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Dyes and Pigments 43 (1999) 197–201

DYES and PIGMENTS

The synthesis and properties of some unsaturated triazinylstilbene fluorescent brightening agents

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Received 26 February 1999; accepted 10 May 1999

Abstract

Eleven unsaturated triazinylstilbene fluorescent brightening agents were synthesized. They were capable of copolymerization with styrene and acrylonitrile, giving colourless fluorescent polymers having good stability to wet treatments and solvents. The spectral and thermal properties, brightening effect on cotton and CIE coordinates were evaluated. © 1999 Elsevier Science Ltd. All rights reserved.

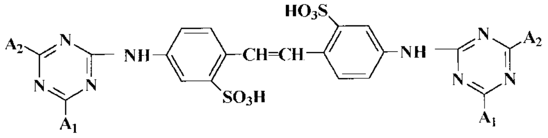
Keywords: Polymerizable fluorescent brightening agents; Triazinylstilbene derivatives

1. Introduction

Among various classical fluorescent brightening agents (FBAs), triazinylstilbene derivatives play an important role [1]. We have previously reported [2–4] the synthesis of some triazinylstilbene derivatives containing unsaturated groups, which enabled them to undergo copolymerization with styrene (St) and acrylonitrile (AN), providing colourless fluorescent polymers which were stable to wet treatments and solvents, due to the covalent bond of the FBAs in the polymer molecule. Therefore, it was of interest to synthesize other derivatives of this type and to study their properties as FBAs for polymers.

2. Results and discussion

The FBAs synthesized in this present study were of general formula **I**; A_1 and A_2 are designated in Table 1:



I

2.1. Synthesis

The synthesis of the compounds under investigation can be achieved by two methods: (a) 4,4′-diaminostilbene-2,2′-disulfonic acid (DASSA) is initially reacted with cyanuric chloride (CC) and

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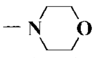
PII: S0143-7208(99)00061-3

Table 1
Characterization data for compounds **I**

No.	A_1	A_2	λ_{max} (nm)	$\log \epsilon$
1	$-NHC_6H_5$	$-NHCH_2CH{=}CH_2$	354	1.3
2	$-NHC_6H_5$	$-N(CH_2CH{=}CH_2)_2$	352	0.8
3	$-NHC_6H_5$	$-NHCOCH{=}CH_2$	350	0.4
4	$-NHC_6H_5$	$-NHCOC(CH_3){=}CH_2$	352	0.5
5	$-NHC_6H_5$	$-OCOC(CH_3){=}CH_2$	352	0.3
6	$-NHC_2H_4OH$	$-NHCH_2CH{=}CH_2$	342	0.4
7	$-NHC_6H_4SO_3H(p)$	$-NHCH_2CH{=}CH_2$	348	1.1
8		$-NHCH_2CH{=}CH_2$	350	0.7
9	$-N(CH_3)_2$	$-NHCH_2CH{=}CH_2$	352	0.8
10	$-N(C_2H_5)_2$	$-NHCH_2CH{=}CH_2$	352	0.6
11	$-NHCH_2CH{=}CH_2$	$-NHCH_2CH{=}CH_2$	350	0.3

the resulting compound $\mathbf{1^a}$ then reacted stepwise with A_1H and A_2H (Scheme 1).

In order to obtain good results from this method, we had to determine which compound should react as A_1H and which as A_2H, bearing in mind that the reaction conditions depended both on the activity of the reagent A_2H and on the influence of the residue A_1 already present in the triazine ring [5,6]. We studied this process based on our previous investigations on the synthesis of triazine derivatives [6]. The data obtained here showed that better results were achieved when *unsaturated* compounds, viz. allyl- or diallylamines, acryl- or methacrylamides and methacrylic acid, were used as an A_2H reagent.

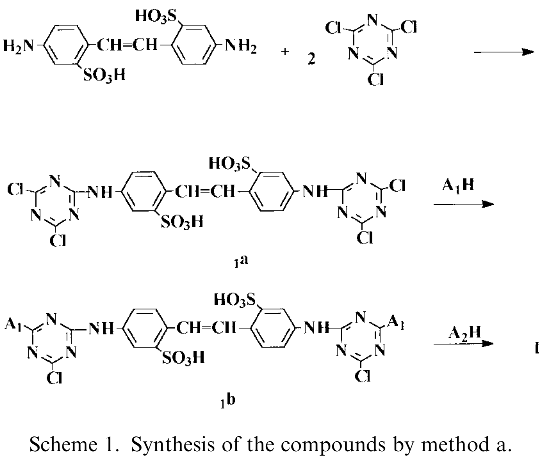
(b) The second method involved CC being initially reacted with compound A_1H. The product obtained ($\mathbf{2^a}$) then firstly reacted with A_2H and then $\mathbf{2^b}$ finally reacted with DASSA (Scheme 2)

A_1H and A_2H were the same as in method (a) (shown in Table 1), i.e. the unsaturated compounds were A_2H reagents.

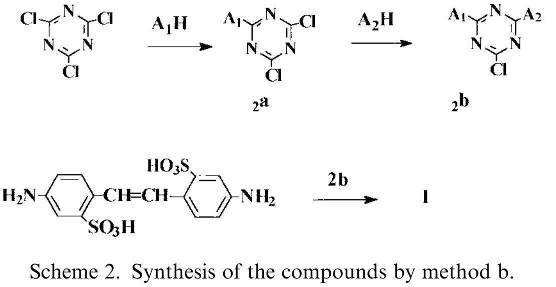
The advantages of this method were that the reaction of the unsaturated compounds with CC could be performed at lower temperature in an organic solvent and the semi-products $\mathbf{2^a}$ and $\mathbf{2^b}$ could be easily isolated and purified before their reaction with DASSA at the final step.

We synthesized all the compounds by these two methods, and comparing the results obtained, bearing in mind both their advantages and disadvantages, we concluded that the first method was the better method.

According to Scheme 1, 2 mol of CC reacted with 1 mol of DASSA in dioxan-water (1:1, v/v) at 0–5°C. The course of the reaction was monitored by TLC on silica gel (under UV light) and the pH was maintained at 7 by adding 30% aq NaOH. After 1 h, when the first stage was completed, 2 mol of the corresponding amine A_1H was added to the mixture, the temperature was increased to 30–40°C and pH was maintained at 7.5–8, depending on the character of the amine A_1H. The reaction was complete in 1.5 h, and 2 mol of the corresponding A_2H reagent (allyl- or diallylamine, acryl- or methacrylamide or sodium methacrylate) was then added. This last stage was carried out at reflux temperature, keeping pH 7–9 (addition of 30% aq NaOH) and in the presence of an inhibitor, i.e. *t*-butylcatechol. After 2 h the product **I** was isolated and dried under vacuum at 30°C. The compounds were soluble in water, dioxan, DMF and methanol and their solutions showed a very intense blueish fluorescence. They were characterized and identified by elemental analysis, UV/Vis



Scheme 1. Synthesis of the compounds by method a.



Scheme 2. Synthesis of the compounds by method b.

and ^{1}H NMR spectra. Some of these data are presented in Table 1 and other data is given in Experimental section.

2.2. *Spectral and thermal data*

The UV/Vis absorption of the compounds in DMF and water were recorded and the data received is presented in Table 1. All compounds absorbed in the UV region between 340 and 355 nm, which is characteristic for this type of FBAs; in DMF a bathochromic shift of 10–15 nm was observed. Based on the results thus obtained, compounds containing anilino or sulfoanilino–allylamino residues offered the best results.

In order to evaluate the thermal properties of the FBAs, which are of importance for their application to polymers, thermal analysis of the compounds was carried out. Their thermo-oxidative destruction began above 310°C and proceeded over the range 315–470°C. This showed that the compounds were sufficiently stable in order to be applied in polymer materials.

2.3. *Polymerization with styrene and acrylonitrile*

The ability of the synthesized FBAs to copolymerize with styrene and acrylonitrile was studied. The polymerization of styrene was carried out in bulk at 80°C in the presence of ABIN as an initiator (0.5 wt%) and 0.1 wt% of the corresponding FBAs. The polymerization of AN was performed at 70°C in DMF solution at the same concentrations of FBAs and ABIN as above. After 8h polymers with an intense bluish fluorescence were obtained. They preserved their fluorescence after four-fold precipitation, thus indicating that the FBAs were chemically bonded to the polymer chain.

The electronic spectra of the precipitated polymers showed the same $\lambda_{\max}$ as the parent FBAs, either during the polymerization or as a result of its bonding into the polymer molecule. It was established spectrophotometrically, using the standard calibration curve method, that between 75 and 85% of the initial amount of the FBAs in the monomer mixture was incorporated into the polymer. Having in mind that these results were for severalfold precipitated polymers and that a part of FBA reacted with formation of oligomers that were removed during the precipitation, we can assume that this amount is acceptable and sufficient to preserve a good whiteness and fluorescence.

It was of interest to study also whether, when incorporated in the polymers, the FBAs exert an effect on their thermal properties. Thermal analysis of the polymers showed that the course of their thermooxidative destruction was identical with that of the corresponding homopolymers (polystyrene or polyacrylonitrile) obtained and studied under the same conditions. From these results it may be assumed that the synthesized FBAs may be suitable for the preparation of chemically brightened polystyrene and PAN.

2.4. *Colour assessment*

The compounds were applied at a concentration of 0.4 wt% to 100% cotton by the previously described procedure [7]. The degree of the whiteness and the CIE $L^*a^*b^*$ coordinates were determined. The data obtained are presented in Table 2. It is apparent that all the compounds impart a high degree of whiteness (twice that of the unbleached material) with a greenish tint. Their effect of whiteness increased in the order:

$$9 \Rightarrow 7, 5 \Rightarrow 11 \Rightarrow 4 \Rightarrow 10, 3 \Rightarrow 2 \Rightarrow 8 \Rightarrow 6 \Rightarrow 1$$

3. Conclusion

On the basis of the results obtained we can conclude that the synthesized triazinylstilbene

Table 2
Degree of whiteness and colour data for 100% cotton treated with FBAs (**I**)

No.	Degree of whiteness		Tint value	CIE coordinates		
	CIE	Berger		L^*	a^*	b^*
1	149.9	154.2	−0.27G	93.3	3.7	−14.5
2	135.2	134.4	−1.34G	92.2	3.7	−11.8
3	131.4	130.7	−1.57G	92.6	3.6	−10.8
4	125.5	124.7	−0.83G	92.1	2.8	−9.8
5	124.3	123.4	−0.68G	91.6	2.6	−10.0
6	146.3	147.8	−1.87G	93.2	4.6	−13.5
7	122.4	118.6	−2.47G	91.3	3.7	−9.3
8	138.5	138.6	−1.27G	92.5	3.8	−12.4
9	108.2	107.9	0.12G	92.2	1.3	−5.8
10	131.8	132.3	−0.83G	92.9	3.2	−10.7
11	122.1	120.5	−1.29G	92.0	2.9	−9.0

FBAs are suitable for the whitening of polymers and cotton, providing a high degree of whiteness, for polymers stable to solvents.

4. Experimental

4.1. Materials and analysis

Materials and solvents were of p.a. or analytical grade (Fluka). 4,4′-bis-aminostilbene-2,2′-disulfonic acid (98%, Bulcolour Co., Bulgaria).

TLC analysis were performed on silica gel plates (Fluka F60 254, 20×10 cm, 0.1 mm thickness) using chloroform–methanol–ammonia (11:5:1, v/v) as eluent. Electronic spectra were recorded in DMF and water for the compounds, and in DMF for polymers, on a Hewlett Packard 8452A UV/Vis spectrophotometer, ^{1}H-NMR in DMF were recorded on JEOL-JNM PS100 spectrometer. Thermal analysis was accomplished on a derivatograph "MOM-Q" (Hungary) under stationary conditions in air; the temperature range was 20–500°C and the heating rate was 10°C min^{-1}. The degree of whiteness and the CIE values were measured using a "Data Color" equipment under illuminant D_{65}.

4.2. Synthesis of the compounds

The same procedure described below for compound **1** was used to obtain compounds **2** and **6–10**.

4.2.1. Synthesis of the compound no **1**.

A solution of cyanuric chloride (0.02 mol) in 100 ml of dioxan was added to 100 ml of a cold aq solution of 4,4′-diaminostilbene-2,2′-disulfonic acid (0.01 mol). The mixture was stirred at 0–5°C, maintaining pH 7 by addition of 30% aq sodium hydroxide. The course of the reaction was monitored by TLC on silica gel, using chloroform: methanol:ammonia (25%) 11:5:1 as eluent. After 1 h, the reaction was complete and 0.02 mol of aniline was then added. The temperature was increased to 30°C and pH was maintained at 7.5. After 1.5 h, 0.02 mol of allylamine was added and the mixture was stirred at reflux temperature, while keeping pH 8.5. After 2 h, the product was isolated by filtration and the precipitate was dried under vacuum at 30°C (yield 80%). The product was purified by column chromatography on silica gel, using the above eluent system.

Elemental analysis: calculated N 19.48%, found 19.70%; ^{1}H NMR [DMF]: δ: 3.8 (d, 4H), 4.8–5.2 (tr, 4H), 5.5–5.8 (m, 2H) 6.8–8 (m, 18H), 8.8–9.2 (s, 6H).

4.2.2. No. **2**

Yield 85%, elemental analysis: calculated N 18.66%, found 18.35%; ^{1}H NMR [DMF] δ: 3.8–4 (d, 8H), 4.9–5.5 (tr, 8H), 5.8–6 (m, 4H), 6.8–7.8 (m, 18H), 9.0–9.2 (s,4H).

4.2.3. No. **6**

Yield 75%, elemental analysis: calculated N 21.89%, found 21.80%; ^{1}H NMR [DMF] δ: 2.8–3 (d, 4H), 3.5–3.8 (d, 4H), 4.0–4.2 (m, 4H), 4.8–5.0 (tr, 4H), 5.3–5.6 (m, 2H), 7.0–7.8 (m, 8H), 8.6–8.8 (s, 6H).

4.2.4. No. **7**

Yield 85%, elemental analysis: calculated N 17.31%, found 17.50; ^{1}H NMR [DMF] δ: 3.6–3.8 (d, 4H), 4.8–5.2 (tr, 4H), 5.5–5.8 (m, 2H), 6.9–7.5 (m, 16H), 10.5 (s, 6H).

4.2.5. No. **8**

Yield 90%, elemental analysis: calculated N 20.79%, found 20.48%; ^{1}H NMR [DMF] δ: 3.4–3.6 (d, 16H), 3.8 (d, 4H), 4.8–5.2 (tr, 4H), 5.5–5.8 (m, 2H), 7.6–8.6 (m, 8H), 9.7 (s, 4H).

4.2.6. No. **9**

Yield 90%, elemental analysis: calculated N 21.90%, found 21.60%; ^{1}H NMR [DMF] δ: 2.4 (s, 12H), 3.9–4.1 (d, 4H), 4.9–5.1 (tr, 4H), 7.8–8.0 (m,8H), 8.7–9.1 (s, 4H).

4.2.7. No **10**

Yield 85%, elemental analysis: N calculated 21.53%, found 21.40%; ^{1}H NMR [DMF] δ: 0.9–1.1 (tr, 12H), 3.0–3.6 (m, 8H), 3.8–4.0 (d, 4H), 4.8-5.2 (tr, 4H), 5.5–5.8 (m, 2H).

4.2.8. Sythesis of compounds nos **3,5** *and* **11**

Compound no. **3** was obtained following the same procedure as for **1**, but the pH for the final stage was maintained at 8. Yield 75%, elemental analysis: calculated N 19.81%, found 19.80%; ^{1}H NMR [DMF] δ: 3.3–3.5 (m, 4H), 4.7–5.0 (m, 2H), 6.5–8 (m, 18H), 9.5–9.8 (d, 2H), 10.5 (s, 4H).

Under the same conditions compound **4** was obtained in 80% yield. Elemental analysis: calculated N 19.18%, found 19.20%; ^{1}H NMR [DMF] δ: 1.6 (s, 6H), 4.5–5 (m, 4H), 6.5–7.9 (m, 18H), 9.5–9.7 ((d, 2H), 10.6 (s, 4H).

Compound no. **5** was obtained according to the procedure for **1**, but pH at the final stage was maintained at 7. Yield 85%, elemental analysis: calculated N 15.94%, found 16.20%; ^{1}H NMR [DMSO] δ: 1.1 (s, 6H), 4.2–4.8 (m, 4H), 6.5–8 (m, 18H), 9.6–9.8 (s, 4H).

Compound no. **11** was obtained following the general procedure for **1**, but the temperature for the second stage was 40°C at pH 8, and for the final stage pH was 9. Yield 85%, elemental analysis: calculated N 22.46%, found 22.90%; ^{1}H NMR [DMSO] δ: 3.8–3.9 (d, 8H), 5.0-5.2 (tr, 8H), 5.5–6.0 (m, 4H).

4.3. *Polymerization with styrene*

In an ampoule flushed with pure dry nitrogen, 10 g of pure styrene, 0.05 g of ABIN and 0.01 g of the corresponding FBA of formula I were mixed. After sealing, the ampoules were heated at 80°C. After 8h, solid transparent polymers with an intense bluish fluorescence were obtained. They were dissolved in chloroform and reprecipitated 4–5-fold by methanol or aq NaOH, until filtrates free of fluorescence (under UV light) were obtained. The polymers thus purified were dried under vacuum at 30°C to constant weight.

4.4. *Polymerization with AN*

Polymerization was carried out in an ampoule with a solution of AN in DMF (20 vol%) in the presence of 0.5 wt% of ABIN and 0.1 wt% of FBAs at 70°C. After 8 h the polymers were purified by 4-fold precipitation by aq NaOH and dried under vacuum to constant weight.

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