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Synthesis and properties of disperse dyes containing a built-in triazine stabilizer

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Abstract

Novel monoazo disperse dyes containing a built-in triazine moiety have been synthesized and evaluated for their ability to give protection against the harmful effects of UV radiation. The results showed that some of the new dyes have the properties needed to provide enhanced skin protection following their incorporation into polyester fabric. It was also found that in certain cases, protection against UV radiation diminished slightly after washing the fabric.

Keywords: Triazine photostabilizer; UV radiation protection; Disperse dyes

1. Introduction

Skin cancer is the most common type of cancer in certain countries and is increasing in incidence [1]. It was projected that in 2004, more than 1 million people would be diagnosed with squamous cell carcinoma and more than 2200 deaths would occur [2]. It was also projected that another 54,200 people would be diagnosed with melanoma, the most lethal of all skin cancers, and 7600 persons would die from this disease during 2004. It is evident that high levels of exposure to ultraviolet radiation (UVR) increase the risk of three major forms of skin cancer, with approximately 65–90% of melanomas caused by UVR exposure [3].

UV absorbers having intramolecular hydrogen bonding include 2-(2-hydroxyaryl)benzotriazoles and 2-(2-hydroxyaryl)-1,3,5-triazines that are widely employed for protecting polymers against photodegradation [4,5]. The application of UV absorbers to textiles was studied by Strobel [6,7], who showed that co-applying UV absorbers and dyestuffs to fabrics could be achieved. However, the efficiency with which UV absorbers were exhausted during the dyeing process was only 50% on polyester (PET) fibers, and even lower when the dyeing was carried out on nylon. This can prevent the co-dyeing process from being cost effective. In order to enhance cost effectiveness and dye photostability, and to develop fabrics that can be used simultaneously to protect the human body from ultraviolet (UV) radiation, a hydroxyphenyl-1,3,5-triazine moiety was incorporated into disperse dye structures. This concept led to the synthesis of monoazo disperse dyes as shown in Scheme 1.

2. Experimental

2.1. General

Cyanuric chloride was obtained from Longsheng Chemical Engineering Company and was of reagent grade. Other chemicals were commercial products of analytical grade.

Melting points were determined with a Mel-Temp capillary melting point apparatus (made in Shanghai, China) and are uncorrected. IR spectra were obtained on an FT/IR-430 Infrared

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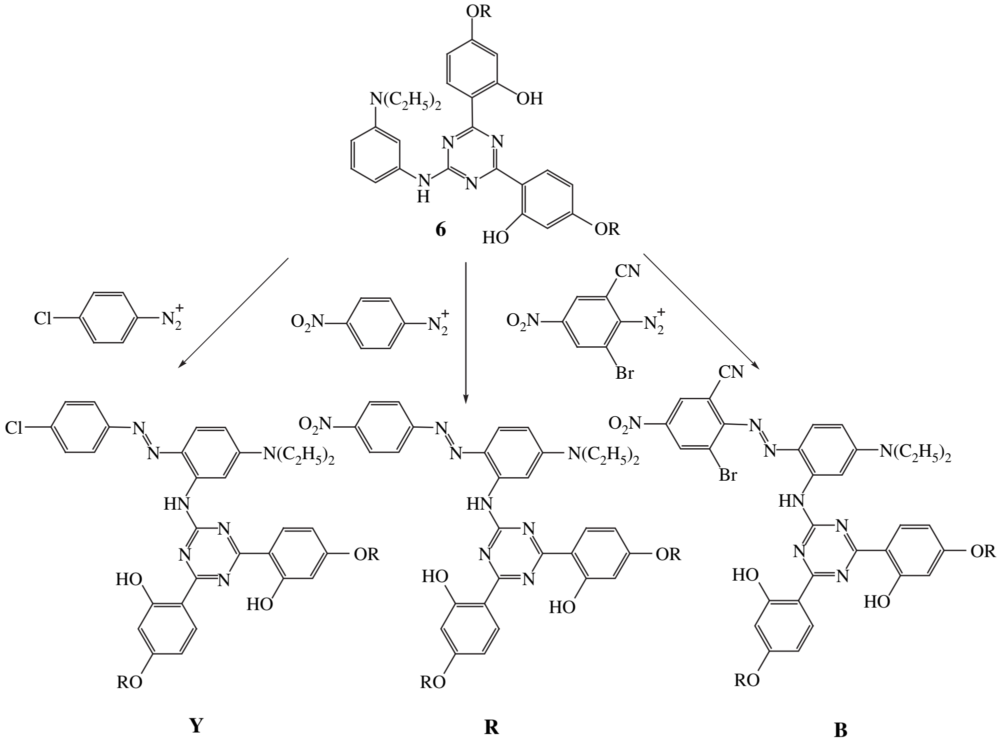
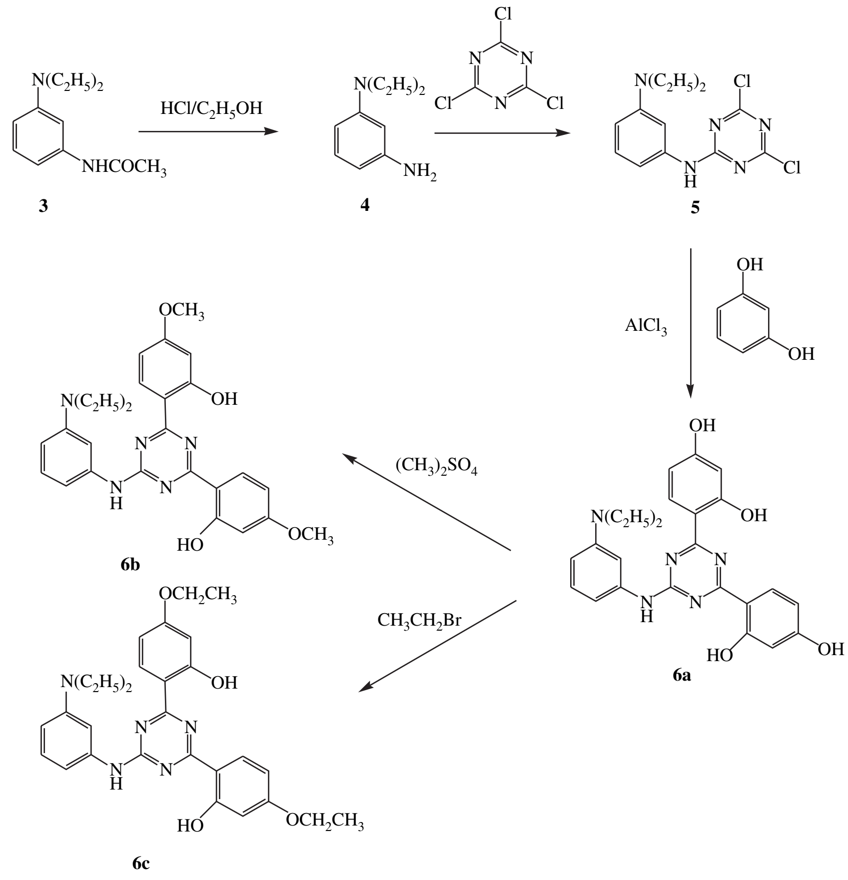
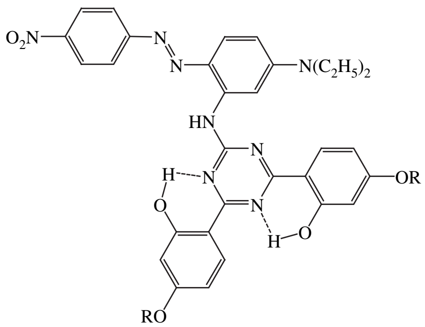


Scheme 1. Synthesis of monoazo disperse dyes containing a triazine photostabilizer, where R = H, Me, Et.



Scheme 2. Synthesis of compounds **6a–c**.



Scheme 3. Intramolecular H-bonding in dyes **Y**, **R**, and **B**, where R = H, Me, Et.

spectrophotometer (JASCO Ltd. Co., Japan). Mass spectra were recorded at CID = 50–200 V with an HP 1100 HPLC/MS system from Hewlett Packard Ltd. Co., USA. ^1H NMR spectra were recorded in DMSO-d_6, using TMS as the internal standard, on a Varian INOVA 400 MHz spectrometer (Varian INOVA. Ltd. Co., USA).

2.2. Dyebath preparation and dyeing

Dyebath dispersions were prepared by dissolving the dye in minimum amount of DMF and adding this solution to 250 ml of distilled H_2O containing as much as dispersing agent MF as dye. The dispersions were adjusted to pH 5.5 using 1% HOAc, and diluted with distilled H_2O to give a final volume of 280 ml.

Dyeings were produced at 1% (on weight of fiber) concentrations, using a liquor ratio of 40:1. Dyeings were carried out in a Roaches S-1002 dyeing machine (Roaches Ltd. Co., England) at 130 °C for 3 h. After the dyeing process was complete, the fabrics were rinsed in water and air-dried.

2.3. Test methods

Fastness testing was conducted according to Chinese test methods GB/T3921-97 (for wash fastness) and GB/T5718-97 (for sublimation fastness). The rating system used was 1 (poor) to 5 (excellent). Light fastness was conducted according to test method GB8427-47 (ISO 105-B2: 1994) and the rating system was 1 (poor) to 7 (excellent).

2.4. Synthesis

2.4.1. Compound **4**

N-(3-Diethylaminophenyl)acetamide (22 g, 0.11 mol) was added to 80 ml CH_3CH_2OH and the mixture was cooled below 20 °C. The mixture was stirred vigorously as 40 ml conc. HCl was slowly added and the resultant solution was stirred at 70 °C for 10 h. The organic layer was dried ($MgSO_4$) and concentrated to give 13.8 g (78.8%) of compound **4** as a viscous oil.

2.4.2. Compound **5**

Cyanuric chloride (18.4 g, 0.1 mol) was added to 50 ml toluene and the solution was cooled below 5 °C, and the mixture was stirred, as compound **4** (16.4 g, 0.1 mol) in 30 ml toluene was slowly added. The resultant solution was stirred for 1 h at 0–5 °C and the solid was collected by filtration and dried to give 28 g (89.7%) of compound **5** as an off-white solid.

2.4.3. Compound **6a**

Compound **5** (9 g, 0.03 mol) was added to 150 ml mixed (*o*/*p*)-dimethylbenzenes and the mixture was stirred as $AlCl_3$ (8 g, 0.06 mol) and resorcinol (6.7 g, 0.06 mol) were added. The resultant solution was heated slowly to 60 °C, held at this temperature for 3 h, heated slowly to 90 °C, and held at this temperature for 5 h. Finally the mixture was stirred under reflux for 10 h, cooled, and poured over 500 g ice. Dimethylbenzene was removed and the pH was adjusted to 1–2 using 15% HCl. The solid was collected by filtration and washed with 500 ml H_2O, then dried to give 11.2 g (84.6%) of compound **6a** as a light green solid.

2.4.4. Compound **6b**

Compound **6a** (2 g, 4 mmol) was added to a mixture of 25 ml acetone and 25 ml H_2O, and the solution was adjusted

Table 1
Analytical data recorded on dye intermediates used in this study

Compounds	R_f (eluent)	Mp (°C)	IR spectrum (KBr) (cm^{-1})	Proton NMR data (ppm)	API-ES MS[a]
5	0.72 (3:1/hexane:EtOAc)	209–212	N–H (3436, 3239); Ar–H (3048); C–H (2987, 2943); C=N (2415, 2389); C=C (1616, 1542, 1501)	(DMSO-d_6): 1.0–1.2 (t, 6H); 3.2–3.8 (s, 4H); 7.2–7.9 (m, 4H)	312
6a	0.65 (4:1/hexane:EtOAc)	>300	N–H and O–H (3164); C=N (2360); C=C (1602, 1504); C–O (1384); C–N (1332)	(DMSO-d_6): 1.1–1.2 (t, 6H); 3.5–3.7 (s, 4H); 6.4–6.6 (m, 4H); 7.64–7.72 (m, 2H); 7.74–7.80 (d, 1H); 8.02–8.22 (m, 3H); 10.9–11.1 (s, 1H)	460
6b	0.5 (5:1/hexane:EtOAc)	196–198	N–H and O–H (3164); C=N (2360); C=C (1602, 1504); C–O (1384); C–N (1332)	(DMSO-d_6): 1.0–1.2 (t, 6H); 3.3–3.4 (s, 4H); 3.7–3.9 (d, 6H); 6.4–6.7 (m, 5H); 6.8–7.0 (m, 2H); 7.1–7.3 (t, 1H); 8.1–8.2 (d, 1H); 8.2–8.3 (d, 1H); 10.4–10.5 (s, 1H); 12.9–13.1 (s, 1H); 13.3–13.9 (s, 1H)	488
6c	0.46 (5:1/hexane:EtOAc)	204–206	N–H and O–H (3164); C=N (2360); C=C (1602, 1504); C–O (1384); C–N (1332)	(DMSO-d_6): 1.0–1.2 (t, 6H); 1.3–1.4 (s, 6H); 3.3–3.5 (s, 4H); 4.0–4.2 (s, 4H); 6.4–6.7 (m, 5H); 6.8–7.0 (m, 2H); 7.1–7.3 (t, 2H); 8.1–8.2 (d, 1H); 8.2–8.3 (d, 1H); 10.2–10.6 (s, 1h); 12.8–13.2 (s, 1H); 13.2–13.6 (s, 1H)	516

[a] (M + 1).

Table 2
Analytical data recorded on dyes **Y**, **R**, and **B**

Dyes	Yield (%)	API-ES MS[a]	λ_{max}[b]	ε_{max}[b]
Y1	78.3	598	466	24,700
Y2	71.7	626	465	23,100
Y3	95.3	654	450	15,700
R1	79.1	609	521	31,400
R2	76.8	634	516	30,200
R3	97.1	665	521	25,200
B1	64.3	712	583	19,000
B2	61.8	740	579	17,500
B3	75.4	768	583	11,300

[a] (M + 1).

[b] Recorded in 90% DMF and 10% H_2O.

Table 3
$L^*a^*b^*$ values for PET dyed with dyes **Y**, **R**, and **B**

Dyes	L^*	a^*	b^*
Y1	52.32	13.81	47.60
Y2	52.23	9.14	42.19
Y3	57.84	3.21	30.27
R1	33.11	26.71	9.68
R2	39.34	29.51	6.69
R3	42.12	28.68	−1.23
B1	39.69	−9.23	−11.87
B2	39.06	0.85	−10.77
B3	41.57	−8.82	−16.15

to pH 8 using K_2CO_3. The mixture was stirred as dimethyl sulfate (1.4 g, 0.011 mol) in 30 ml CH_3OH was slowly added. The resultant solution was stirred for 20 h at 20 °C and the reaction mixture was cooled and adjusted to pH 5–6 using 10% HCl. Acetone was removed and the product was collected by filtration, washed with 30 ml H_2O, and dried to give 1.5 g (70.7%) of compound **6b** as a pale yellow solid.

2.4.5. *Compound **6c***

Compound **6b** (1.5 g, 3 mmol) was added to a mixture of 30 ml acetone and 10 ml H_2O, and adjusted to pH 9 using K_2CO_3. The mixture was stirred as 1 ml CH_3CH_2Br was slowly added and the resultant solution was stirred for 15 h at 35 °C. The reaction mixture was cooled and adjusted to pH 5–6 using 10% HCl and acetone was removed. The solid was collected by filtration, washed with 30 ml H_2O, and dried to give 1.2 g (71.3%) of **6c** as a pale yellow solid.

2.4.6. *Dyes **Y1–Y3***

The method used is illustrated in the synthesis of **Y1**.

p-Chloroaniline (0.56 g, 4.3 mmol) was added to 10 ml of 25% HCl and the mixture was stirred vigorously for 1 h at 10 °C. The resultant solution was cooled below 5 °C with the aid of an ice bath and stirred as $NaNO_2$ (0.31 g, 4.5 mmol) in 2 ml H_2O was added rapidly. The reaction mixture was stirred at 5 °C until a clear solution was formed. The solution was added to 50 ml DMF containing compound **6a** (2 g, 4.3 mmol) and 2 ml conc. HCl at a rate such that the temperature did not exceed 5 °C, and the resultant solution was stirred for 2 h at 5 °C. The solution was poured cautiously into 500 g ice and adjusted to pH 7 by adding 10% NaOH. The solid was collected by filtration, washed with 100 ml H_2O, and dried to give 2.0 g (78.3%) of **Y1** as brown solid.

2.4.7. *Dyes **R1–R3***

The method used is illustrated in the synthesis of **R1**.

p-Nitroaniline (0.6, 4.3 mmol) was added to 10 ml of 25% HCl and the mixture was stirred vigorously for 1 h at 10 °C. The resultant solution was cooled below 5 °C with the aid of an ice bath and stirred as $NaNO_2$ (0.31 g, 4.5 mmol) in 2 ml H_2O was added rapidly. The reaction mixture was stirred at 5 °C until a clear solution was formed. The solution was

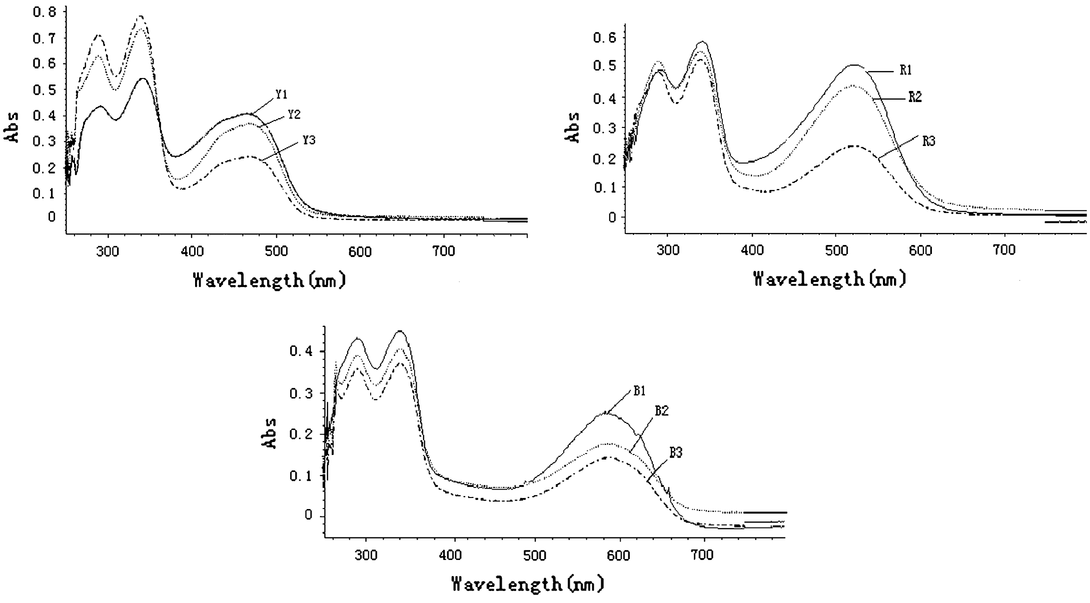


Fig. 1. UV–vis spectra of dyes **Y**, **R**, and **B** in 90% DMF/10% H_2O.

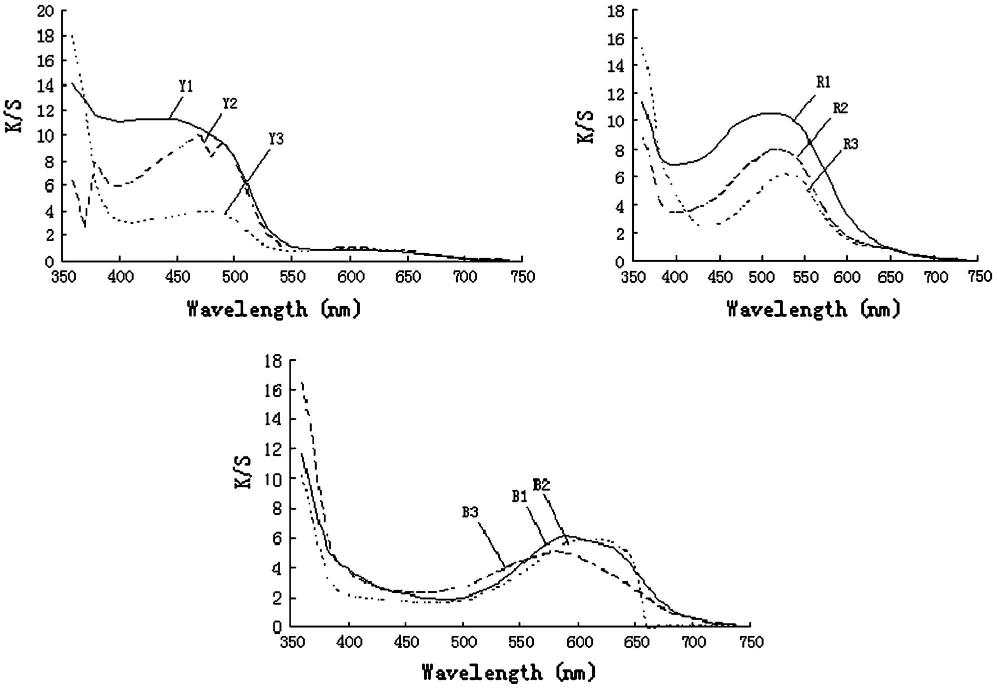


Fig. 2. *K/S* data recorded for 1% shades of dyes **Y**, **R**, and **B** on PET fabric.

added to 50 ml DMF containing compound **6a** (2 g, 0.0043 mol) and 2 ml conc. HCl at a rate such that the temperature did not exceed 5 °C, and the resulting solution was stirred for 2 h at 5 °C. The reaction solution was poured cautiously into 500 g ice and adjusted to pH 7 by adding 10% NaOH. The solid was collected by filtration, washed with 100 ml H_2O, and dried to give 2.1 g (79.1%) of **R1** as a reddish-black solid.

2.4.8. Synthesis of dyes *B1–B3*

The method used is illustrated in the synthesis of **B1**.

Finely powdered $NaNO_2$ (0.31 g, 4.5 mmol) was added slowly with stirring to 6 ml conc. H_2SO_4. The mixture was heated to 70 °C, held at this temperature for 10 min, and then cooled below 10 °C. 2-Cyano-4-nitro-6-bromoaniline was added slowly to this suspension, keeping the temperature below 20 °C. The resultant solution was stirred at 40 °C for 1 h. The

Table 4
Light- and wash-fastness data for dyes **Y**, **R**, and **B** on PET[a]

Dyes	Light fastness	Wash fastness		
		Color change	Staining	
			Cotton	PET
Y1	4	3–4	3	4
Y2	4–5	4–5	4–5	4–5
Y3	5	4–5	3	4
R1	4–5	4	3	3
R2	5	4–5	4–5	4–5
R3	5	4–5	4–5	4–5
B1	5	4	4–5	4–5
B2	5	4–5	4–5	4–5
B3	5	4–5	4–5	4–5

[a] Using a dyebath containing 1% (o.w.f.) dye and 1% disperse agent.

Table 5
Sublimation fastness data for dyes **Y**, **R**, and **B** on PET[a]

Dyes	Sublimation fastness								
	150 °C			180 °C			210 °C		
	Color change	Staining		Color change	Staining		Color change	Staining	
		PET	Cotton		PET	Cotton		PET	Cotton
Y1	4	4–5	4–5	4	3–4	4–5	3	3–4	4–5
Y2	4–5	4–5	4–5	4–5	4	4–5	3–4	3–4	4–5
Y3	4–5	4–5	4–5	4–5	4–5	4–5	3–4	4–5	4–5
R1	4–5	4–5	4–5	4	4	4–5	3–4	4	4–5
R2	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
R3	4–5	4–5	4–5	4–5	4	4–5	4	3–4	4–5
B1	4–5	4–5	4–5	4–5	4–5	4–5	3	3–4	4–5
B2	4–5	4–5	4–5	4–5	4–5	4–5	4	4	4–5
B3	4–5	4–5	4–5	4–5	4–5	4–5	4	4	4–5

[a] Using a dyebath containing 1% (o.w.f.) dye and 1% disperse agent.

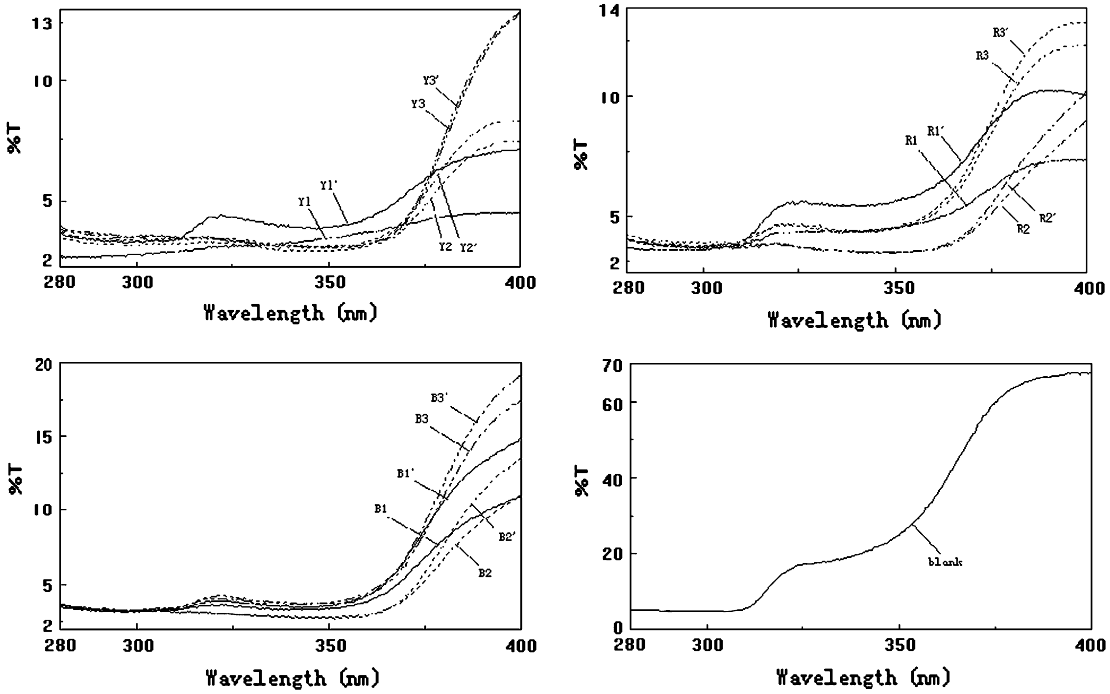


Fig. 3. Spectral transmittance results from dyed and undyed PET, where **Y/R/B** and **Y′/R′/B′** correspond to dyed fabrics before and after washing, respectively. Blank = undyed PET.

filtrate was added dropwise to a solution of compound **6a** (2 g, 4.3 mmol) in 50 ml DMF below 5 °C and stirred for 2 h at this temperature. The solution was poured cautiously into 500 g ice and adjusted to pH 7 by adding 10% NaOH. The solid was collected by filtration, washed with 100 ml H_2O, and dried to give 3 g of (97.1%) **B1** as a bluish-black solid.

3. Results and discussion

3.1. Synthesis and characterisation

The target disperse dyes containing triazine moiety required the synthesis of type **6** compounds. These novel couplers were prepared in 3–4 steps from compound **3** (Scheme 2). Compound **3** was hydrolyzed with HCl in CH_3CH_2OH to give diamine **4**. In turn, diamine **4** was condensed with cyanuric chloride in toluene to give compound **5**, which was condensed with resorcinol in the presence of $AlCl_3$ to give **6a** [8–11]. The fourth step involved alkylation with $(CH_3)_2SO_4$ or CH_3CH_2Br in acetone in the presence of K_2CO_3 to give couplers **6b** and **6c**. The selectivity of the alkylation reaction is due to intramolecular H-bonding, which ties up the *o*-OH group (Scheme 3). Reacting novel couplers **6** with the diazonium salt derived from *p*-chloroaniline, *p*-nitroaniline, and 2-cyano-4-nitro-6-bromoaniline gave nine disperse dyes **Y**, **R**, and **B** (Scheme 1).

Table 6
$T(\mathrm{UVA})_{\mathrm{AV}}$, $T(\mathrm{UVB})_{\mathrm{AV}}$ and $\mathrm{UPF}_{\mathrm{AV}}$ data recorded on PET dyed with **Y**, **R**, and **B**

Dyes	$T(\mathrm{UVA})_{\mathrm{AV}}$	$T(\mathrm{UVA})_{\mathrm{AV}}$[a]	$T(\mathrm{UVB})_{\mathrm{AV}}$	$T(\mathrm{UVB})_{\mathrm{AV}}$[a]	$\mathrm{UPF}_{\mathrm{AV}}$	$\mathrm{UPF}_{\mathrm{AV}}$[a]
Y1	3.5	4.8	2.5	3.1	36.9	30.6
Y2	4.1	4.5	2.9	3.2	33.8	31.7
Y3	5.3	5.3	3.3	3.3	29.9	29.4
R1	3.9	4.9	3.1	3.1	34.1	30.3
R2	4.3	4.6	3.3	3.1	30.9	30.6
R3	6.6	6.9	3.4	3.1	26.7	26.5
B1	4.3	4.9	3.3	3.3	32.5	30.4
B2	4.8	4.8	3.2	3.3	30.6	30.4
B3	7.3	7.8	3.3	3.3	26.9	26.3
Blank[b]	38.7	/	4.9	/	10.4	/

[a] Washed PET.
[b] Undyed PET.

Table 1 contains R_f, Mp, IR spectrum, MS and NMR data that were generated from intermediates prepared in this study. It is clear that the data support the structures of all compounds.

Analytical data recorded on disperse dyes prepared in this study are summarized in Table 2. UV–vis absorption spectra of dyes **Y**, **R**, and **B** are shown in Fig. 1, which shows the contribution of a built-in triazine group. We found that the incorporation of a triazine moiety resulted in dyes having strong absorption in the UVA (315–400 nm) and UVB (280–315 nm) regions. Extinction coefficients ($\varepsilon_{\max}$) of the new dyes were <35,000. We also found that $\varepsilon_{\max}(\mathbf{R}) > \varepsilon_{\max}(\mathbf{Y}) > \varepsilon_{\max}(\mathbf{B})$ and that $\varepsilon_{\max}(\mathbf{1}) > \varepsilon_{\max}(\mathbf{2}) > \varepsilon_{\max}(\mathbf{3})$.

3.2. Dyeing properties

3.2.1. Color data

Table 3 and Fig. 2 provide a summary of $L^*a^*b^*$ and *K*/*S* values recorded on the nine new disperse dyes on PET fabric. It can be seen that the deepest shades were obtained when R = H. Also, we found that *K*/*S* decreases in the order R = H > Me > Et, which correlates with increasing molecular mass. The same trend was observed when comparing *K/S* values for the three dye colors, with *K/S* for **Y** > **R** > **B**. The latter results suggest that the molecular sizes of the blue dyes have approached the limit for disperse dyes for PET.

3.2.2. Fastness data

Fastness properties of the disperse dyes on PET are listed in Tables 4 and 5. It can be seen that the presence of a built-in stabilizer moiety led to good light fastness, as ratings of 4–5 were obtained. As would be anticipated, wash fastness was generally very good for these large hydrophobic dyes. When R = H, the wash fastness of dyes **Y** and **R** was lower than the other members of the respective groups. It is possible that the −OH groups undergo ionization in the somewhat alkaline wash bath, enhancing dye solubility in water. We also found that incorporating a triazine moiety into disperse dye structure affords good sublimation fastness. These results are not surprising, since the molecular weight of the dyes is quite high (598–768), making them high-energy dyes.

3.3. UV radiation protection

Ultraviolet radiation protection capability of PET dyed with dyes **Y**, **R**, and **B** was evaluated according to test method GB/T18830-2002. $T(\lambda)$ (spectral transmittance) is summarized in Fig. 3. Also, Table 6 contains $T(\mathrm{UVA})_{\mathrm{AV}}$, $T(\mathrm{UVB})_{\mathrm{AV}}$ and $\mathrm{UPF}_{\mathrm{AV}}$ (ultraviolet protection factor) values that were calculated according to Eqs. (1)–(3).

$$T(\mathrm{UVA})_i = \frac{1}{m}\sum_{\lambda=315}^{400} T_i(\lambda) \tag{1}$$

$$T(\mathrm{UVB})_i = \frac{1}{k}\sum_{\lambda=290}^{315} T_i(\lambda) \tag{2}$$

$$\mathrm{UPF}_i = \frac{\sum\limits_{\lambda=290}^{\lambda=400} E(\lambda)\times\varepsilon(\lambda)\times\Delta\lambda}{\sum\limits_{\lambda=290}^{\lambda=400} E(\lambda)\times\varepsilon(\lambda)\times T(\lambda)\times\Delta\lambda} \tag{3}$$

Solar irradiance $E(\lambda)$ and erythematic action spectrum $\varepsilon(\lambda)$ are based on method prEN 13758 [12].

We found that PET dyed with disperse dyes containing a triazine stabilizer was effective, providing protection against ultraviolet radiation when R = H and Me, and that the improvement over untreated fabric was quite apparent from GB/T18830-2002. When R = Et, values of $T(\mathrm{UVA})_{\mathrm{AV}} > 5\%$ and $\mathrm{UPF}_{\mathrm{AV}} < 30$ were observed, which did not represent a performance improvement. Untreated PET exhibited $T(\mathrm{UVA})_{\mathrm{AV}} = 38.7\%$ and $\mathrm{UPF}_{\mathrm{AV}} = 10.4$, both of which are poor, though, expected outcomes. All dyed PET fabrics were washed according to method GB/T3921-97. After the washing process was complete, ultraviolet radiation protection capability of PET dyed with **Y1**, **R1**, **B1** declined somewhat, perhaps due to the removal of small amounts of residual surface dye.

4. Conclusions

Monoazo disperse dyes containing a built-in triazine photostabilizer can be synthesized and then applied to PET fabric via pressure dyeing. Owing to polarity and high molecular weight, these disperse dyes have high sublimation fastness. Their light fastness and water fastness properties are generally good as well. It has also been shown that the UV radiation protection capability of PET is improved by applying these dyes.

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