°C. The resultant polymers were dissolved in toluene and reprecipitated by addition of ethanol. This procedure was repeated several times and then the polymers were finally dried under vacuum at 40°C.

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