Dyeing of Nylon 6 and Silk Fabrics with Novel Polyfunctional Disazo Reactive Disperse Dye

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Abstract: The synthesis of a new polyfunctional disazo reactive disperse dye containing bis (sulphatoethylsulphone) /monochlorotriazine reactive system is described. The structure of the synthesized dye was established and confirmed by TLC, elemental analysis and spectral data (IR and ^{1}H-NMR).The dye has been applied to nylon 6 and silk fabrics at a variety of pH. Optimum dye exhaustion and fixation were achieved at pH 8 and 100 °C. The introduction of two temporarily anionic sulphatoethylsulphone and monochlorotriazine reactive groups into the reactive disperse dye molecule was found to promote the fixation and the build up, as a result of the combination between two different reactivity in the dye a complementary behavior achieved to resist variations in dyeing conditions. The results of dyeings on both substrates indicate that the model polyfunctional disazo reactive disperse dye shows a higher degree of exhaustion and fixation on silk than on nylon 6. All the dyed fabrics tested displayed high light fastness and excellent fastness properties.

1. Introduction

Different studies have been investigated about the use of a single dye type for different fibre types. This goal have been achieved by the use of reactive disperse dyes which possessed the features needed for the affinity for any of the widely used fibre types without the need to conduct separate reactions outside the dyebath (Suwanruji, 2004). Attempts have been made to produce different types of reactive disperse dyes for example reactive disperse dyes carrying monochlorotriazine (Stapleton and Waters, 1981, De Giorgi and Cerniani, 1987, De Giorgi, 1989), vinylsulphone (Nishida *et al*., 1980, Nishida *et al*., 1981) and disulphide bis (ethylsulphone) (Mousa and Youssef, 2003) reactive groups. Reactive disperse dyes containing β-sulphatoethylsulphone (SES) group have been extensively reported. In an earlier study, Dohmyou *et al.* applied reactive disperse dyes containing SES group to silk, polyester and nylon fabrics (Dohmyou *et al.,* 1990). Later, Burkinshaw and Collins reported that the wet fastness of dyed nylon fabrics could be improved by the use of SES reactive disperse dyes (Burkinshaw and Collins, 1994). Lee *et al*. synthesised SES reactive disperse dyes and investigated their dyeing properties on wool (Lee *et al.,* 2001), polyester (Lee and Kim, 1999, Lee and Kim, 1999, Lee and Kim, 2000, Lee *et al.*, 2002, Koh *et al.*, 2003, Lee *et al.*, 2005) and polyester/cotton blend fabrics (Lee *et al.*, 2003) as temporarily solubilised disperse dyes. These studies investigated reactive disperse dyes as monofunctional dyes.
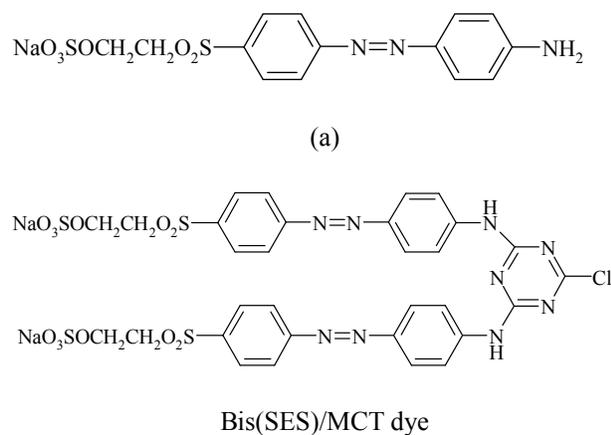
In our previous studies we reported the synthesis of homobifunctional reactive disperse dyes having bis (SES) reactive groups applied on nylon 6 (Youssef *et al.*, 2007) and silk (Youssef *et al.*, 2009) fabrics. These studies illustrated that the bifunctional dye fixed effectively to silk and nylon 6 with improved application properties being accounted to its highly nonionic reactive bis-vinylsulphone system under alkaline conditions (pH 8). By virtue of the characteristic dye structure reactivity, excellent leveling and fastness properties were also obtained. Also the neutral dyeing of wool, polyester and wool/polyester blend fabrics has been investigated using this type of reactive disperse dyes (Mousa *et al.*, 2011).

In other studies we reported heterobifunctional reactive disperse dye having SES reactive group combined with disulphide bis(ethylsulphone) reactive group which have been applied on nylon 6 fabric (Mousa *et al.*, 2006). This bifunctional reactive disperse dye exhibited high exhaustion and fixation values at pH 6 and 120 °C. The results also indicate that the combination of temporarily anionic and nonionic reactive groups of the bifunctional dye provided great enhancement in dyeing performance compared to that of the monofunctional dye. The dyes also showed very good leveling and fastness properties on nylon 6 fabric.

For further study, we investigated hetero-bifunctional reactive disperse dye having SES reactive group combined with monochlorotriazine (MCT) reactive group. The dye was applied on nylon

6 fabric and compared with a new monoazo polyfunctional reactive disperse dye containing bis(SES)/MCT reactive system (Mousa *et al.*, 2007).The merit of these dyes relied on its applicability in alkaline medium, which would increase the ability to build up further with good application properties.

The present study reports the synthesis and evaluation of related disazo polyfunctional reactive disperse dye based on bis(SES)/MCT reactive system using a simple monoazo SES dye (a) which twice condensed with cyanuric chloride forming the target disazo polyfunctional reactive disperse dye.

$NaO_3SOCH_2CH_2O_2S$—⟨phenyl⟩—$N{=}N$—⟨phenyl⟩—NH_2

(a)

$NaO_3SOCH_2CH_2O_2S$—⟨phenyl⟩—$N{=}N$—⟨phenyl⟩—NH—(triazine)—Cl

$NaO_3SOCH_2CH_2O_2S$—⟨phenyl⟩—$N{=}N$—⟨phenyl⟩—NH—(triazine)

Bis(SES)/MCT dye

2.Experimental
General

Dye purity was assessed by thin layer chromatography (TLC) using eluent system, ethylacetate: n-propanol (2:1, v/v) on silica gel plates. Infrared (IR) spectra were recorded on a Nexus 670 FTIR Spectrometer (KBr; Thermo Nicolet). ^{1}H-NMR spectra were recorded on a JEOL JNM-EX 500 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. The maximum absorption wavelength (λ_{max}) was measured on a Shimadzu UV-2401PC UV/Vis spectrophotometer. Dyed samples were evaluated for their colour properties using an UltraScan PRO spectrophotometer (Hunter Lab) with a D_{65} illuminant and 10° standard observer.

Materials

Scoured and bleached single jersey knitted polyamide 6 (nylon 6) fabric, 114 g/m^2, 135 d/30f was obtained from El-Shourbagy Co., Egypt. Before dyeing, the fabric was treated with a solution containing 2 g/l nonionic detergent (Hostapal CV, Clariant, Egypt) at 80 °C for 1 h, thoroughly washed in water and air dried at room temperature.

Degummed and bleached silk fabric, 80 g/m^2 was obtained from El-Khateib Co. Before application, the fabric was treated in an aqueous solution containing 2 g/L (Hostapal CV, Clariant, Egypt) for 1 h at 80 °C and a 50:1 liquor ratio (LR), then washed thoroughly in water and air dried at room temperature (RT).

Aniline was obtained from Fluka Chemie AG. 1-Aminobenzene-4-β-sulphatoethylsulphone was obtained from Amar Impex, Mumbai, India. Cyanuric chloride was obtained from Merck. All other chemicals and solvents used in this study were of laboratory reagent grade.

Synthesis of polyfunctional disazo reactive disperse dye

A solution of diazotised 1-aminobenzene-4-β-sulphatoethylsulphone (14.8 g at 95% purity, 0.05 mol), prepared by the method previously described (Lewis *et al*., 2000), was supplied with aniline solution (4.9 g at 95% purity, 0.05 mol) in distilled water (25 ml) and hydrochloric acid (6 ml, 36%) over 30 min at 0-5°C. The mixture was stirred for 3 hrs, maintaining the temperature below 5°C and the pH at 3.5-4.

The pH of the resultant azo dye (a) solution was adjusted to 6-7, then poured by ratio 2:1 there into a freshly prepared suspension of cyanuric chloride (4.85 g at 95% purity, 0.025 mol) in acetone (25 ml) and crushed ice (15-20 g) the reaction mixture was stirred at 0-5 °C for 4 hrs while controlling the pH at 4-5 using 2M aqueous solution of sodium carbonate, for completing the first condensation reaction for the half amount of the prepared dye used, then the temperature of the reaction mixture was then raised up to 30 °C and adjusting the pH 5-5.5 for 5 hrs, in order to complete the second condensation reaction for the second half of the prepared dye.

The dye was then filtered off and dried at room temperature under vacuum (yield 84.5%). The dye was characterised by TLC (R_f = 0.57) and λ_{max} (50% DMF) = 372.60 nm.

Bis(SES)/MCT dye: $C_{31}H_{26}N_9 O_{12}S_4Na_2Cl$ (926.29) [M$^+$-1] = 925.00. Calcd.: C, 40.19; H, 2.80; N, 13.61 ; S, 13.83%, Found: C; 44.23; H, 2.63; N, 13.50; S, 13.12 %. IR (ν, cm^{-1}): 3441 (NH), 1616 (-N=N-), 1137 (-SO$_2$-), 1227, 1051, and 999 cm^{-1} (-OSO$_3^-$). ^{1}H-NMR: δH (ppm) in [$_2$H^6]DMSO: 3.63-3.65 (4H, *t*, J = 6.8 Hz, α-CH$_2$ $_{(SES)}$), 3.92-3.94 (4H, *t*, J = 6.8 Hz, β-CH$_2$ $_{(SES)}$), 6.71 (2H, *d*, J = 7.6 Hz, phenyl H), 7.71 (2H, *d*, J = 8.4 Hz, phenyl H), 7.87 (2H, *d*, J = 8.4 Hz, phenyl H), 7.97 (2H, *d*, J = 7.6 Hz, phenyl H).

Dyeing procedure

Silk and Nylon 6 fabrics were dyed using the synthesized polyfunctional reactive disperse dye in an Ahiba dyeing machine with 2-g samples at a liquor ratio 50:1. The dyebath was prepared at room

temperature in the presence of dye concentrations (1-5 % owf). The dyebath was prepared at pH 4, 5, 6, 7 and 8 in 0.2 *M* disodium hydrogen phosphate/0.1 *M* citric acid buffer solutions. Dyeing was started at 40°C and then the temperature raised to 100 °C over 60 min. Dyeing was continued at the desired temperature for a further 45 min (105 min total dyeing time) unless otherwise specified. After dyeing, all dyed samples were rinsed with water and air dried. Dye exhaustion and total dye fixation on silk and nylon 6 fabrics were evaluated spectrophotometrically.

Measurements and testing
Dye exhaustion
The uptake of the reactive disperse dye by nylon 6 and silk fabrics were measured by sampling the dyebath before and after dyeing. The dye concentration (g/L) of the dyebath, diluted 20-fold with 50% aqueous DMF, was measured spectrophotometrically at the λ_{max} value using a calibration curve previously obtained using known dye concentrations (g/L) in 50% aqueous DMF. The percentage of dyebath exhaustion (%*E*) was calculated using Eq. 1 (Burkinshaw *et al.*, 2001):

$$\%E = \left[1 - \left(C_2 \Big/ C_1 \right) \right] \times 100 \qquad (1)$$

$C1$ and $C2$ are the dye concentrations in the dyebath before and after dyeing, respectively.

Dye fixation
The dye fixation (%*F*), the percentage of the exhausted dye chemically bound on the fiber, was measured by refluxing the dyed samples in 50% aqueous DMF (20:1 LR) for 15 min to extract the unfixed dye. This procedure was repeated until the extract was clear. The concentration of the extract was then measured spectrophotometrically at the λ_{max} value of each dye and the dye fixation ratio calculated using Eq. 2 (Burkinshaw *et al.*, 2001):

$$\%F = \frac{\left(C_1 - C_2 - C_3 \right)}{\left(C_1 - C_2 \right)} \times 100 \qquad (2)$$

Where, C_3 is the concentration of extracted dye.
From the dyebath exhaustion (*E*) and dye fixation (*F*), the total dye fixation (*T*), which is the percentage of dye chemically bound relative to the total amount of dye used, was calculated for all dyeings using Eqn 3 (Burkinshaw *et al.*, 2001):

$$\%T = \frac{\left(\%E \times \%F \right)}{100} \qquad (3)$$

Fastness testing
The dyed samples, after washing-off using 2 g/l nonionic detergent (Hostapal CV: Clarient, Egypt) at 80°C for 15 min, were tested by the standard ISO methods (Methods of test, 1990). The tests were as follows: Colour fastness to washing, ISO 105-C02 (1989); fastness to rubbing, ISO 105-X12 (1987); fastness to perspiration, ISO 105-E04 (1989); and fastness to light (ISO 105-B02 (1988).

3. Results and Discussions
**Characterization of reactive disperse dye**
The purity of the dye was evaluated by TLC using ethylacetate: n-propanol as eluent system. IR spectrum of the dye showed absorption bands at 1227, 1137, 1051 and 999 cm^{-1}, relative to the stretching of -SO$_3^-$ and SO$_2$ groups. The ^{1}H NMR spectrum of the synthesized dye shows two triplets at 3.63 and 3.93 ppm, each integrated to four protons, assignable to the α- and β-methylene protons of the bis(SES) group, respectively.

Effect of pH
The effect of pH on the exhaustion and fixation of the ployfunctional reactive disperse dye on silk and nylon 6 fabrics was studied using 2% owf dye concentration. For this purpose, a series of dyeings were carried out by varying the dyebath pH from 4 to 8. The results given in Figure 1 clearly show that the exhaustion values and the total fixation yield significantly increased up to pH 6 then slightly vary over the pH range between 6 and 8 reaching maximum values at pH 8, this feature appeared for both fabrics. This reflects the advantages of the combination of two reactive groups having different reactive levels, because the two reactive groups being complement each other for variations in dyeing conditions. Applying the dye at pH 8 generate two important advantages, firstly would increase the β-elimination of the temporarily anionic sulphatoethylsulphone groups, secondly maximize the concentration of the nucleophilic amino end-groups on the fiber. This may suggest that the nonionic bifunctional vinylsulphone derivative of the dye, generated from the β-elimination reaction of the two temporarily anionic sulphatoethylsulphone groups, in addition to the presence of the monochlorotriazine reactive group, can maximize the nucleophilic reaction with the amino groups on both fabrics.
The results also clearly show that the exhaustion and total fixation yield on silk fabric was higher than that on nylon 6 fabric. This can be attributed to the higher amino group content of silk than nylon 6 (Cookson and Harrigan, 1992), which results in better

fixation of the nonionic reactive bis(VS)/MCT form on silk.
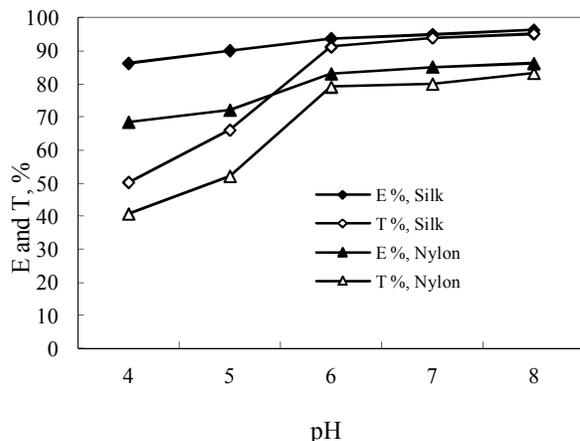
Figure 1: Effect of pH on the exhaustion (E) and total fixation (T) of the polyfunctional reactive

disperse dye (2% owf) at 100 ˚C on silk and nylon 6 fabrics.

Effect of dyeing time

Having established that the optimum dyeing pH was 8 for the polyfunctional dye on both fabrics, the extent of exhaustion and total fixation yield was investigated at different dyeing time and at 100Cº using 2% owf dye concentration. The results given in Figure 2 clearly show that the dye displays good build up and exhibits high rate of exhaustion especially on silk fabric then equilibrate at dyeing time (105 min) for both fabrics, probably due to its high substantivity. It is also clear that the total fixation yield of the dye increases as the dyeing proceeds. This may be due to that the hydrophobic character of the nonionic bis(vinylsulphone)/ MCT reactive system in the dye, generated from β-elimination reaction of the temporarily anionic bis(SES) groups, not only imparts high substantivity under the alkaline dyeing but also effectively exhibits high fixation efficiency.
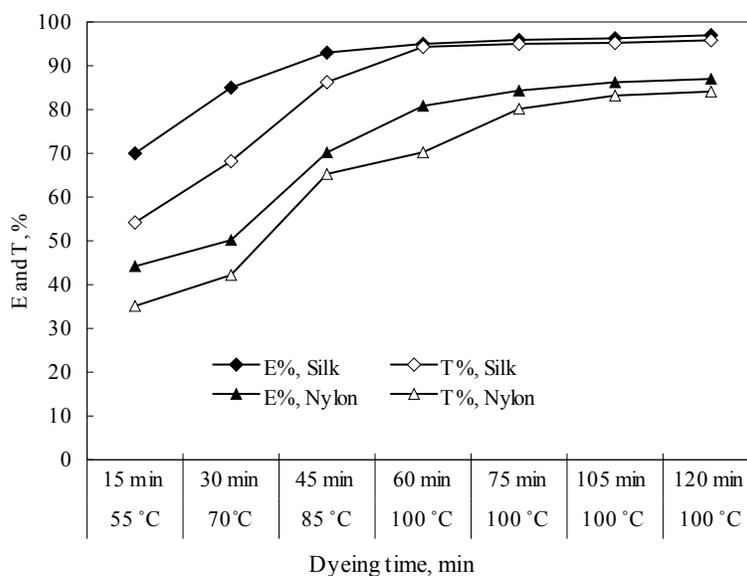

F**igure 2**: Effect of dyeing time on the exhaustion and total fixation of the dye (2% owf) at pH 8 and 100 ˚C on silk and nylon 6 fabrics.

Effect of dye concentration

The study was investigated further by carrying out dyeings with concentrations from 1 to 5 % owf with the optimum dyeing pH 8 and 100Cº. The results of the extent of the exhaustion and total fixation yield of the dye on silk and nylon 6 fabrics are given in figure 3. From which, it can be seen that the extent of exhaustion and fixation yield of the dye on both fabrics decrease with increasing dye concentration. This is due to lowering of dye substantivity at higher dye concentrations as a result of increasing dye aggregation, which lowers dye

penetration in the fiber. Additionally, at high dye concentrations the number of available dye sites on the fiber decreases and competitive hydrolysis increases, resulting in a lower extent of exhaustion and fixation yield of the dye.

It is also seen that the dye exhibits a higher degree of exhaustion and fixation values on silk than on nylon 6. This results from the higher proportion of amino groups on silk, which allow a greater degree of dipole–dipole interaction with the nonionic bis(VS)/MCT reactive system, resulting in higher dye–fibre fixation.
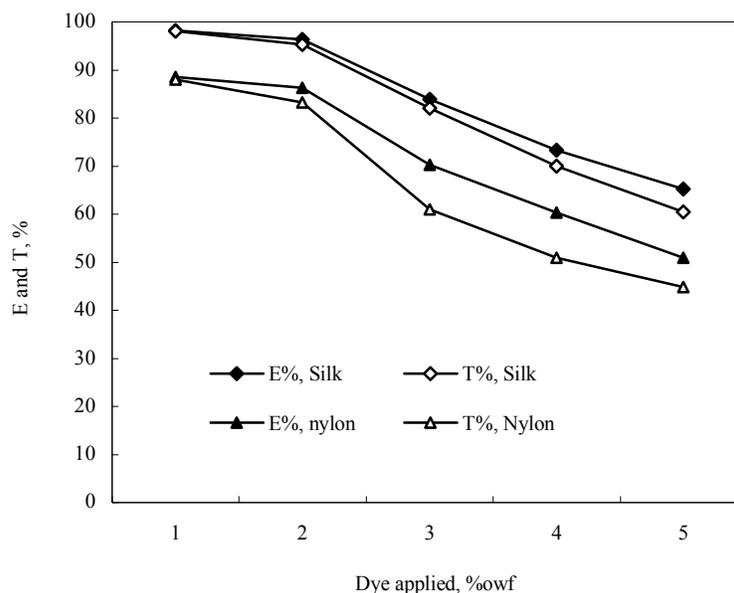
Figure 3: Exhaustion and total fixation at different dye concentrations, pH 8 and at 100 ˚C on silk and nylon 6 fabrics.

Fastness properties

The colour strength and fastness properties of the polyfunctional reactive disperse dye on both silk and nylon 6, dyed at 2% owf, liquor ratio 50:1, pH 8 and 100 °C, were investigated and are given in Table 1. The results show that all the dyed fabrics tested displayed high light fastness and excellent fastness to washing, rubbing and perspiration.

Table 1. Colour strength (K/S) and fastness properties of the polyfunctional reactive disperse dye on silk and nylon 6 fabrics

Fabric	K/S	Fastness to rubbing		Wash fastness			Fastness to Perspiration						Light
							Alkaline			Acidic			
		Dry	Wet	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW	
Silk	**18.57**	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	6
Nylon 6	21.07	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	6

Alt = alteration; SC = staining on cotton; SW = staining on wool

Conclusion

A new disazo polyfunctional reactive disperse dye, containing two temporarily anionic SES and MCT reactive groups, has been synthesised and shown to have good dyeing performance on silk and nylon 6 fabrics. Optimum exhaustion and fixation on both fabrics was achieved by dyeing at pH 8 and 100 °C. The β-elimination of the two temporarily anionic SES groups under alkaline conditions results in the formation of a nonionic reactive vinylsulphone derivative in combination with monochlorotriazine as having different reactivity level, achieving a complementary behavior to resist variations in dyeing conditions, which in turn increasing the dye–fibre interaction and improving the fixation on both silk and nylon 6 fabrics. The dyeing performance of this type of reactive disperse dye may lead to the design of novel reactive disperse dyes with good application properties.

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