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Dyeing of nylon with reactive dyes. Part 3: Cationic reactive dyes for nylon

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Abstract

Several reactive dyes, solubilised by the incorporation of one or two cationic groups were synthesised. Each possessed either a single mono- or dichlorotriazine reactive group, or a hetero-bifunctional (monochlorotriazine/sulphatoethylsulphone) reactive system. All dyes fixed efficiently to nylon under alkaline dyeing conditions with fixation and build up being fully comparable to market's leading anionic reactive dyes.
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Keywords: Reactive dyes; Nylon; Fixation efficiency; Cationic dyes

1. Introduction

Anionic (acid) dyes are commonly used to colour nylon [1,2]. These attach to nylon via electrostatic linkages between the cationic, protonated amino end groups of the nylon (NH_3^+) and the anionic sulphonate groups of the dye ($Dye{-}SO_3^-$). However, in this type of attachment the wet fastness is usually less than ideal and some staining of adjacent fabrics takes place during laundering. The first commercially successful covalent attachment of dyes to textiles is generally attributed to Rattee and Stephen [3–6] who demonstrated that dyes containing a dichlorotriazine reactive group could be covalently attached to cotton [7–10]. Nowadays reactive dyes, which incorporate one or more electrophilic reactive groups, are the dominant class used for dyeing cellulosic fibres. However, only relatively small quantities of reactive dye are used on nylon and the focus of most of the published work has been a comparison of the relative efficacies, on nylon, of existing water soluble cellulose reactive dyes possessing electrophilic reactive groups such as chlorodifluoropyrimidines [11], bromoacrylamides [12], chlorotriazines and vinylsulphones [13,14], as well as some disperse types [15].

The most notable commercial reactive dyes for nylon have probably been the *Stanalan* [16] and *Eriofast* [17] ranges. In order to render reactive dyes for nylon attractive to potential customers it is necessary that any such products exhibit a useful balance of technical and commercial properties. Desirable technical features include high fixation, good build-up and fastness properties.

We have recently reported that molecular size and shape, as well as degree of sulphonation, are important determinants of anionic reactive dye fixation [18,19] on nylon. Greater sulphonic acid group concentration leads to greater electrostatic attraction with the positively charged fibre ($nylon{-}NH_3^+$ under acidic conditions), and final exhaustion $(K/S)_2$ and fixation efficiency were observed to increase with increasing degree of sulphonation [19]. Additionally, the build up of anionic reactive dyes is limited by the number of amino sites present on the fibre and also by steric hindrance.

Reactive groups, capable of reacting with the terminal amino groups of nylon, belong to one of the two major classes. Hetero-aryl halides react by a bimolecular activated hetero-aromatic nucleophilic substitution (S_NAr) reaction. Activated Michael type acceptors function by the nucleophilic addition

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of a terminal amino group to the β-carbon of an activated double bond of the reactive dye. Such reactions would be expected to occur only when the amino end groups in the fibre are non-protonated and nucleophilic. Under the usual acidic application the effective concentration of un-protonated amino groups on nylon is low and fixation tailed off before all the formally available amino groups had reacted with dye.

Lewis and Ho [20] proposed that when dyeing at 95 °C, the pK_a of the amino conjugate acid in nylon 6.6 would be about 8. At high pH, the carboxylic acid group of nylon will be essentially fully de-protonated and the fibre will be strongly anionic. Thus anionic dyes will experience strong electrostatic repulsion from the nylon. Conversely cationic dyes would be expected to be strongly attracted to anionic fibre, via ion−ion attractive forces, whilst at the same time maximising the concentration of nucleophilic amino end groups and thus the number of sites for reaction with electrophilic reactive groups. In order to test this postulate some reactive cationic dyes were prepared and evaluated.

2. Experimental

Visible absorption spectra were recorded using a Phillips model PU 8700 UV/visible spectrophotometer. Thin layer chromatography (TLC) was performed using aluminium plates coated with silica gel 60 F254 (Merck) as stationary phase, and a mixture of isobutanol:*n*-propanol:ethyl acetate:water in the ratio 2:4:1:3 as mobile phase. The developed plates were visualised under visible, short and long wavelength ultraviolet light (254 nm, 365 nm). High performance liquid chromatography (HPLC) was performed using a Hewlett-Packard 1100 liquid chromatograph with a 10 cm, Purospher RP-18 (5 μm) packing and LiChroCART 125-4 HPLC column cartridges. The mobile phases used were aqueous 0.25% CHAP solution (dicyclohexylammonium phosphate) as solvent A and acetonitrile (HPLC grade) as solvent B. These solvents were passed through the column, maintained at 40 °C, in a fixed ratio A:B (70:30) at the standard gradient rate 2 ml/min, and the samples were analysed spectroscopically using a diode array detector at a wavelength range from 250 to 650 nm. Elemental analyses for carbon, hydrogen, nitrogen and sulphur were carried out at the Department of Chemistry, University of Manchester, on a Carlo Erba 1108 element analyser. Mass spectrometry was performed using two different techniques, fast atomic bombardment and MALDI (matrix assisted laser adsorption ionisation) at Hall Analytical, Manchester. Scoured, modified nylon 6.6 *Tactel Coloursafe* fabric was supplied by Du Pont (UK).

Commercial reactive dyes invariably contain additional materials such as dedusting agents, salt and water. The effective agent (e.a.) content of each dye was determined by titration against titanium(III) chloride [13−15]. As titanium(III) chloride is readily oxidised by air it was standardised prior to use by titration against a standard dye (*Procion Orange MX-2R*). The dye (0.1 g) was dissolved in distilled water (100 ml) and potassium sodium tartrate buffer (20 ml, 20% w/v) was added. The solution was boiled under argon and titrated against titanium(III) chloride solution (0.1 N) and the strength of each dye described by its *Mole In*, that is, the mass in grams of dye which contains one mole of dye.

2.1. Preparation of dyes

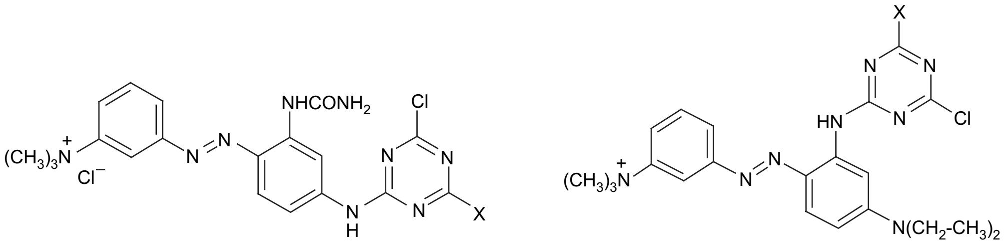
A series of dyeings were conducted using the novel reactive dyes listed in Table 1. These were prepared as described below.

2.1.1. m-Aminophenyltrimethylammonium salt

This was prepared by the two routes depicted in Schemes 1 and 2.

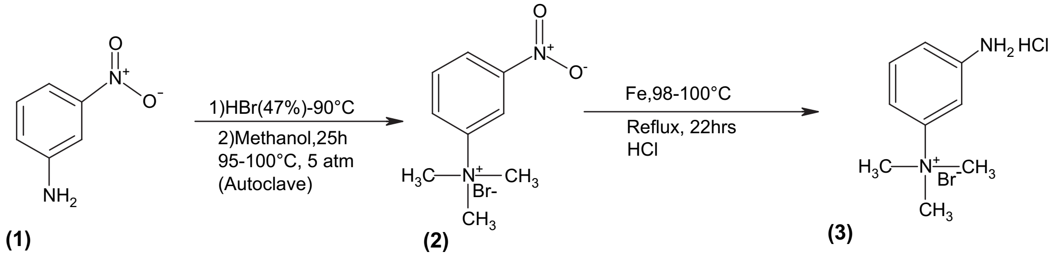
2.1.1.1. *m-Aminophenyltrimethylammonium salt (method 1). meta*-Nitroaniline (**1**) (0.945 mol, 130 g), was stirred

Table 1
Synthesised novel reactive dyes used for dyeing, *Tactel Coloursafe*

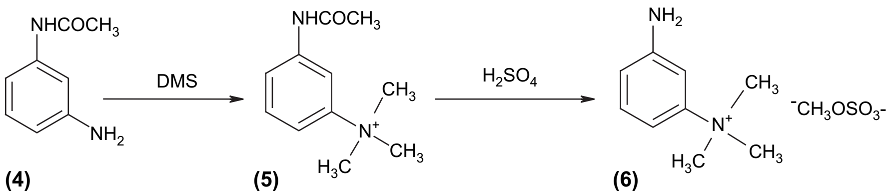


(Dye **1** to Dye **3**) (Dye **4** to Dye **7**)

Dye	No. of cationic groups	XH (A)	Reactive group
1	1	Cl	Dichlorotriazinyl
2	2	*m*-(Trimethylammonio-)phenylamino	Monochlorotriazinyl
3	1	4-(2-Sulphatoethylsulphonyl)phenylamino	Monochlorotriazinyl and vinylsulphone
4	1	Cl	Dichlorotriazinyl
5	1	Phenylamino	Monochlorotriazinyl
6	2	*m*-(Trimethylammonio-)phenylamino	Monochlorotriazinyl
7	1	4-(2-Sulphatoethylsulphonyl)phenylamino	Monochlorotriazinyl and vinylsulphone



Scheme 1. Synthesis of *m*-aminophenyltrimethylammonium salt (method 1).

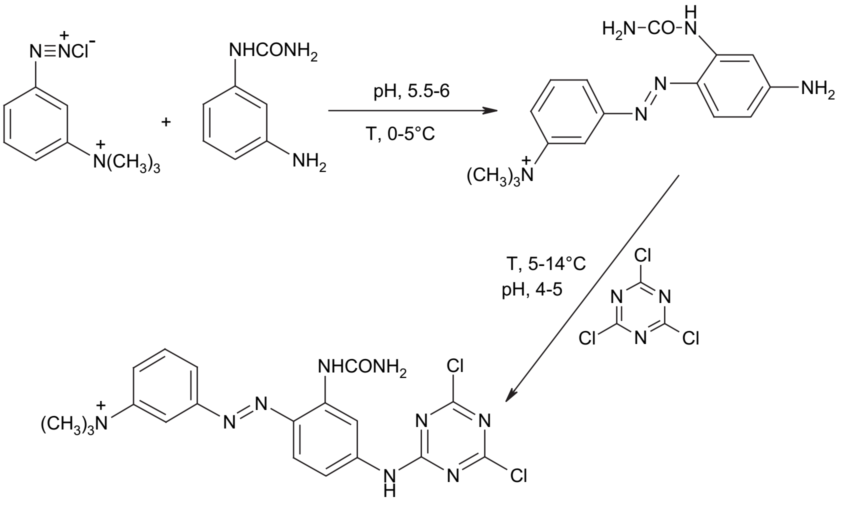


Scheme 2. Synthesis of *m*-aminophenyltrimethylammonium salt (method 2).

with aqueous hydrogen bromide solution (47%, 156 ml, 0.72 mol/mol), with good agitation at 30 °C. The suspension was then heated to 90 °C for 30 min. On cooling to room temperature, the solid was collected, washed with acetone (200 ml), and dried under reduced pressure, at 20 °C. This was stirred with methanol (200 ml), and heated in an autoclave for 25 h at 95–100 °C and at 5 atm pressure. The resulting pale brown crystalline solid was collected, stirred with methanol (250 ml), collected and washed with further methanol (100 ml). The almost dry solid was stirred with dilute aqueous ammonia (5 g + 250 ml water), for 5 min and collected, stirred with methanol (200 ml), followed by diethyl ether (200 ml) and the resulting 3-nitrophenyl-trimethylammonium bromide was dried at room temperature. 3-Nitrophenyl-trimethylammonium bromide (50 g, 0.19 mol), was added slowly to a previously prepared suspension of iron dust (57.5 g), in distilled water (191 ml), and hydrochloride acid (12 N, 3.5 ml). The mixture was heated under reflux for 45 min, maintaining the temperature by controlling the rate of addition. The resulting suspension was refluxed for 22 h, cooled to 25 °C and sodium carbonate (~20 g) was added very carefully with stirring, to pH 8. The resulting suspension was filtered through "Hyflo" to give a clear brown solution of filtered *m*-aminophenyltrimethylammonium bromide (**3**) which was used directly.

2.1.1.2. m-Aminophenyltrimethylammonium salt (method 2).

3-Aminoacetoanilide hydrochloride (**4**), (18 g, 0.12 mol), was dissolved in distilled water, and the pH was raised to 7. Dimethylsulphate (DMS) (50.4 g, 0.4 mol) was added to the



Scheme 3. Synthesis of Dye **1**.

resulting suspension of 3-aminoacetoanilide and the mixture heated to 50 °C; the pH was maintained at 7 by the slow addition of sodium hydroxide (2 N). The reaction was monitored by TLC and HPLC and the product hydrolysed without isolation. Concentrated sulphuric acid was slowly added dropwise to the stirred solution of 3-(acetylaminophenyl)trimethylammonium chloride (**5**) at room temperature; the mixture was stirred at 90–100 °C for 1 h, with control by HPLC and TLC, to produce a solution of *m*-aminophenyltrimethylammonium methosulphate (**6**), which was used directly without isolation.

2.1.2. 1-(3-Trimethylammoniophenylazo)-2-ureido-4-(4,6-dichloro-[1,3,5]triazin-2-ylamino)benzene (Dye *1*)

This was prepared by the route depicted in Scheme 3.

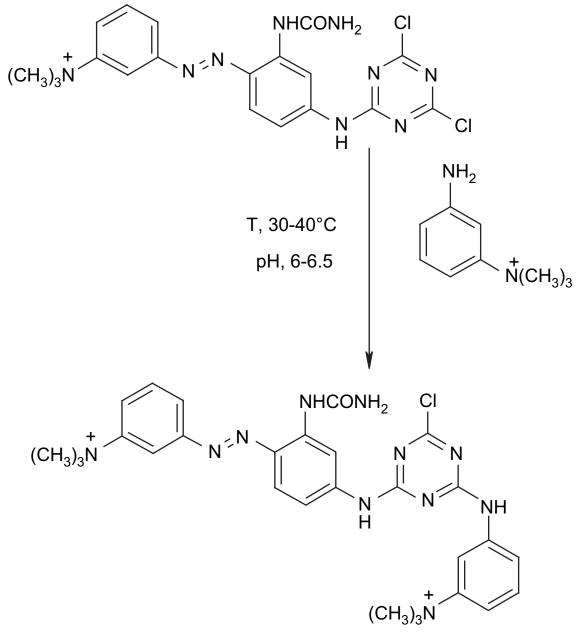
A solution of sodium nitrite (2.5 g, 0.036 mol), in distilled water (20 ml), was slowly added, at 0–5 °C, to a solution of the above *m*-aminophenyltrimethylammonium salt (4.8 g, 0.032 mol) in water (20 ml) and hydrochloric acid (36%, 40 ml, 0.08 mol). After stirring for 30 min at 0–5 °C and pH less than 2, excess nitrous acid was destroyed by adding a small amount of sulphamic acid. The resulting solution of diazonium salt was added slowly to a solution of *m*-ureido-aniline (4.8 g, 0.032 mol), at pH 5.5–6. The mixture was stirred for 30 min at pH 6 and at 0–5 °C. The resulting yellow solid, 1-(3-trimethylammoniophenylazo)-2-ureido-4-aminobenzene, was collected after removing some of the solvent under reduced pressure.

A freshly prepared suspension of 2,4,6-trichloro-*s*-triazine (5.9 g, 0.032 mol) was made by adding a solution of this material in acetone (20 ml) to crushed ice (10–20 g). The solution of 1-(3-trimethylammoniophenylazo)-2-ureido-4-aminobenzene, in distilled water (100 ml), at 5 °C and at pH 4 was added to this suspension. The mixture was stirred for 30 min with control by TLC ($R_f = 0.64$) and h.p.l.c. ($t_R = 1.2$ min). The resulting solid, 1-(3-trimethylammoniophenylazo)-2-ureido-4-(4,6-dichloro-[1,3,5]triazin-2-ylamino)benzene, was collected by filtration. The dye was very sparingly soluble in water. Calc. for $C_{19}H_{20}N_9OCl_2$: C, 49%; N, 27%. Found: C, 26%; N, 14%. Mol. In was 885 (52% e.a.). Mass *m*/*e*: [(460–463) = M].

2.1.3. 1-(3-Trimethylammoniophenylazo)-2-ureido-4-[4-chloro-6-(3-trimethylammoniophenylamino)-[1,3,5]triazin-2-ylaminobenzene (Dye *2*)

This was prepared by the route depicted in Scheme 4.

A solution of *m*-aminophenyltrimethylammonium chloride (4.8 g, 0.032 mol) in distilled water was slowly added to a solution of 1-(3-trimethylammoniophenylazo)-2-ureido-4-(4,6-dichloro-[1,3,5]triazin-2-ylamino)benzene prepared as described above (Section 2.1.2) at 30–40 °C, and at pH 6, with control by HPLC ($t_R = 1.4$ min) and TLC ($R_f = 0.68$). The desired product, 1-(3-trimethylammoniophenylazo)-2-ureido-4-[4-chloro-6-(3-trimethylammoniophenylamino)-[1,3,5]triazin-2-ylamino]benzene, was collected by filtration. Calc. for $C_{28}H_{34}N_{11}OCl_2$: C, 55%; N, 25.2%. Found: C, 19.2%; N, 8.76%. Mol. In = 1754 (35% e.a.). Mass *m*/*e*: 611 (M + H).



Scheme 4. Synthesis of Dye **2**.

2.1.4. 1-(3-Trimethylammoniophenylazo)-2-ureido-4-[4-chloro-6-[4′(β-sulphatoethylsulphonyl)phenylamino]-[1,3,5]triazin-2-ylaminobenzene (Dye *3*)

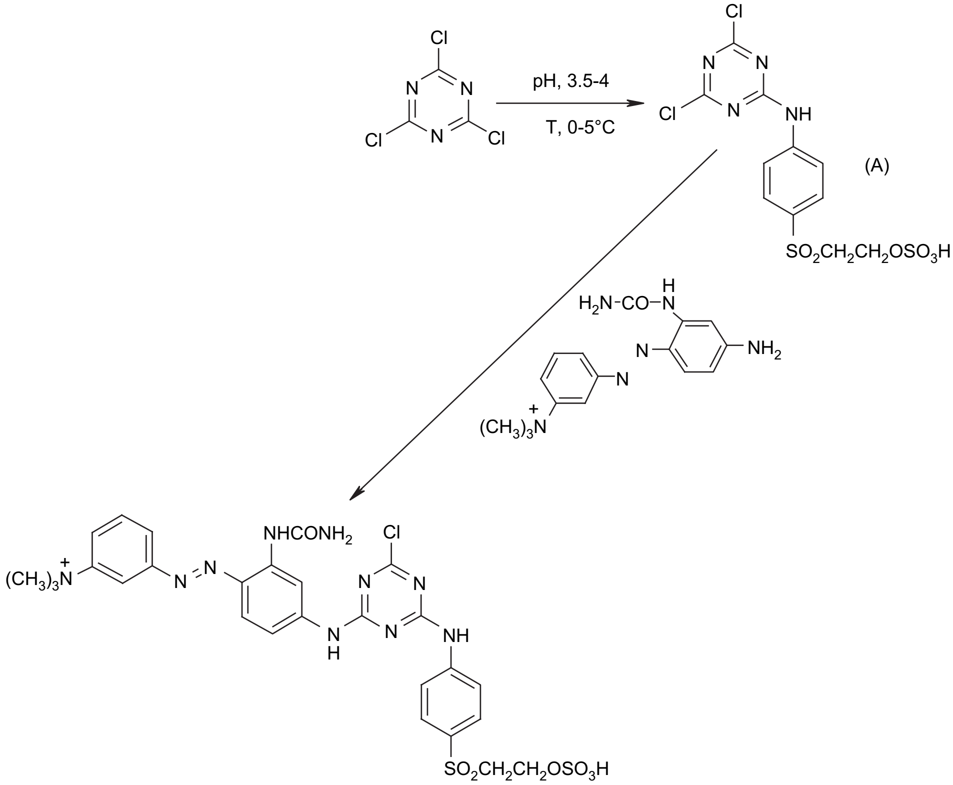
This was prepared by the route depicted in Scheme 5.

Sodium hydroxide (2 N) was added slowly to a suspension of 4-(2-sulphatoethylsulphonyl)aniline (PABSES) (9 g, 0.032 mol), in distilled water (200 ml), at 0–5 °C up to pH 2, followed by the slow addition of sodium carbonate solution (2 N) up to pH 4. A freshly prepared suspension of 2,4,6-trichloro-*s*-triazine (5.9 g, 0.032 mol), in acetone (30 ml), and crushed ice (10–20 g), was added very slowly to the resulting stirred solution of 4-(2-sulphatoethylsulphonyl)phenylamino at below 5 °C and at pH 3.5. After 1 h the reaction was essentially complete and 2,4-chloro-6-[4′(β-sulphatoethylsulphonyl)phenylamino]-[1,3,5]triazin-2-ylaminobenzene, so produced, was used without further isolation.

A solution of 1-(3-trimethylammoniophenylazo)-2-ureido-4-aminobenzene prepared as described above (Section 2.1.2) was added slowly to a solution of 2,4-dichloro-6-[4′(β-sulphatoethylsulphonyl)phenylamino]-[1,3,5]triazin-2-ylaminobenzene, at 30–40 °C and at pH 5. The mixture was stirred for 30 min at pH 6 and the resulting yellow product 1-(3-trimethylammoniophenylazo)-2-ureido-4-[4-chloro-6-{4′(β-sulphatoethylsulphonyl)}phenylamino]-[1,3,5]triazin-2-ylaminobenzene was collected by filtration (HPLC ($t_R = 4.1$ min) and TLC ($R_f = 0.58$)). The dye was very sparingly soluble in water and the Mol. In was determined by elemental analysis: 832 (87% e.a.). Calc. for $C_{27}H_{29}N_{10}S_2O_7ClNa$ (725.5): C, 44.6%; N, 19.2%; S, 8.8%. Found: C, 38.9%; N, 19.24%; S, 7.55%. Mass spectrum *m*/*e*: 607 (M − SO_4Na), 667 (M − N_2H_3CO), 711 (M − CH_3), 726 (M).

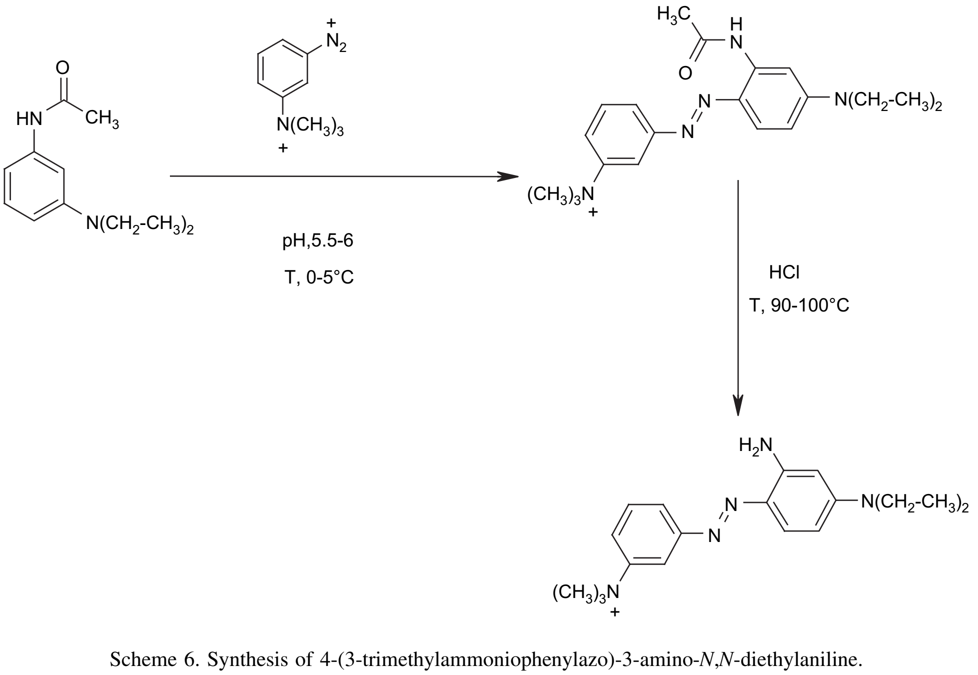
2.1.5. 4-(3-Trimethylammoniophenylazo)-3-amino-*N*,*N*-diethylaniline

This was prepared by the route depicted in Scheme 6.



Scheme 5. Synthesis of Dye **3**.

A solution of 3-trimethylammoniophenyl diazonium chloride (2.475 g, 0.015 mol), prepared as described (Section 2.1.2), was added slowly to a solution of *N*,*N*-diethyl *m*-amino acetanilide (3.09 g, 0.015 mol), at pH 5.5–6. The mixture was stirred for 30 min at pH 6 and at 0–5 °C, with control by TLC and HPLC Concentrated hydrochloric acid (2 N) was added dropwise to a stirred solution of the resulting 4-(3-trimethylammoniophenylazo)-3-acetylamino-*N*,*N*-diethylaniline, under reflux, at 90–100 °C for 30 min with control by TLC ($R_f = 0.33$) and HPLC ($t_R = 0.651$ min) to obtain an orange solid, 4-(3-trimethylammoniophenylazo)-3-amino-*N*,*N*-diethylaniline.



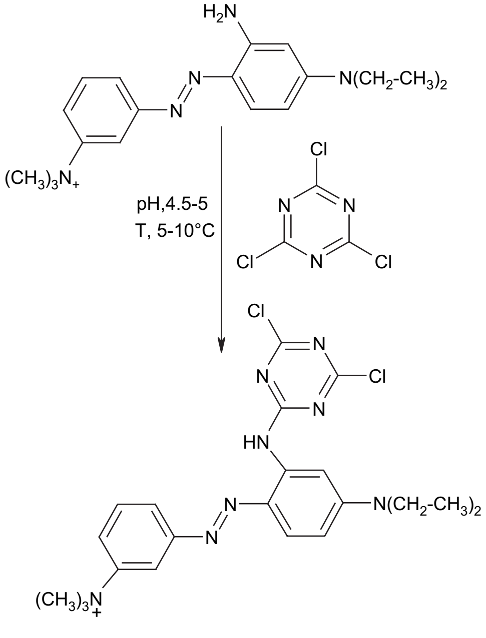
Scheme 6. Synthesis of 4-(3-trimethylammoniophenylazo)-3-amino-*N*,*N*-diethylaniline.

The Mol. In was determined by titration against titanium(III) chloride [21–25] (400) and microanalysis (405). Microanalysis, Calc. for $C_{19}H_{28}N_5$ (326): C, 69.9%; N, 21.47%. Found: C, 55.6%; N, 17.4% (80% e.a.). Mass *m*/*e*: 326/327 (M + H).

*2.1.6. 4-(3-Trimethylammoniophenylazo)-3-(4,6-dichloro-[1,3,5]triazin-2-ylamino)-N,N-diethylaniline (Dye **4**)*

This was prepared by the route depicted in Scheme 7.

A solution of 2,4,6-trichloro-*s*-triazine (1.15 g, 0.006 mol) in acetone (10 ml) was added to crushed ice (5 g) and the resulting suspension was added to a stirred solution of 4-(3-trimethylammoniophenylazo)-3-amino-*N*,*N*-diethylaniline (2 g, 0.006 mol), in distilled water (50 ml), at below 5 °C and at pH 4. The mixture was stirred for 30 min at pH 4–5 with control by TLC and HPLC and the resulting product, 4-3-trimethylammoniophenylazo)-3-(4,6-dichloro-[1,3,5]triazin-2-ylamino)-*N*,*N*-diethylaniline, was precipitated by slow addition of potassium chloride (KCl, 20% w/v), and isolated by filtration. The product was essentially homogeneous as judged by TLC ($R_f = 0.64$) and HPLC ($t_R = 4.89$ min). Calc. for $C_{22}H_{27}N_8Cl_2$ (474): C, 55.7%; N, 23.62%. Found: C, 37.2%; N, 15.75% corresponding to Mol. In = 710 (67% e.a.). Mol. In by titanous titration 704. Mass *m*/*e*: 472–475 (M).



Scheme 7. Synthesis of Dye **4**.

*2.1.7. 4-(3-Trimethylammoniophenylazo)-3-[4-chloro-6-(phenylamino)-[1,3,5]triazin-2-ylamino]-N,N-diethylaniline (Dye **5**)*

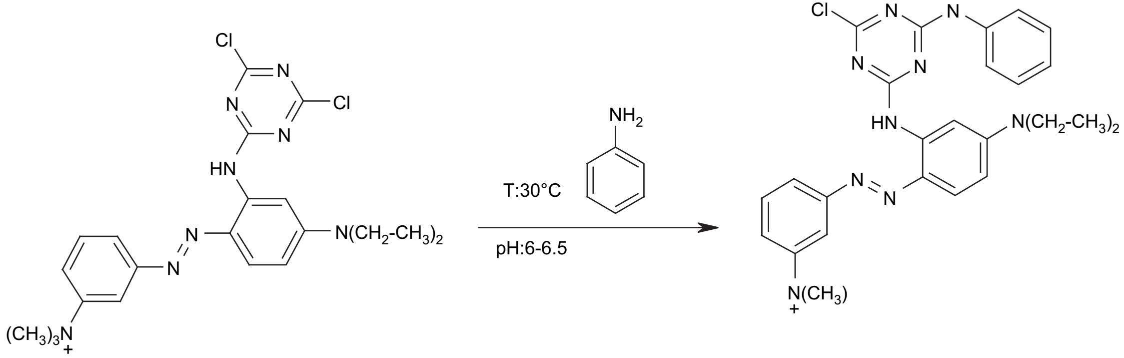
This was prepared by the route depicted in Scheme 8.

Aniline (0.558 g, 0.006 mol) was slowly added to a solution of dichlorotriazinyl orange reactive dye, 4-(3-trimethylammoniophenylazo)-3-(4,6-dichloro-[1,3,5]triazin-2-ylamino)-*N*,*N*-diethylaniline, prepared as described above at 30–40 °C and at pH 6 with control by TLC ($R_f = 0.44$), and HPLC ($t_R = 1.027$ min). The desired monochlorotriazinyl orange reactive dye, 4-(3-trimethylammoniophenylazo)-3-[4-chloro-6-(phenylamino)-[1,3,5]triazin-2-ylamino]-*N*,*N*-diethylaniline, was precipitated by slow addition of potassium chloride (15% w/v), isolated by filtration. Mol. In by titanous titration 995. Calc. for $C_{28}H_{33}N_9$ Cl (530): C, 63.7%; N, 23.7%. Found: C, 33.6%; N, 12.5% corresponding to Mol. In = 1006 (53% e.a.). Mass *m*/*e*: 531 (M).

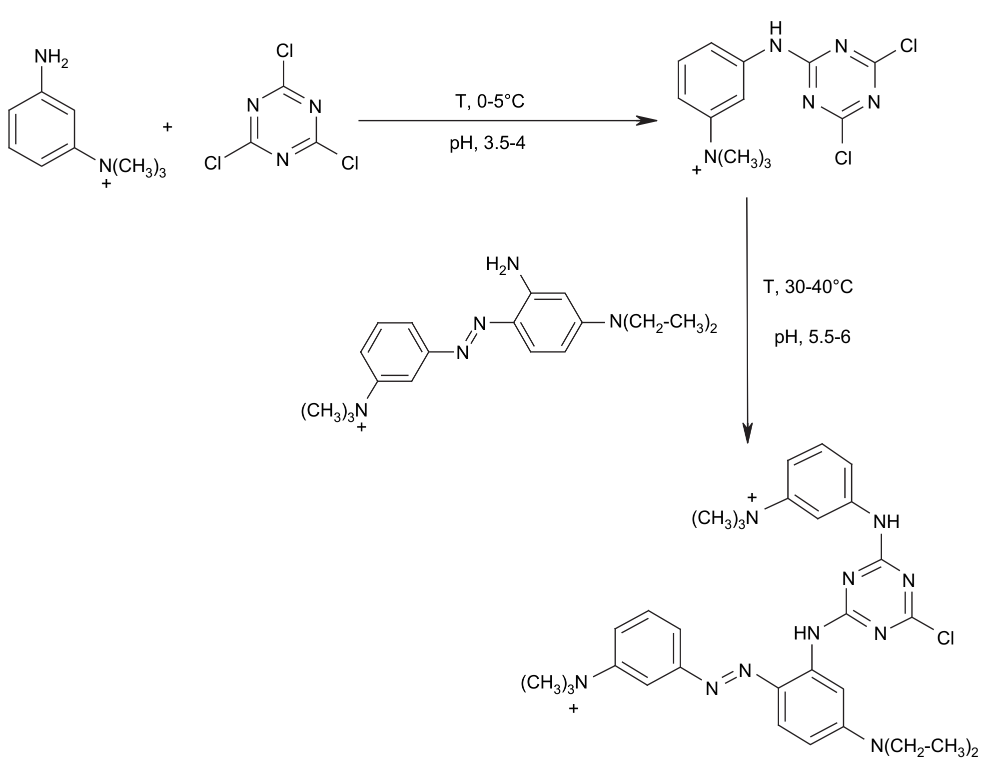
*2.1.8. 4-(3-Trimethylammoniophenylazo)-3-[4-chloro-6-(3-trimethylammoniophenylamino)-[1,3,5]triazin-2-ylamino]-N,N-diethylaniline (Dye **6**)*

This was prepared by the route depicted in Scheme 9.

A freshly prepared suspension of 2,4,6-trichloro-*s*-triazine in ice/acetone (1.15 g, 0.006 mol) was added to a stirred solution of *m*-aminophenyltrimethylammonium chloride (0.91 g, 0.006 mol), in distilled water (100 ml), at below 5 °C and at pH 4. The mixture was stirred for 30 min, at pH 4–5, to give a solution of 3-[*N*-(4,6-dichloro-[1,3,5]triazine-2-ylamino)]phenyltrimethylammonium chloride. A solution of 4-(3-trimethylammoniophenylazo)-3-amino-*N*,*N*-diethylaniline, (2 g, 0.006 mol), in distilled water, was slowly added and the resulting solution stirred at 30–40 °C, and at pH 6, for 2 h. The product, 4-(3-trimethylammoniophenylazo)-3-[4-chloro-6-(3-trimethylammoniophenylamino)-[1,3,5]triazin-2-ylamino]-*N*,*N*-diethylaniline, was precipitated by slow addition of



Scheme 8. Synthesis of Dye **5**.



Scheme 9. Synthesis of Dye **6**.

potassium chloride (KCl, 25% w/v) to the stirred solution and collected to give a product which was essentially homogeneous, as judged by TLC Calc. for $C_{31}H_{41}N_{10}Cl$ (588): C, 63.2%; N, 23.7%. Found: C, 36.2%; N, 12.6% corresponding to Mol. In = 1069 (55.5% e.a.). Mol. In by titanous titration 970. Mass *m*/*e*: 295(M + H), corresponding to a strong doubly charged ion.

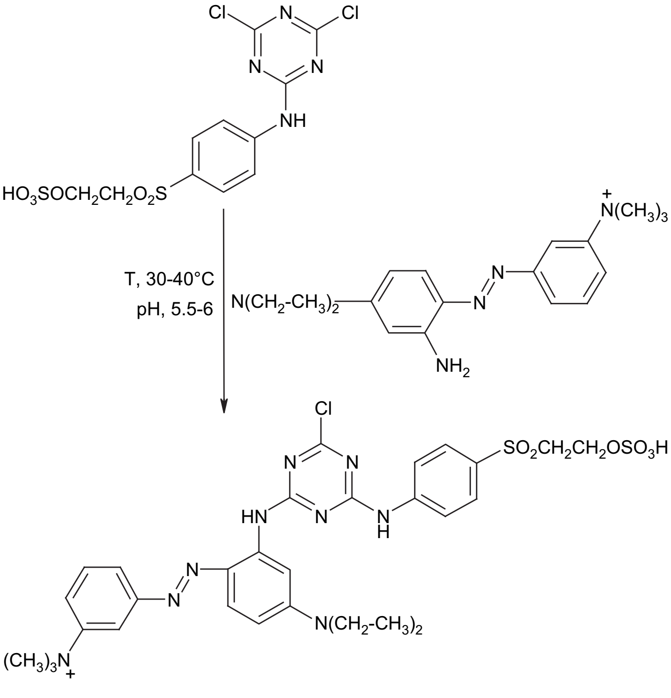
2.1.9. 4-(3-Trimethylammoniophenylazo)-3-[4-chloro-6-[4′(β-sulphatoethylsulphone)phenylamino]-[1,3,5]triazin-2-ylamino]-N,N-diethylaniline (Dye 7)

This was prepared by the route depicted in Scheme 10.

A solution of 2,4-dichloro-6-[4′(β-sulphatoethylsulphonyl)-phenylamino]-[1,3,5]triazine (2.5 g, 0.006 mol), (Section 2.1.4, Scheme 5) was added slowly to a solution of 4-(3-trimethylammoniophenylazo)-3-amino-*N*,*N*-diethylaniline (2 g, 0.006 mol) (Section 2.1.5, Scheme 6), at 30–40 °C and at pH 4–5.5 and the mixture was stirred for 30 min. The orange product, 4-(3-trimethylammoniophenylazo)-3-[4-chloro-6-[4′(β-sulphatoethylsulphonyl)phenylamino]-[1,3,5]triazin-2-ylamino]-*N*,*N*-diethylaniline, was precipitated by slow addition of potassium chloride (KCl, 25% w/v) and isolated by filtration. The product was essentially homogeneous as judged by TLC ($R_f = 0.35$) and HPLC ($t_R = 4.99$ min). Calc. for $C_{30}H_{37}N_9S_2O_6Cl$ (718.5): C, 50.1%; N, 17.53%; H, 5.14%. Found: C, 48.4%; N, 17%; H, 5.1% corresponding to Mol. In = 748 (96% e.a.). Mol. In by titanous titration 774. Mass *m*/*e*: 740(M − H + Na), 600(M − SO_4Na).

2.2. Dyeing

Dyeings were carried out using a Roaches dyeing machine (Mathis Labomat BFA 12): 5 g pieces of fabric were dyed at a liquor ratio of 20:1, using stainless steel dye pots, each of



Scheme 10. Synthesis of Dye **7**.

200 cm^3 capacity. The dyeing method used is depicted in Fig. 1. At the end of dyeing, the dyed fabric was removed and rinsed in cold tap water for 5 min. An initial series of dyeings was carried out at four different pH values using McIlvaine buffers, as shown in Table 2 [24], for pH values of 4, 6 and 8 and by adding sodium hydroxide to disodium hydrogen phosphate (pH 10). No additional electrolyte, levelling agent or alkali was used. Having determined the optimum pH, subsequent dyeings were carried out on 5 g pieces of fabric, at four depths of shade (0.18%, 0.36%, 0.72%, and 1.44% o.m.f.).

Dyes **1–3** and **7** were sparingly soluble and were dispersed by milling overnight with pea gravel in the presence of dispersing agent (Zetex DA-N, 0.5 cm^3) to give very finely divided dispersions.

2.2.1. Colour strength (*K*/*S*) of dyes on fabric

Reflectance measurements on the dry dyed fabrics were carried out using a Datacolor Spectraflash 600 specrophotometer using D_{65} illumination; the dyed fibre was folded twice so as to provide four layers and the average of three reflectance measurements, taken at different positions, was used.

2.2.2. Dye exhaustion

The extent of dye exhaustion was determined spectrophotometrically. The absorbance of each dye bath solution before and after the dyeing process was measured using 1 cm quartz cells housed in a Philips PU 8720 UV/visible scanning spectrophotometer at the λ_{max} of each dye. The percentage dye bath exhaustion (%*E*) was calculated using Eq. (1), where A_0 and A_1 are the absorbances of the dye bath before and after dyeing, respectively.

$$\%E = \frac{A_0 - A_1}{A_0} \times 100 \tag{1}$$

As Dyes **1–3** and **7** were only sparingly soluble in water, %*E* could not be determined.

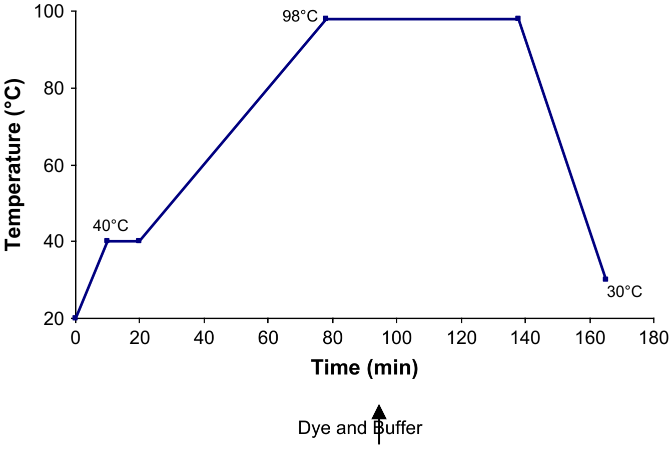


Fig. 1. Dyeing profile used.

Table 2
Composition of McIlvaine buffers in a total volume of 80 cm^3

pH	0.2 M Na_2HPO_4/cm^3	0.1 M citric acid/cm^3
4	30.9	49.1
6	50.6	29.4
8	77.8	2.2

2.2.3. Dye fixation

Only a proportion of the total dye, which exhausts onto the substrate, reacts to form covalent linkages, whilst the remaining dye is attached by ionic bonds and by van der Waals' forces. Therefore, in order to determine the degree of dye fixation the following procedure was used. A sample (1 g) of dyed fabric was immersed in 150 cm^3 of 20% aqueous pyridine solution, the temperature was raised rapidly to boiling and the treatment continued under reflux until no further dye was removed from the fibre, which took approximately 3 h. The stripped dyeing was thoroughly rinsed in tap water and allowed to dry at room temperature. The percentage of exhausted dye fixed was determined by a method used by several earlier workers [11–15,18,19] using Eq. (2), where $(K/S)_1$ and $(K/S)_2$ represent the colour strength of dyeing before and after stripping, respectively.

$$\%F = \frac{(K/S)_2}{(K/S)_1} \times 100 \tag{2}$$

This method assumes, at least at the concentrations of dyes employed, that (*K*/*S*) values are proportional to the concentration of dye on fabric. The overall percentage fixation, %*T*, was evaluated from Eq. (3).

$$\%T = \frac{\%F \times \%E}{100} \tag{3}$$

However, exhaustion (%*E*) could not be readily determined for the dyes of sparing solubility (Dyes **1–3** and **7**); therefore in the place of percentage of total fixation (%*T*), the percentages of fixation (%*F*) were calculated.

2.2.4. Determination of effective agent content of dyes

The effective agent content of each dye was determined by titration against titanium(III) chloride as previously described [18,19,21–24]. Invariably, the products as isolated contained salt and water, Mole In (MI) represents the mass, in grams of dye as isolated, which contains 1 mol of "pure" dye. To confirm the results obtained by titration against titanium(III) chloride, the percentage effective agent contents of the dyes were also determined by microanalysis. In the latter method the average of the figures for carbon and nitrogen only were used. As Dyes **1–3** and **7** were only sparingly soluble in water the effective agent content of each dye was determined by microanalysis.

2.2.5. Visible absorption spectra of dyes

Solutions of the seven novel dyes, achieved in the cases of Dyes **1–3** and **7** in acetone and, for Dyes **4–6** in distilled water, were prepared in the concentration range 0.01–0.12 $g\,l^{-1}$ and the absorbance of each solution was measured at the λ_{max}

of the dye, using 1 cm cells and a Philips model PU 8720 spectrophotometer. The molar extinction coefficients (ε_{max}) of the dyes were determined and are shown in Table 3.

3. Results and discussion

3.1. Visible absorption spectra of dyes

Dyes **1–3** were all yellow; Dyes **4–7** were all orange. The λ_{max} of the former group varied from 390 nm (Dye **2**) to 400 nm (Dye **3**) and the latter from 481 nm (Dye **6**) to 486 nm (Dye **7**). The individual members of each of the two groups were based on a common chromophore, and reactive group (single monochlorotriazine) but differed only in "second leg" substituent attached to the halotriazine. The introduction of successively more powerfully electron-withdrawing groups into the "second leg" attached to the halotriazine resulted in a slight hypsochromic shift. The order of reducing λ_{max} for the group comprising Dyes **1–3** was as follows: Dye **3**, λ_{max} 400 nm, 4-(2-sulphatoethylsulphonyl)aniline (PABSES) as "second leg" is more bathochromic than Dye **1**, chlorine as "second leg", λ_{max} 392 nm, and Dye **2** *m*-aminophenyltrimethylammonium chloride as "second leg" substituent, λ_{max} 390 nm. In the second group (Dyes **4–7**) λ_{max} reduces as follows: Dye **7**, λ_{max} 486 nm, 4-(2-sulphatoethylsulphonyl)aniline as "second leg", Dye **4**, chlorine λ_{max} 392 nm, Dye **5**, aniline λ_{max} 482 nm and Dye **6** *m*-aminophenyltrimethylammonium λ_{max} 481 nm.

The molar extinction coefficient of two groups of dyes varied slightly, but was approximately 13,000–14,000 ($mol^{-1}\,cm^{-1}$) and 20,000–28,000 ($mol^{-1}\,cm^{-1}$), respectively.

3.2. Effect of pH on dyeing performance

In the presence of water, depending on the pH within the fibre, the amino and carboxylic acid groups will be ionised to a greater or lesser extent, according to the equilibrium shown in Fig. 2.

$$\text{NH}_2\text{-PA-COO}^- \xrightleftharpoons{H^+} \text{HOOC-PA-NH}_2 \xrightleftharpoons{H^+} \text{HOOC-PA-NH}_3^+$$

Fig. 2. Protonation/deprotonation of nylon with varying acidity.

Under basic conditions, the cationic reactive dye will be adsorbed onto the anionic carboxylate groups in the fibre via ion–ion linkages. Consequently pH is a key parameter in influencing the level of exhaustion and therefore probably final fixation of the cationic reactive dye to nylon. It was thus necessary to determine the best application pH for each dye type in order to achieve optimum colour yield and dye fixation. A series of dyeings were evaluated, in buffers of different pHs, so as to determine the optimum application pH. Buffers of pH 4, 6, 8 and 10 were made as described above (Section 3) and the dyes applied for over 60 min at 98 °C.

Table 3
Molar extinction coefficients ε_{max} and absorption maximum λ_{max} of dyes

Dye	λ_{max}/nm	ε_{max}/mol^{-1} cm^{-1} l
1	392	13 625
2	390	12 500
3	400	14 690
4	485	27 512
5	482	20 985
6	481	20 157
7	486	28 649

As the results in Table 4 indicate, Dye **1** (at 0.18% o.m.f.), Dyes **3–5** (at 0.36% o.m.f.), fix more efficiently at pH 8, whilst Dye **2** (at 0.72% o.m.f.) and Dye **6** (at 1.44%, o.m.f.) fix best at pH 10. Dyes **1–3** are only sparingly soluble, thus measurement of the absorbance of each dye bath both before and after the dyeing process was not accurate. Therefore in these cases the percentage of exhaustion (%*E*) could not be determined and in the place of percentage of total fixation (%*T*), the percentages of fixation (%*F*) were calculated. Very low values of colour strength $(K/S)_1$ were not recorded. Dye **7** possesses the same mixed monochlorotriazinyl/vinylsulphone hetero-bifunctional reactive system as Dye **3**; with the former dye the optimum dyeing yield was obtained at pH 8 and because of the difficulties associated with sparing solubility, Dye **7** was also applied at pH 8.

The dependence of exhaustion and fixation on pH for the different dyes is shown in Figs. 3–8.

The optimum pH for dyeing nylon 6.6 with cationic reactive dyes was found to be between pH 8 and 10, where good exhaustion and fixation were achieved without the need for electrolyte or proprietary levelling agent.

As all the dyes (Dyes **1–7**) carried cationic groups, the observed increase in dye uptake (*K*/*S* value) that accompanied the increase in pH of application can be attributed to

Table 4
$(K/S)_1$, $(K/S)_2$, %*F* of all dyes and also %*E*, %*T* of soluble dyes (Dyes **4–6**) at different pH values

Dye	pH	4	6	8	10
1 (0.18% dye o.m.f.)	$(K/S)_1$	0.51	0.73	1.22	1.15
	$(K/S)_2$	0.37	0.52	1.2	0.74
	%*F*	72.5	71.2	98.4	64.3
2 (0.72% dye o.m.f.)	$(K/S)_1$	–	–	1.2	1.9
	$(K/S)_2$	–	–	1.1	1.8
	%*F*	–	–	91.6	94.7
3 (0.36% dye o.m.f.)	$(K/S)_1$	1.61	2.2	2.3	2.4
	$(K/S)_2$	0.87	1.6	2	1.7
	%*F*	54	72.7	87	71
4 (0.36% dye o.m.f.)	$(K/S)_1$	–	4.4	6	5.9
	$(K/S)_2$	–	3	5.4	4.4
	%*E*	–	60	100	90
	%*T*	–	40	90	67.7
5 (0.36% dye o.m.f.)	$(K/S)_1$	–	–	5.88	6.5
	$(K/S)_2$	–	–	4.83	5.6
	%*E*	–	–	68	70
	%*F*	–	–	82	86
	%*T*	–	–	56	60.3
6 (1.44% dye o.m.f.)	$(K/S)_1$	2.89	3.16	3.31	2.33
	$(K/S)_2$	1.85	2.5	2.8	1.88
	%*E*	90	90	100	80
		64	79	84.6	80.7
	%*T*	57.6	71.2	84.6	64.5

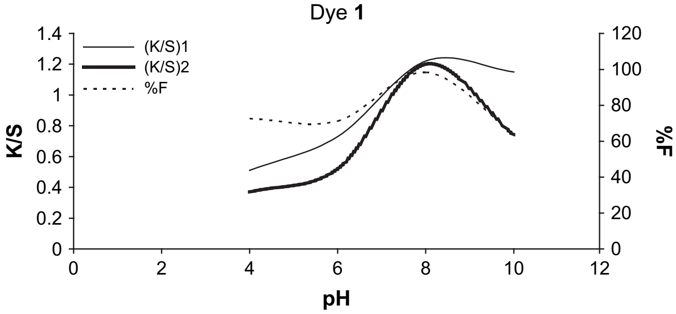


Fig. 3. $(K/S)_1$ (exhaustion), $(K/S)_2$ (fixed dye) and % fixation (%*F*) for Dye **1** at different pHs (0.18% dye o.m.f.).

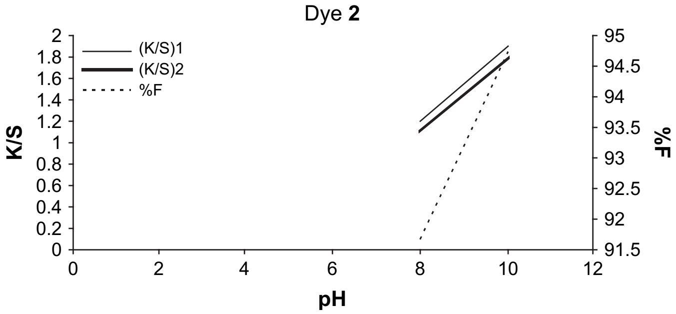


Fig. 4. $(K/S)_1$ (exhaustion), $(K/S)_2$ (fixed dye) and % fixation (%*F*) for Dye **2** at different pHs (0.72% dye o.m.f.).

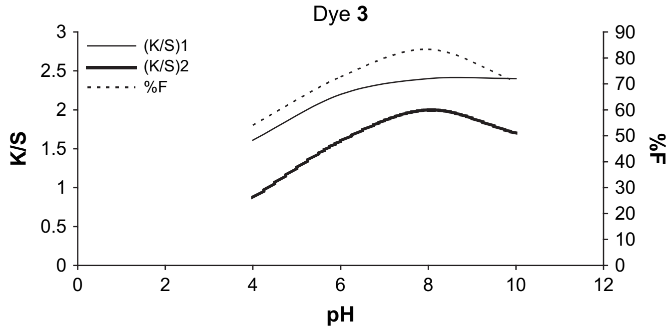


Fig. 5. $(K/S)_1$ (exhaustion), $(K/S)_2$ (fixed dye) and % fixation (%*F*) for Dye **3** at different pHs (0.36% dye o.m.f.).

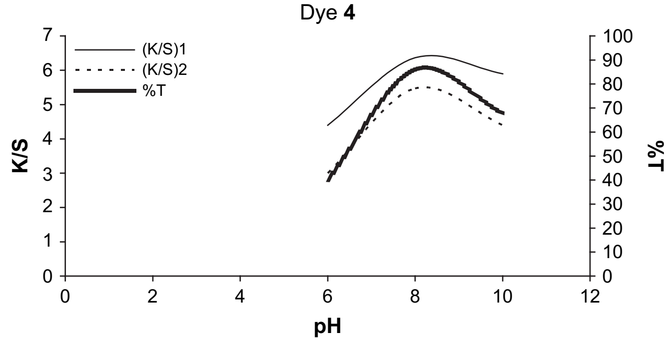


Fig. 6. $(K/S)_1$ (exhaustion), $(K/S)_2$ (fixed dye) and % total fixation (%*T*) for Dye **4** at different pHs (0.36% dye o.m.f.).

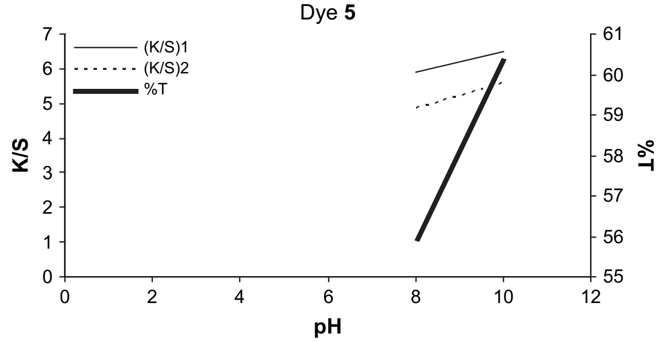


Fig. 7. $(K/S)_1$ (exhaustion), $(K/S)_2$ (fixed dye) and % total fixation (%*T*) for Dye **5** at different pHs (0.36% dye o.m.f.).

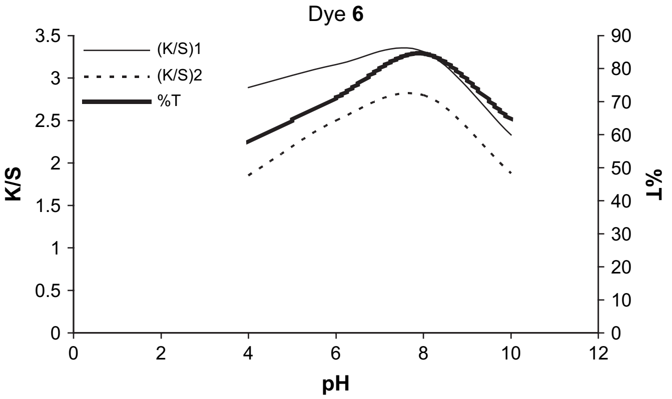


Fig. 8. $(K/S)_1$ (exhaustion), $(K/S)_2$ (fixed dye) and % total fixation (%*T*) for Dye **6** at different pHs (0.36% dye o.m.f.).

a corresponding increase in the attractive ion–ion interaction operating between the cationic groups in the dye molecule and the anionic carboxylate groups present in the fibre.

3.3. Build-up properties of dyes on nylon

Having established that the optimum dyeing pH was 8 for Dyes **1**, **3**, **4** and **5** and assumed to be 8 for Dye **7** (by comparison with Dye **3**) and pH 10 for Dyes **2** and **6**, the build-up properties of the dyes (Dyes **1**–**7**) were determined using the dyeing profile shown in Fig. 1. The strengths of the dyes were determined by microanalysis and/or titration against titanium(III) chloride [25] and the results are shown in Table 5.

Table 5
Effective agent contents of dyes

Dye	M_r	Mol. In	Strength/%
1	463	885	52
2	611	1754	35
3	725.5	832	87
4	474	707	67
5	531	1000	53
6	588	1019	58
7	719	774	93

Table 6 lists the build up (K/S data values) and percentage fixation (%F), exhaustion (%E) and percentage of total fixation (%T) obtained on dyeing nylon 6.6 with all novel cationic reactive dyes and two commercial products, Eriofast Red B and Eriofast Yellow R. It shows the percentage obtained on dyeing nylon with soluble dyes (Dyes **4**–**6**, Eriofast Red B and Eriofast Yellow R) at optimum application pH.

Results are depicted graphically in Figs. 9–17. In order to obviate discrepancies arising from the different molecular weights and effective agent contents of the dyes, build-up data were plotted using milli-molar concentrations of dye o.m.f.; therefore the dye concentration on the *x*-axis has been expressed in milli-moles of dye per kilogram of fibre.

Initially, the three hypsochromic dyes were based on a common chromophore, Dye **1** possesses a single dichlorotriazinyl reactive group and one cationic group, Dye **2** possesses a single monochlorotriazinyl reactive group and two cationic groups, while Dye **3** possesses a single cationic

Table 6
$(K/S)_1$, $(K/S)_2$, %F, of all dyes and %E and %T of soluble dyes (Dyes **4**–**6** and commercial dyes) at optimum pH

Dye	%Depth/o.m.f.				
		0.36	0.72	1.44	1.8
1	$(K/S)_1$	2.23	3.57	5.71	6.8
	$(K/S)_2$	1.8	2.7	4.2	5.1
	%F	81	75.6	73.5	75
2	$(K/S)_1$	0.99	1.9	2.8	3.4
	$(K/S)_2$	0.99	1.8	2.5	3
	%F	100	94.7	89.3	88
3	$(K/S)_1$	2.3	3.13	4.7	5.01
	$(K/S)_2$	2	2.9	4	4.2
	%F	87	86	85.1	84
4	$(K/S)_1$	6	11.3	19.4	21.5
	$(K/S)_2$	5.4	9.7	16.5	18.2
	%E	100	95	88	84
	%F	90	86	85	84.6
	%T	90	81.7	75	71.1
5	$(K/S)_1$	3.75	7.5	14.81	17
	$(K/S)_2$	3.54	7.13	13.17	15.43
	%E	100	100	99	96
	%F	94.4	95	89	90.76
	%T	94.4	95	88	87.13
6	$(K/S)_1$	3.31	5.6	11.1	12.93
	$(K/S)_2$	2.8	4.5	8.76	10
	%E	100	85	85	81
	%F	84.6	78.9	79	77.34
	%T	84.6	69.5	67	62.6
7	$(K/S)_1$	2.24	3.57	5	5.65
	$(K/S)_2$	2	3.1	4.3	4.45
	%F	89.3	86.8	86	78.76
Commercial yellow dye	$(K/S)_1$	2.9	5.8	11.3	13.4
	$(K/S)_2$	2.87	5.6	10.5	12.5
	%E	100	100	96	95
	%F	98.9	96.5	93	93.3
	%T	98.9	96.5	89	88.62
Commercial orange dye	$(K/S)_1$	2.64	5.28	9.9	12.6
	$(K/S)_2$	2.54	5.05	9	11.5
	%E	100	100	96	94
	%F	96.2	95	90	91
	%T	96.2	95	86	85

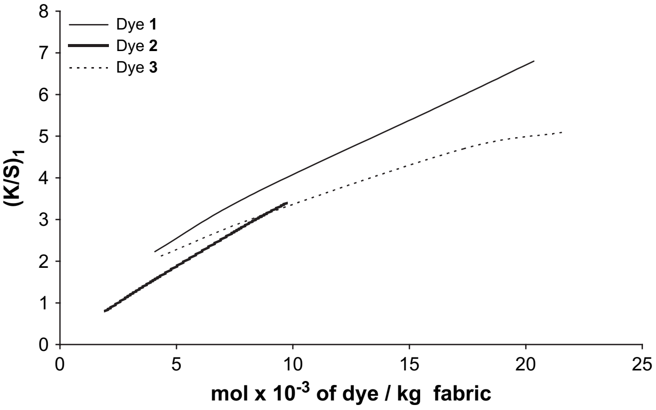


Fig. 9. $(K/S)_1$ values of Dyes **1**–**3**.

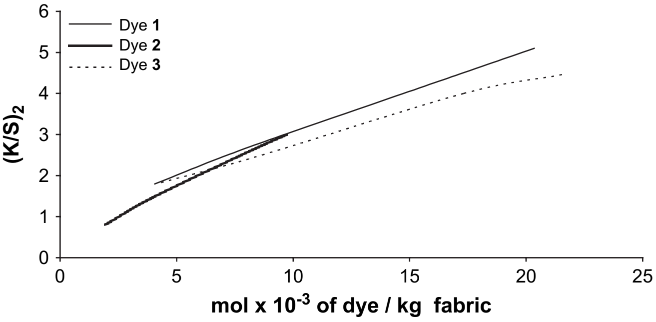


Fig. 10. $(K/S)_2$ values of Dyes **1**–**3**.

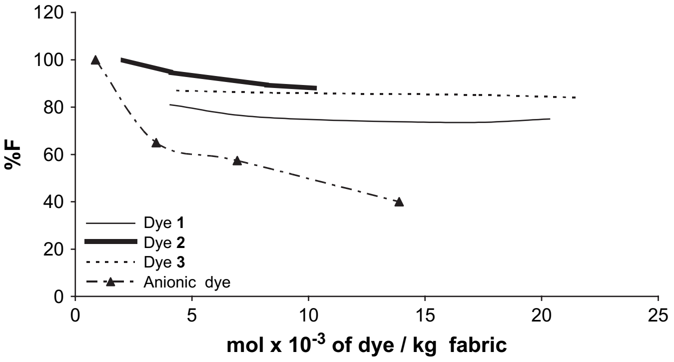


Fig. 11. %F values for Dyes **1**–**3** and an anionic reactive dye.

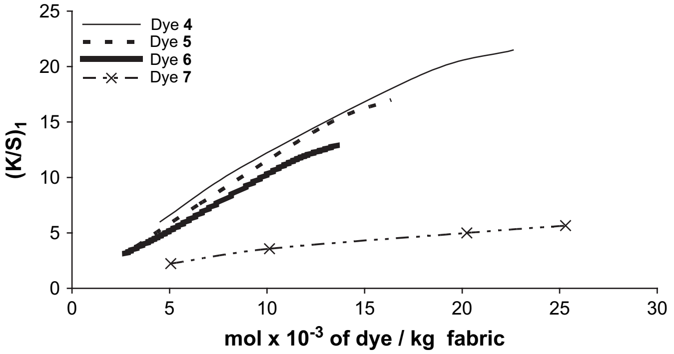


Fig. 12. $(K/S)_1$ values of Dyes **4**–**7**.

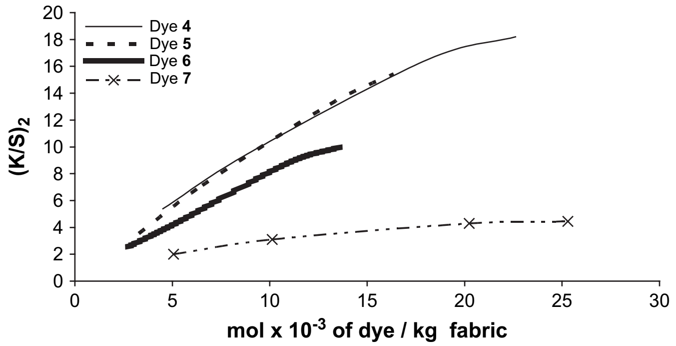


Fig. 13. $(K/S)_2$ values of Dyes **4**–**7**.

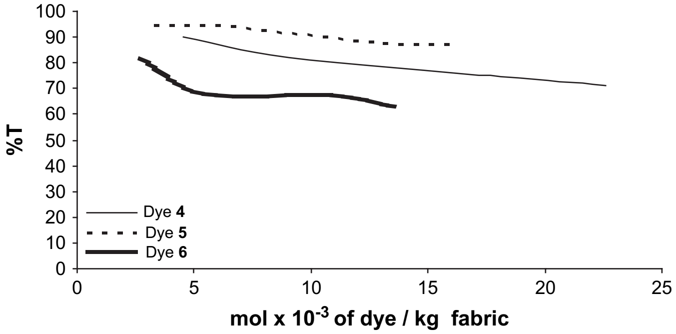


Fig. 14. (%T) values of Dyes **4**–**6**.

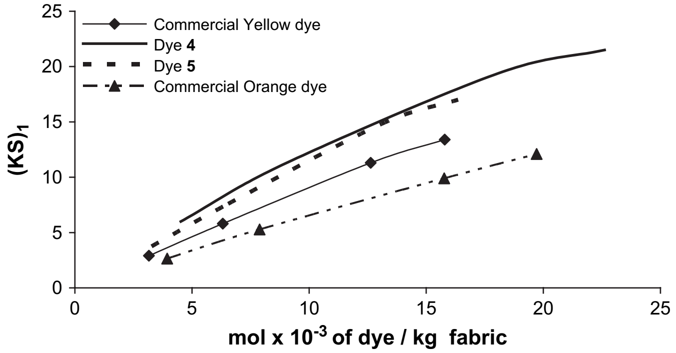


Fig. 15. $(K/S)_1$ values of the commercial dyes and Dyes **4** and **5**.

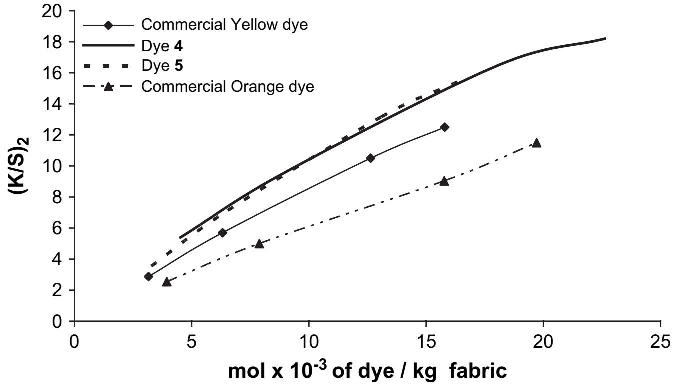


Fig. 16. $(K/S)_2$ values of two commercial reactive dyes for nylon and Dyes **4** and **5**.

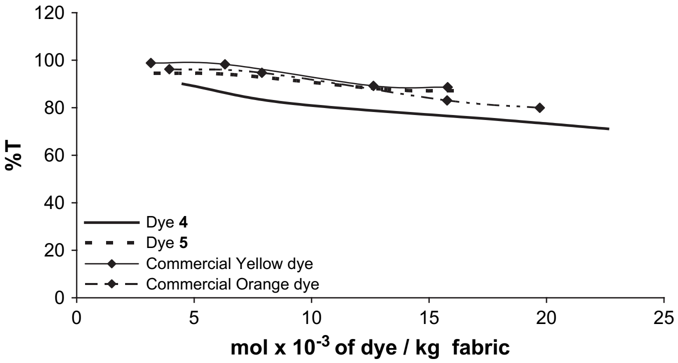


Fig. 17. %T values for two commercial reactive dyes for nylon and Dyes **4** and **5**.

group but has an additional reactive group (vinylsulphone). Dyes **1**–**3** are sparingly soluble and gave very low visual colour yield (K/S) due to the hypsochromic nature of the chromophore. The vinylsulphone group of reactive dyes, including hetero-bifunctional types Dye **3**, is usually formed, in situ, during dyeing in the presence of alkali. The most important precursor for dyes of this type is the β-sulphatoethylsulphone, which forms the corresponding reactive, vinylsulphone in the alkaline dye bath by elimination of sulphate. At a lower dye bath pH value, the sulphatoethylsulphone is relatively stable and an alkali-moderated, β-elimination step is required to generate the reactive vinylsulphone form [26,27].

From the results displayed in Table 6 and Figs. 9–11, it can be seen that the initial exhaustion $(K/S)_1$ of Dye **1** is higher than that of Dyes **2** and **3**, but that all dyes behave very similarly in terms of fixed dye $(K/S)_2$. Fig. 11 suggests that cationic dyes exhibit better fixation efficiency compared with anionic dyes (Dye **4**), from an earlier study [18,19] in which it was shown that the build up and fixation of anionic dyes tail off long before all the formally available amine groups were reacted with dye; that its build up was likely to be limited, not by the number of amino sites present, but more by steric hindrance and/or electrostatic repulsion. Thus at pH (8–10) essentially most of the amino groups will be present in the free, un-protonated form and hence highly nucleophilic and reactive towards electrophilic reactive groups. Additionally at this high pH essentially all of the carboxylate acid groups will be de-protonated and hence anionic. Under these conditions, therefore, both electrostatic attraction between dye and fibre and availability of nucleophilic amino groups will be maximised. It was readily demonstrated that high F/E values were attainable with cationic dyes relative to anionic dyes and thus four novel orange, cationic reactive dyes (Dyes **4**–**7**) were evaluated. All dyes were monocationic, except Dye **6** which was a bis-cationic species. Both Dyes **5** and **6** possess a single monochlorotriazinyl reactive group; Dye **4** a single dichlorotriazinyl reactive group and Dye **7** a bifunctional (monochlorotriazinyl and sulphatoethylsulphone) reactive group. The evaluation of this series of novel dyes was hindered by widely varying solubility. Dyes **4**–**6** were readily soluble in water whereas Dye **7** was only sparingly soluble; therefore, measurement of the absorbance of the dye bath (Dye **7**) before and after the dyeing process was not accurate, and so the percentage of exhaustion (*%E*) could not be readily determined.

Fig. 12 shows that the initial exhaustion of Dye **4** is marginally higher than that of Dyes **5** and **6**, but that all of these are much greater than that of Dye **7**. Build up, initial and final exhaustion of Dye **7** were very much lower than the other dyes; this might be related to lack of solubility of Dye **7**. Figs. 12–14 show that the bis-cationic monochlorotriazinyl (MCT) dye, Dye **6**, shows less build up, than Dyes **4** and **5**; less initial and final exhaustion than the monocationic monochlorotriazinyl (MCT) dye, Dye **5**. It is possible that one cationic group interacts efficiently with one anionic carboxylate group of nylon, whereas with the bis-cationic Dye **6** a greater build-up of positive charge, as dye fixes, impedes approach of further bis-cationic dye. This suggests that, although the monochlorotriazins, Dyes **5** and **6**, are significantly less reactive than the dichlorotriazine, Dye **4**, they are still sufficiently reactive to react efficiently with the amino end groups of nylon under the chosen application conditions. Dye **7** was only sparingly soluble and conclusions about the stability of the second reactive group were thus difficult to draw. In the next step, Dyes **4** and **5** were compared with two commercially available reactive dyes for nylon.

Figs. 15–17 show that the initial and final exhaustion of monocationic MCT (Dye **5**) and monocationic DCT (Dye **4**) were better than the two commercial dyes. They (especially Dye **5**) gave very high fixation, similar to the commercial dyes.

3.4. Wash fastness properties of dyes

The wash fastness of Dyes **1**–**7** were assessed using the ISO 105CO6/C2S wash fastness test at 60 °C [28]. The change in shade and the degree of cross-staining were assessed visually using grey scales and the results are presented in Table 7. The wash fastness, as expected, of each dye fixed to nylon 6.6 fabrics was very good at each of the four depths of shade employed.

Table 7
Wash fastness results of dyes in the ISO 105CO6/C2S

Dye	Staining					
	Secondary cellulose acetate	Bleached un-merc. cotton	Nylon 6.6	Polyester	Acrylic	Wool
1	5	5	5	5	5	5
2	5	5	5	5	5	5
3	5	5	5	5	5	5
4	5	5	5	5	5	5
5	5	5	5	5	5	5
6	5	5	5	5	5	5
7	5	5	5	5	5	5

4. Conclusions

At high pH the build up and fixation of anionic reactive dyes on nylon is limited by electrostatic repulsion between dye and anionic carboxylate groups present in the nylon.

At low pH the effective concentration of anionic carboxylate groups is greatly reduced, and that of cationic protonated amino groups increased, leading to electrostatic attraction between dye and fibre but a massive reduction in the concentration of free amino groups, the nucleophilic species responsible for reactive with dye.

Under alkaline conditions the fixation and build up of cationic reactive dyes on nylon are excellent. Because covalent bond formation between dye and nylon is efficient, the resulting dyeing exhibit excellent wet fastness. Monocationic dyes appear to build up better than bis-cationic types; this may be associated with the build up of positive charge on the fibre as more dye fixes leading to reduced electrostatic attraction between dye and fibre at heavy depths of shade.

Acknowledgement

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