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The Synthesis and Properties of Some Triazine–Stilbene Fluorescent Brighteners

Ivo Grabchev

Institute of Polymers, Bulgarian Academy of Sciences,
BG-1113 Sofia, Bulgaria

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ABSTRACT

New triazine–stilbene fluorescent brighteners containing an acrylamide group have been synthesized. Their absorption and fluorescence characteristics in aqueous solution were investigated and their fluorescence quantum yields (0·24–0·36) estimated. The compounds gave a high degree of whiteness on polyamide-6.

1 INTRODUCTION

Triazine–stilbene fluorescent brighteners (FBs) are known to be effective compounds for attaining high degrees of whiteness[1] and we have previously reported the synthesis of some triazine–stilbene FBs containing unsaturated polymerizing groups, and their copolymerization with acrylonitrile and styrene.[2–5]

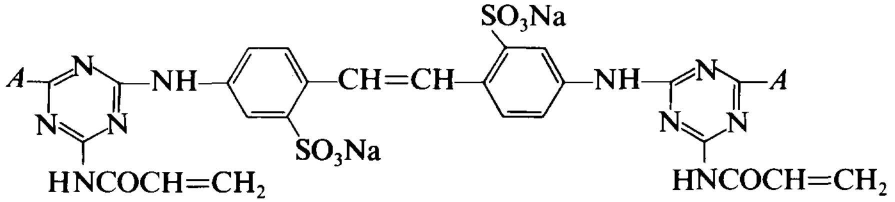
We report here the synthesis of some triazine–stilbene FBs containing an acrylamide group, and an evaluation of their properties.

2 RESULTS AND DISCUSSION

2.1 Synthesis

The FBs synthesized were of general formula **1**.

They were prepared by established methods, whereby 1 mol of 4,4'-diaminostilbene-2,2'-disulphonic acid was reacted with 2 mol of cyanuric



1

A = $NHCOCH{=}CH_2$ **1a** morpholino **1b**
$N(CH_3)_2$ **1c** $N(C_2H_5)$ **1d**
$NHC_6H_4SO_3Na\text{-}2'$ **1e** $NHC_6H_4SO_3Na\text{-}4'$ **1f**
$NHC_6H_3SO_3Na\text{-}3'$ **1g** $NHC_6H_3(SO_3Na)_2\text{-}2'4'$ **1h**

chloride at 0–5°C, while maintaining the pH at 6 by addition of 10% aqueous sodium hydroxide. The reaction mixture was stirred for 2 h, the temperature increased to 55–60°C and 2 mol of acrylamide was then added. Stirring was continued for a further 4 h at pH 7 and after this second acylation stage the temperature was increased to 75–80°C and 2 mol of the respective amine (AH) was added. The mixture was stirred for 4 h at pH 8 and then cooled to ambient temperature. The product was isolated by addition of sodium chloride. Relevant characterization data are shown in Table 1.

2.2 Spectral data

The absorption and fluorescence characteristics of the FBs were studied in aqueous solution at ambient temperature and in anhydrous ethanol at 77 K (Table 2).

In aqueous solution, the FBs absorbed in the UV region (λ_{max} 342–348 nm). Fluorescence emission was observed in the region 380–490 nm with a well pronounced maximum at 430–442 nm. The difference between absorption and emission values for the different FBs was not very large, indicating that the nature of the third substituent does affect the main fluorescence of the chromophoric system. By estimating the intersection of the fluorescence and absorption spectra it was found that the fluorescence emission values in the anhydrous ethanol were close to those in aqueous solution. The FBs studied did not phosphoresce either in aqueous solution or in anhydrous ethanol at 77 K, indicating that when excited they were in the singlet state (S_1).

The quantum yields of fluorescence were determined in aqueous solution using sodium salycilate as standard.[6] The results were in the region 0·24–0·36, which shows that the fluorescence involves non-emission deactivation of the S_1 state.

TABLE 1
Characterization Data for FBs

FB	*Yield (%)*	*Elemental analysis (N%)*	*FT-IR (KBr) (cm^{-1})*	*^1H NMR δ (ppm) (DMSO)*
1a	76	Calculated: 19·80 Found: 19·69	3248 [ν(—NH)] 1660 [ν(C=O)] 1621 [ν(CH_2=)] 1580 [ν(C=N)] 1236 [ν(SO_2)] 770 [δ(CH-Ar)]	10·6 (s, 2H NH) 7·6–8·1 (m, 8H) 6·3 (s, 4H NHCO) 4·6–4·9 (m, 4H CH=) 5·4–5·5 (m, 8H CH_2=)
1b	84	Calculated: 19·08 Found: 18·96	3251 [ν(—NH)] 1663 [ν(C=O)] 1624 [ν(CH_2=)] 1584 [ν(C=N)] 1236 [ν(SO_2)] 1061 [ν(C—O—C)] 770 [δ(CH-Ar)]	10·7 (s, 2H NH) 7·4–8·2 (m, 8H) 6·4 (s, NHCO) 5·3–5·8 (m, 4H CH_2=) 4·6–4·9 (m, 2H CH=) 3·2–3·5 (t, 16H —CH_2—)
1c	83	Calculated: 21·09 Found: 20·96	3261 [ν(—NH)] 1679 [ν(C=O)] 1624 [ν(CH_2=)] 1590 [ν(C=N)] 1230 [ν(SO)] 1350 [δ(CH_3)] 770 [δ(CH-Ar)]	10·8 (s, 2H NH) 7·5–8·4 (m, 8H) 6·5 (s, NHCO) 5·6–5·9 (m, 4H CH_2=) 4·7–5·0 (m, 2H CH=) 1·3 (t, 12 H—CH_3)
1d	83	Calculated: 19·71 Found: 19·63	3267 [ν(—NH)] 1678 [ν(C=O)] 1621 [ν(CH_2=)] 1583 [ν(C=N)] 1351 [δ(CH_3)] 1231 [ν(SO_2)] 772 [δ(CH-Ar)]	10·7 (s, 2H NH) 7·5–8·5 (m, 8H) 6·6 (s, 2H NHCO) 5·4–6·0 (m, 4H CH_2=) 4·8–5·1 (m, 2H CH=) 3·3–3·6 (q, 8H $\underline{CH_2}CH_3$) 1·1 (s, 12H CH_2—$\underline{CH_3}$)
1e	79	Calculated: 15·30 Found: 15·20	3281 [ν(—NH)] 1678 [ν(C=O)] 1622 [ν(CH_2=)] 1581 [ν(C=N)] 1230 [ν(SO_2)] 771 [δ(CH-Ar)]	10·9 (s, 4H NH) 7·6–8·6 (m, 16H) 6·4 (s, 2H NHCO) 5·3–5·7 (m, 4H CH_2=) 4·7–5·2 (m, 2H CH=)
1g	80	Calculated: 15·30 Found: 15·19	3282 [ν(—NH)] 1674 [ν(C=O)] 1620 [ν(CH_2=)] 1583 [ν(C=N)] 1232 [ν(SO_2)] 770 [δ(CH-Ar)]	10·8 (s, 4H NH) 7·4–8·4 (m, 16H) 6·2 (s, 2H NHCO) 5·5–5·9 (m, 4H CH_2=) 4·6–5·2 (m, 2H CH=)

continued

TABLE 1—*contd.*

FB	*Yield (%)*	*Elemental analysis (N%)*	*FT-IR (KBr) (cm^{-1})*	*^1H NMR δ (ppm) (DMSO)*
1f	76	Calculated: 15·30 Found: 15·18	3279 [ν(—NH)] 1672 [ν(C=O)] 1622 [ν(CH_2=)] 1579 [ν(C=N)] 1233 [ν(SO_2)] 771 [δ(CH-Ar)]	10·9 (s, 4H NH) 7·3–8·1 (m, 16H) 6·1 (s, 2H NHCO) 5·4–5·8 (m, 4H CH_2=) 4·5–5·0 (m, 2H CH=)
1h	68	Calculated: 12·90 Found: 12·78	3283 [ν(—NH)] 1670 [ν(C=O)] 1619 [ν(CH_2=)] 1583 [ν(C=N)] 1231 [ν(SO_2)] 770 [δ(CH-Ar)]	11·0 (s, 4H NH) 7·6–8·6 (m, 14H) 6·6 (s, 2H NHCO) 5·2–5·6 (m, 4H CH_2=) 4·5–5·0 (m, 2H CH=)

IR spectra showed intense absorption at 1663–1640 cm^{-1} (C=O group), and weak vibrations at 1624–1619 cm^{-1} (double bond of the acrylamide group). Strong bands were also observed at 1585–1579 cm^{-1} (triazine C=N). The ^{1}H NMR spectra showed a multiplet at 4·6–5·0 (=CH_2), a multiplet at 5·4–5·9, and a singlet at 6·4 (proton of amide nitrogen atom on acrylamide group).

2.3 Whitening of nylon-6

Whitening of nylon-6 was carried out for 30 min at a concentration of 0·6% with respect to the material, at pH 4–4·5 (CH_3COOH) and 75–80°C using a liquor ratio of 40:1.[7] The degree of whiteness was determined, together with

TABLE 2
Absorption and Fluorescence Characteristics of FBs in Water

	1a	*1b*	*1c*	*1d*	*1e*	*1f*	*1g*	*1h*
λ_{abs} (nm)	343	348	346	346	348	346	344	348
log ε	4·01	4·05	4·06	4·06	4·04	4·02	4·03	4·05
λ_{fl} (nm)	430	436	438	438	442	440	438	436
λ_{s_1} (nm)	382	394	398	396	400	396	398	400
E_{s_1} (KJ mol^{-1})	313·9	303·8	300·8	302·3	299·3	302·3	300·8	299·3
Stokes' shift (cm^{-1})	5898	5800	6070	6070	6111	6174	6238	5800
Quantum yield of fluorescence	0·24	0·31	0·33	0·36	0·34	0·34	0·28	0·25

TABLE 3
Degree of Whiteness and Color Data for Nylon-6 Treated with FBs

FB	*Whiteness (CIE)*	*Coordinates*			*Tint value*	*Light fastness*
		x	*y*	*Y*		
1a	142·1	0·295	0·308	82·549	−0·9 R1	4–5
1b	146·8	0·293	0·305	83·149	−1·3 R1	5
1c	152·1	0·292	0·305	84·106	−1·0 R1	5
1d	151·3	0·296	0·300	84·006	−1·1 R1	5
1e	148·2	0·294	0·298	85·142	−0·6 R1	4–5
1f	152·4	0·292	0·299	85·004	−0·6 R1	4–5
1g	150·1	0·298	0·300	84·518	−0·8 R1	4–5
1h	149·2	0·249	0·304	83·398	−0·8 R1	4–5

respective color data and light fastness. Results are shown in Table 3. It can be seen that the FBs studied impart a high degree of whiteness with a weak violet hue R1 and that they have good resistance to light.

2.4 Copolymerization with styrene

Styrene was copolymerized with 0·2 wt% **1b** and **1c** for 8 h in an inert atmosphere at 80°C. Benzoyl peroxide was used as an initiator for the radical polymerization.[3] The obtained polystyrene was transparent, having a blue fluorescence. The polymer chain contained about 90% of the FB introduced, as determined spectrophotometrically. The presence of FBs in the polymer chain did not significantly affect the molecular mass or polydispersity of the polystyrene.

3 EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 1600 FT-IR, UV/Vis spectra on a Hewlett Packard 8452A, using aqueous solutions of concentration 5×10^{-5}mol l^{-1}, and fluorescence spectra on Perkin-Elmer MPF 44. The color coordinates of the fabrics were determined using a Texflach ACS/ Datacolor spectrophotometer.

3.1 Preparation of 4,4'-bis[(4-morpholino-6-acrylamid-2-yl-amino)]stilbene-2,2'-disulphonic acid

Cyanuric chloride (0·02 mol) was dissolved in 50 ml acetone and the solution was added to a 50 ml aqueous solution of 0·01 mol 4,4'-diaminostilbene-2,2'-disulphonic acid at 0–5°C. After stirring for 2 h, whilst maintaining pH 6 by addition of 10% aqueous sodium hydroxide, the liquor was heated to 55–60°C; 0·02 mol acrylamide was added and stirring continued for 4 h at pH 7. The temperature was then raised to 80–85°C, 0·02 mol morpholine was added and the mixture stirred for 4 h at pH 8. The reaction mixture was cooled and the product isolated by addition of sodium chloride. The precipitate was filtered, washed with cold (0°C) aqueous acetone (1:1) and dried under vacuum at 40°C.

The other FBs were similarly prepared.

3.2 Copolymerization with styrene

Styrene (10 g), 0·02 g of the appropriate FB (**1a**, **1b** or **1c**) and 0·01 g dibenzoylperoxide were placed in a glass ampoule, and the system purged with N_2. The sealed ampoule was heated 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 the polymers were finally dried under vacuum at 40°C.

REFERENCES

1. Anliker, R. & Muller, G., *Fluorescence Whitening Agents in Environmental Quality and Safety*. Thieme, Stuttgart; 1975, Vol. IV.
2. Konstantinova, T. & Grabchev, I., *Comp. Rendu. Acad. Bulg. Sci.*, **44**(10) (1991) 59.
3. Grabchev. I., *Dyes and Pigments*, **25** (1994) 249.
4. Konstantinova, T. & Grabchev, I., *Angew. Makromol. Chem.*, **196** (1992) 107.
5. Konstantinova, T., Grabchev, I. & Konstantinov, H., *Angew. Makromol. Chem.*, **221** (1994) 45.
6. Weber, G. & Teale, F., *Trans Faraday Soc.*, **53** (1957) 646.
7. Grabchev, I. & Konstantinova, T., *Mell. Textilber.*, **2** (1994) 125.