# Chemical Science & Engineering Research

## Dyeing of Nylon 6.6 with Polyfunctional Disazo MCT/SES Reactive Disperse dyes derived from Aminothiophene Moiety/1-Aminobenzene-4-B-Sulphatoethylsulphone

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**Abstract:** Synthesis of a new polyfunctional disazo MCT/SES reactive disperse dyes derived from aminothiophene moiety/1-aminobenzene-4-β-sulphatoethylsulphone is described. These disazo polyfunctional reactive disperse dye based on bis(SES)/MCT reactive system was coupled with 4-aryl-2-aminothiophene derivatives using a simple mono-azo SES dye which twice condensed with cyanuric chloride forming the target disazo polyfunctional reactive disperse dye. The synthesized dyes were purified by recrystallization method and the structure was confirmed by TLC, UV-Visible, FT-IR, GC-MS, and NMR studies. The dyes were applied to Nylon 6.6 fabrics. Optimum dye exhaustion and fixation were achieved at pH of 8 and temperature of 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 buildup. The presence of thiophene moiety resulted in excellent brightness of shade. The results of dyeing on nylon 6.6 indicate that the novel polyfunctional disazo reactive disperse dye shows a higher degree of exhaustion and fixation. All the tested dyed fabrics showed good to moderate light fastness ratings of 4 to 5, and very good fastness to washing and perspiration of 4-5.

**Keywords:** Disazo reactive disperse dyes; Polyfuntional; Sulphatoethylsulphone/ monochlorotriazine reactive disperse dye; Aminothiophene Nylon 6.6

## 1. Introduction

In the past decades, several attempts have been made to produce different types of reactive disperse dyes, particularly, reactive disperse dyes carrying monochlorotriazine,[1-3] vinylsulphone[4,5] and disulphide bis (ethylsulphone) reactive groups.[6] 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.[7] Later, Burkinshaw and Collins reported that the wet fastness of dyed nylon fabrics could be improved by the use of SES reactive disperse dyes.[8] Lee et al.[9] synthesized SES reactive disperse dyes and investigated their dyeing properties on wool, polyester[10-12] and Polyester/cotton blend fabrics as temporarily solubilized disperse dyes. The dye was applied on nylon 6.6 fabric and compared with a new monoazo polyfunctional reactive disperse dye containing bis (SES)/MCT reactive system.[13] 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. Khatri et al.,[14-16] utilized various reactive and disperse dye compounds for dyeing of cellulose nanofibers. They found that the dyes are highly effective in the dyeing process. The interaction molecules and the fabrics were also well demonstrated.[17,18]

Interest in the design of azo dyes containing heterocyclic moieties stems from their high degree of brightness compared to azo dyes derived from anilines.[19] The 2-aminothiophene based azo dyes are known as disperse dyes with excellent brightness of shade. This class of dyes was established as an alternative to more expensive anthraquinone dyes.[20] Thiophene belongs to a class of heterocyclic compounds containing a five membered ring made up of one sulphur as heteroatom with the formula $C_4H_4S$. Thiophene and its derivatives exist in petroleum or coal. Thiophene structure can be found in certain natural products and is also incorporated in several pharmacologically active compounds.[21] The thiophene-containing azo dyes have many advantages including a colour deepening effect as an intrinsic property of the thiophene ring and small molecular structure leading to better dye ability. The present research reports the synthesis and evaluation of disazo polyfunctional reactive disperse dye based on bis(SES)/MCT reactive system coupled with 4-aryl-2-aminothiophene derivatives using a simple monoazo SES dye (a) which twice condensed with cyanuric chloride forming the target disazo polyfunctional reactive disperse dye. Synthesized polyfunctional reactive disperse dye were characterized by means of FT-IR and NMR spectral investigation. After being optimized, the polyfunctional reactive disperse dyes were applied for the dyeing process of nylon 6.6.

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**Table 1.** Physical characteristics of polyfunctional dyes based on aminothiophene moiety

| Dye code | Empirical formula | Molecular mass (g mol$^{-1}$) | Melting point ($^{\circ}$C) | Yield (%) | Colour of crystal |
|---|---|---|---|---|---|
| I$_{13}$ | C$_{39}$H$_{32}$O$_{12}$N$_9$S$_6$Cl | 997.5 | 180-182 | 56 | Yellow |
| I$_{14}$ | C$_{39}$H$_{32}$O$_{12}$N$_9$S$_6$Cl$_3$ | 1116.5 | 132-135 | 48 | Orange |
| I$_{15}$ | C$_{39}$H$_{38}$O$_{12}$N$_9$S$_6$Cl | 1051.5 | 150-152 | 51 | Orange |
| I$_{16}$ | C$_{39}$H$_{30}$O$_{12}$N$_9$S$_6$Cl$_5$ | 1185.5 | 190-192 | 49 | Orange |
| I$_{17}$ | C$_{39}$H$_{32}$O$_{12}$N$_9$S$_6$ClBr | 999.4 | 157-160 | 70 | Orange |

# 2. Experimental Section

## 2.1. Materials and Characterization

All the chemicals used in the synthesis of the dyes were of analytical grade and were used without further purification. The melting points of the synthesized compounds were determined by open capillary method using melting point apparatus expressed in degree Celsius and are uncorrected. Small amount of each dye was filled into a capillary each and placed into the apparatus.

The purity of the compound was checked by thin layer chromatography (TLC) on silica gel plates using diethylether: ethanol (75%: 25%) solvent mixture. The UV-Visible absorption spectra were recorded using CARY 630 UV-Visible Spectrophotometer Model: Agilent Technology. The Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded on FTIR Nexus 670 spectrometer in KBr disc (Thermo Nicolet) and absorption bands are expressed in cm$^{-1}$. Gas-chromatography-mass spectroscopy (GC-MS) and nuclear magnetic resonance spectroscopy (NMR) was carried out using Agilent technologies 7890B GC system- 5977A Mass spectrometer and Neutron Magnetic Resonance spectrometer, respectively. The light fastness was carried out using Microsal light fastness tester model no 225 and Blue wool standards.

## 2.2. Synthesis of Polyfunctional Disazo Reactive Disperse Dyes Based On 4-aryl-2-aminothiophene Intermediate (I$_{13}$-I$_{18}$)

A solution of diazotised 1-aminobenzene-4-β-sulphatoethylsulphone (14.8 g at 95 % purity, 0.05 mol), was prepared and reacted with a solution of each of the 2-amino-4-phenylthiophene intermediates (AI1-AI6) (4.9 g, 0.05 mol) respectively, in distilled water (25 ml) and hydrochloric acid (6 ml, 36%) over 30 min at 0-5 °C. The mixture was stirred for 3 hours, maintaining the temperature below 5 °C and the pH at 3.5-4. The six mono reactive azo disperse dyes obtained was filtered off and dried at room temperature under vacuum (Lewis et al., 2000) and weighed respectively. The pH of the mono functional disperse reactive dyes (I$_1$-I$_6$) was adjusted to 6-7, then poured by ratio 2:1 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 hours 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 5.5 for 5 hours, in order to complete the second condensation reaction for the second half of the prepared dye.[22] The polyfunctional disazo reactive dyes were then filtered off and dried at room temperature and weighed.
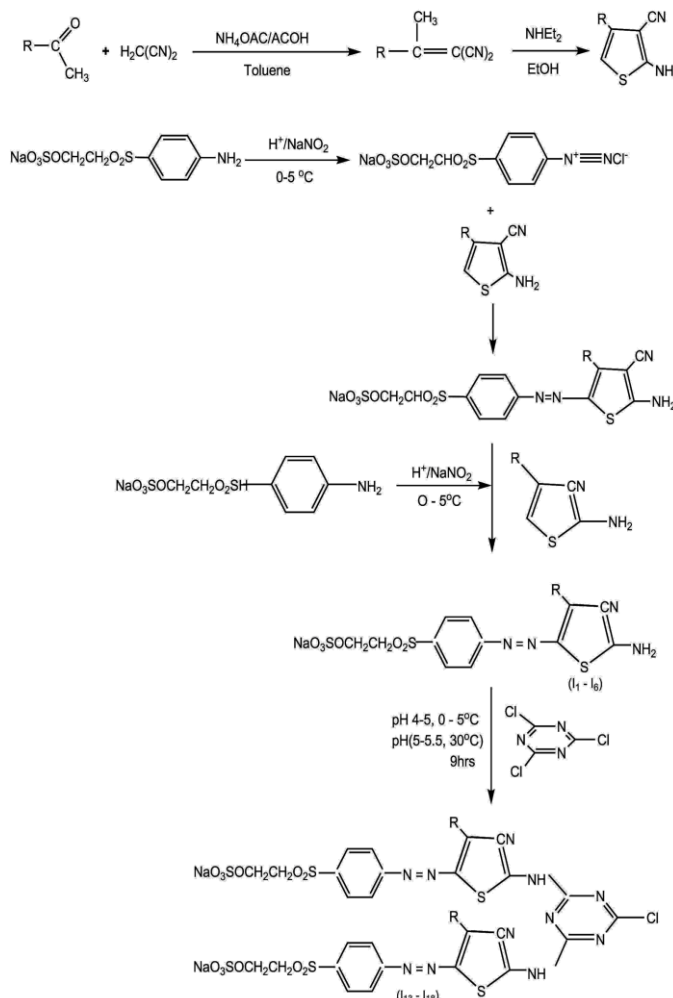


**Scheme 1.** Synthesis of polyfunctional disazo reactive disperse dyes based on 4-aryl-2-aminothiophene Intermediate (R = (I$_{13}$) - C$_6$H$_5$; (I$_{16}$) - C$_6$H$_3$Cl$_2$; (I$_{17}$) - C$_6$H$_4$Br; (I$_{14}$) - C$_6$H$_4$Cl; (I$_{18}$) - C$_6$H$_3$Br$_2$; (I$_{15}$) - C$_6$H$_6$N.

## 2.3. Dyeing of nylon 6.6

The stock solution of each dye was prepared by weighing 0.3g dye powder and adding it to a beaker containing 20ml aqueous DMF. Nylon 6.6 fabrics were dyed using the synthesized azo reactive disperse dye in a dyeing machine with 1g sample at a Liquor ratio 50:1. The dye bath was prepared at room temperature in the presence of dye concentrations (1-5 % owf). The dye bath was prepared at pH 2, 4, 6, 8, 10 and 12 using sodium carbonate and acetic acid solutions. Dyeing started at 40°C and then the temperature was raised to 100 °C over 60 min. Dyeing was continued at the desired temperature for a further 45 min (105 min total dyeing

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**Table 2.** Visible absorption data of the polyfunctional reactive disperse dyes

| Dyes | $\varepsilon_{max}$ $10^5$ L mol$^{-1}$ cm$^{-1}$ in EtOH | Ethanol $\lambda_{max}$ (nm) | Acetone $\lambda_{max}$ (nm) | Ethanol + HCl $\lambda_{max}$ (nm) | Chloroform $\lambda_{max}$ (nm) | Change in $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|
| $I_{13}$ | 1.62 | 451 | 430 | 450 | 400 | +5 |
| $I_{14}$ | 2.51 | 480 | 467 | 454 | 420 | +13 |
| $I_{15}$ | 2.47 | 490 | 445 | 488 | 443 | +2 |
| $I_{16}$ | 1.01 | 448 | 444 | 451 | 442 | -3 |
| $I_{17}$ | 0.56 | 465 | 455 | 460 | 417 | +5 |
| $I_{18}$ | 1.86 | 456 | 453 | 450 | 400 | +6 |

time). After dyeing, all dyed samples were rinsed with running water and air dried. Dye exhaustion and total dye fixation on Nylon 6.6 fabrics was evaluated by means spectrophotometric investigations.

### 2.4. Determination of percentage exhaustion

The uptake of the polyfunctional reactive disperse dyes by nylon 6.6 fabric was measured by sampling the dye bath before and after dyeing. The dye concentration (g/L) of the dye bath, diluted with 25ml acetone, was measured spectrophotometrically at the $\lambda_{max}$ value. The percentage of dye bath exhaustion (%E) was calculated using Equation 1.[23]

$$\%E = \left[1 - \left(\frac{A_2}{A_1}\right)\right] x100 \qquad (1)$$

$A_1$ and $A_2$ are the dye absorbance in the dye bath before and after dyeing respectively.

### 2.5. Dye fixation

The dye fixation (%F), the percentage of the exhausted dye chemically bound on the fibre, was measured by stripping and refluxing the dyed samples in 50% aqueous DMF (20:1) for 30 min at 100oC to extract the unfixed Dye

$$\%F = \frac{(C_1 - C_2 - C_3)}{C_1 - C_2} x100 \qquad (2)$$

Where, $C_3$ is the concentration of extracted dye.

### 2.6. Fastness test

The dyed samples will be tested by the standard ISO methods (Methods of test, 1990). The tests are as follows: Colour fastness to washing, ISO 105-C02 (1989); ISO 105-X12 (1987); fastness to perspiration, ISO 105-E04 (1989); and fastness to light using microsal tester xenon lamp.

## 3. Results and Discussions

### 3.1. Characterization of synthesized dyes (I₁₃-I₁₈)

The condensation of corresponding ketone (0.03 mol, acetophenone) and malonitrile (0.06mol, 3.96 g) in benzene was carried out using a heterocatalytic system. The reaction mixture was refluxed in the
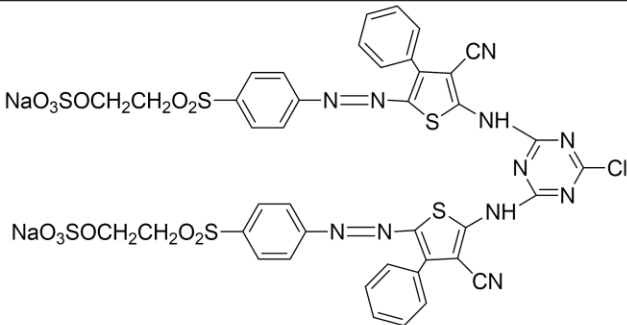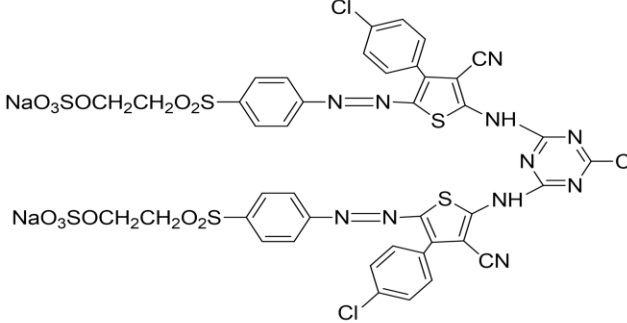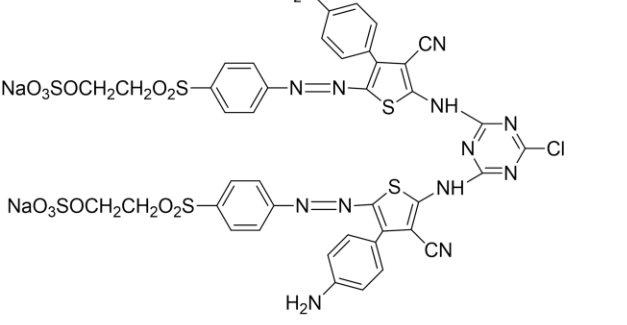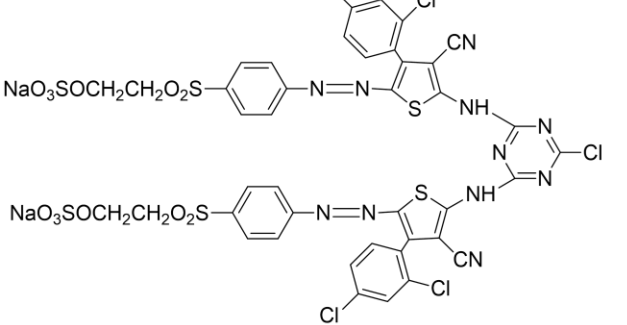
presence of catalytic amount of acetic acid and ammonium acetate to produce arylidenemalononitrile as an intermediate, followed by the cyclisation with sulphur, using diethylamine as catalysts at 65°C for 2- 3 hours to give the desired intermediate. The thick sticky dark product obtained was cooled overnight, filtered, washed with ethanol, ethanol and water 1:1 and dried. It was purified and recrystallized and reacted with the diazotized amine to get the monoazo dyes (I₁–I₆). The six azo reactive disperse dyes (I₁-I₆) freshly synthesized were filtered, dried, weighed and were further adjusted to a pH of 6-7 and was added to a freshly prepared suspension of Cyanuric Chloride by ratio of 2: 1 in acetone and crushed ice. The reaction mixture was stirred at 0-5 °C for 4 hours while controlling the pH at 4-5 using 2M aqueous solution of sodium carbonate (20%), 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 hours, in order to complete the second condensation reaction for the second half of the prepared dye. The poly functional disazo reactive dyes were then filtered off and dried at room temperature under vacuum and weighed.

The yields of the dyes were of acceptable yield ranging from 48% to 70%. This is not suprising inview of the results when comapre to previous and similar works [Table 1]. One of the methods mentioned as a way of overcoming low yield is a prolong reaction time.[24] The basic condition that was pointed out, was also very critical to the cyclisation step as shown in the reaction Scheme 1 for the intermediates. The melting points were also taken and reported in Table 1. All the purified intermediates and dyes exhibited fairly well defined melting points characteristics of pure compounds. Whilst it would be unwise to attempt to explain in detail their relative values, because of the complex dependence of the melting points on a number of factors (e.g, polarity, size, geometry interaction), a few general trend can be a counted for.

The wavelengths of the maximum absorption of the polyfunctional disazo reactivedisperse dyes range from 448 to 490 nm in ethanol, 430 to 467 nm in acetone and 400 to 443 nm in chlorofoam, 450 to 488 nm in ethanol + HCl (Table 2). The maxixmum absorption wavelength increased with increase in solvent polarity. Bathochromic shifts of the visible absorption band were also observed on increasing the solvent polarity where the difference in $\lambda_{max}$ was noticed upon measuring the dyes in Ethanol and acetone. This is of course expected for a system in which the excited state is more polar than the ground state.

The resonance theory gives the reason for the bathochromism of 2-aminothiophene. The first concerns the powerful withdrawing thiophene residue that contains S-atom as a π-excessive heteroatom.

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**Table 3.** Name and structures of the polyfunctional reactive disperse dyes.

| Dye Code | Name And Structure |
|---|---|
| I₁₃ |  sodium (4,4'-((5,5'-((6-chloro-1,3,5-triazine-2,4-diyl)bis(azanediyl))bis(4-cyano-3-phenylthiophene-5,2-diyl))bis(diazene-2,1-diyl))bis(4,1-phenylenesulfonyl))bis(ethane-2,1-diyl) bis(sulfate) |
| I₁₄ |  sodium (4,4'-((5,5'-((6-chloro-1,3,5-triazine-2,4-diyl)bis(azanediyl))bis(3-(4-chlorophenyl)-4-cyanothiophene-5,2-diyl))bis(diazene-2,1-diyl))bis(4,1-phenylenesulfonyl))bis(ethane-2,1-diyl) bis(sulfate) |
| I₁₅ |  sodium (4,4'-((5,5'-((6-chloro-1,3,5-triazine-2,4-diyl)bis(azanediyl))bis(3-(4-aminophenyl)-4-cyanothiophene-5,2-diyl))bis(diazene-2,1-diyl))bis(4,1-phenylenesulfonyl))bis(ethane-2,1-diyl) bis(sulfate) |
| I₁₆ |  sodium (4,4'-((5,5'-((6-chloro-1,3,5-triazine-2,4-diyl)bis(azanediyl))bis(4-cyano-3-(2,4-dichlorophenyl)thiophene-5,2-diyl))bis(diazene-2,1-diyl))bis(4,1-phenylenesulfonyl))bis(ethane-2,1-diyl) bis(sulfate) |

**I₁₇**

sodium (4,4'-((5,5'-((6-chloro-1,3,5-triazine-2,4-diyl)bis(azanediyl))bis(3-
(4-bromophenyl)-4-cyanothiophene-5,2-diyl))bis(diazene-2,1-
diyl))bis(4,1-phenylenesulfonyl))bis(ethane-2,1-diyl) bis(sulfate)



**I₁₈**

sodium (4,4'-((5,5'-((6-chloro-1,3,5-triazine-2,4-diyl)bis(azanediyl))bis(4-
cyano-3-(2,4-dibromophenyl)thiophene-5,2-diyl))bis(diazene-2,1-
diyl))bis(4,1-phenylenesulfonyl))bis(ethane-2,1-diyl) bis(sulfate)
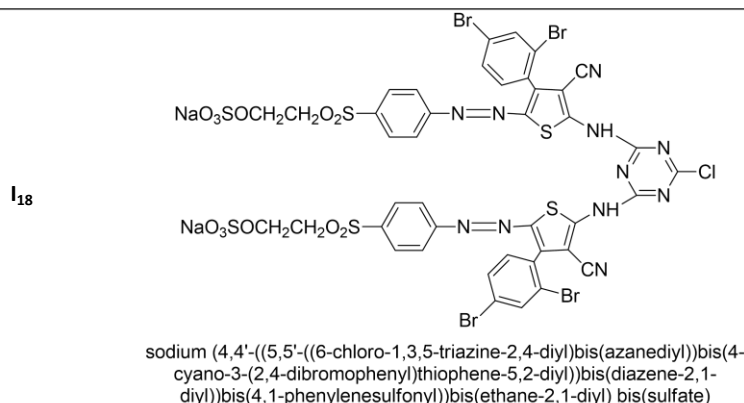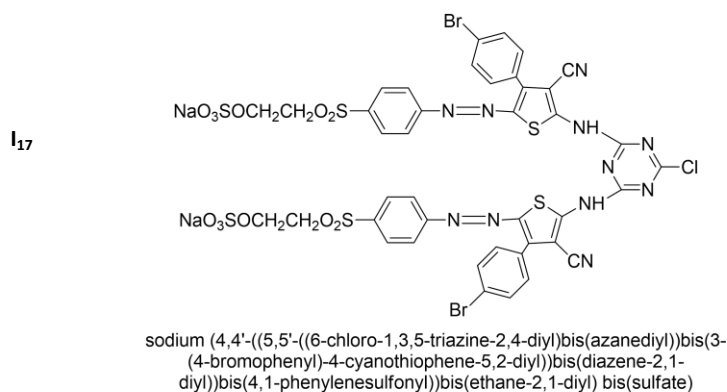
**Table 4.** FT-IR data of the polyfunctional reactive disperse dyes

| Functional group | C=C | C-H | C=C | N-H | Ar-H | C-S | C-N | C-C | N=N | C-H | C-Cl | C-H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| sType of vibration | Bending Ali | Bending aro | Str | Str | Str ar | In-plane bend | Str | Str ali | Str ali | In-plane of Ar-H | | Str ali |
| I₁₃ | 1625 | 827 | 1584 | 3652 | 3049 | 685 | 1039 | 1293 | 1494 | | 723 | 2232 |
| I₁₄ | 1636 | 834 | 1482 | 3324 | - | 693 | 1043 | - | 1587 | | 730 | 2221 |
| I₁₅ | 1625 | 991 | 1446 | 3403 | 3201 | 685 | 1043 | 1312 | 1576 | | 745 | 2202 |
| I₁₆ | - | - | 1490 | 3325 | 3104 | 693 | 1051 | 1282 | 1580 | | 831 | 2214 |
| I₁₇ | 1692 | 838 | 1453 | 3205 | 3056 | 689 | 1051 | 1136 | 1692 | | 630 | 2117 |

**Table 5**: Proton NMR chemical shifts for the polyfunctional reactive disperse dyes (CDCl₃, TMS (CH₃)₄Si)

| Dye code/ type of carbon in ppm (δ) | CH₂/CH | C₆H₅ | NH | OCH₂ | Ar-H |
|---|---|---|---|---|---|
| I₁₄ | 0.622-0.685 | 0.622-0.685 | 2.040 | 2.957 | 7.542-7.81 |
| I₁₃ | | | 8.032 | | |
| I₁₆ | | 6.977 | | 5.885 | 7.220 |
| I₁₇ | 2.177 | | 1.203 | 3.765-3.807 | 7.446 |

The S-atom which is said to act as an additional withdrawing group has as unoccupied orbits available that can accommodate the transfer of charge and stabilize the excited state, resulting in a bathochromic shift. The 3d orbitals on the S atom may also contribute to the first excitement energy.[25] Sulphur also increases the diene character of the thiophene ring, so the π- electrons in the thiophene ring are likely to migrate more easily. This factor is responsible for the large absorption shifts of the thiophene dyes. The purity of the dye was evaluated by TLC using diethyl ether: ethanol as eluent system. The synthesized intermediates and dyes were purified by recrystallization using different solvents based on the principle of recrystallization. The solvent used were ethanol, toluene, acetone and acetic acid. All aminothiophene derivatives and dyes were purified by 3-4 recrystallizations from hot ethanol and other suitable solvents. Table 2 shows the name and structures of the synthesized dyes (Table 3).

FT-IR spectrum of the dyes showed absorption bands at 1625-1692 cm⁻¹ relative to the bending of C=C groups, 827-991 cm⁻¹ for C-H bend, 1446-1584 cm⁻¹ for C=C stretch, 3205-3652 cm⁻¹ for N-H stretch, 685-693 cm⁻¹ for C-S in plane bend, 1039-1051 cm⁻¹ for C-N stretch and 1494-1692 cm⁻¹ for N=N stretch and other relevant peaks (Table 4). These results showing
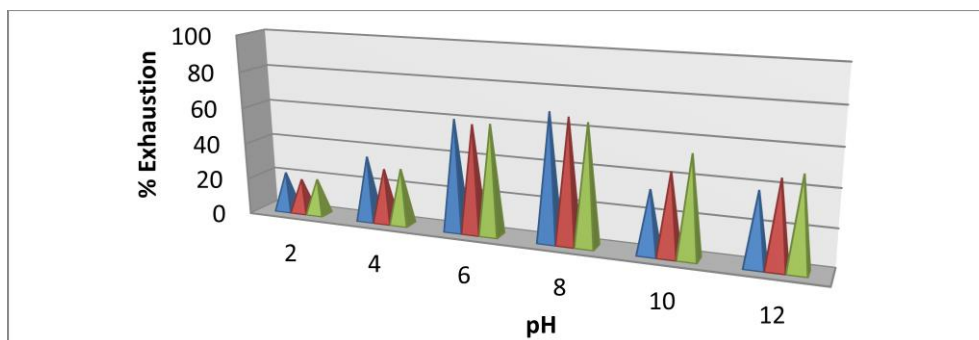
**Fig. 1.** Effect of dye bath pH on dye exhaustion on nylon 6.6 using dyes $I_{13}$ (blue), $I_{15}$ (red) and $I_{18}$ (green).

**Table 6.** Percentage fixation on nylon 6.6

| Dye code | Fixation (%) |
|----------|--------------|
| $I_{13}$ | 71 |
| $I_{14}$ | 72 |
| $I_{15}$ | 78 |
| $I_{16}$ | 76 |
| $I_{17}$ | 72 |
| $I_{18}$ | 78 |

**Table 7.** Fastness to light

| Dye code | Fastness rating on nylon 6.6 |
|----------|------------------------------|
| $I_{13}$ | 5 |
| $I_{14}$ | 5 |
| $I_{15}$ | 5 |
| $I_{16}$ | 5 |
| $I_{17}$ | 5 |
| $I_{18}$ | 4 |

the corresponding peaks are as supported in literature by Coates et al.[26] The FT-IR and NMR spectra of the polyfunctional reactive disperse dyes are provided in the Supporting Information.

The NMR analysis was carried out using chloroform ($CDCl_3$) as solvent and tetramethysilane (TMS) as internal standard. In order to standardize the NMR spectra, the chemical shifts are positioned in relation to a reference proton set at 0.00 ppm. Tetramethylsilane ($CH_3Si$) is the standard for $^1H$ NMR. Table 5 shows the proton NMR chemical shifts for the synthesized compounds ($CDCl_3$, TMS $(CH_3)_4Si$). The H+ NMR spectrum of the synthesized dye $I_{14}$ shows two triplets at 0.622-0.685 ppm, each integrated to protons, assignable to the $CH_2$ and methylene protons and 2.957 ppm for $-OCH_2$ of the bis (SES) group, a peak shows at 2.040 ppm assignable to $NH_2$ attached to the thiophene ring and doublet at 7.542-7.81 ppm which shifted downfield assignable to phenyl ring $C_6H_5$ on the thiophene moiety.

Other relevant peaks were shown as indicated in the Table 6. The chemical shift of the NH group on the aminothiophene shifted downfield upon formation of aminothiophene. It is also important to note that electronegative effect of the N atom was the main reason for the downfield shift in the NMR values of compound $I_{14}$ from the corresponding aminothiophene derivatives. A singlet at 2.957 ppm attributed to the presence of $-OCH_2$ group on the sulphatoethylsulphone on the difunctional dye. This value shifted downfield as a result of the inductive effect of O group attached to the inductive effect of O group attached to more electronegative atoms experience higher chemical shift as electronegative compounds remove electrons from the electron cloud, which decreases their density and results in low/less shielding. This causes deshielding of the proton and cause them to have a higher chemical shift; moving it to downfield. For $^{13}C$ NMR of dye $I_{17}$, peaks at 40, 154, 80 ppm were noticed corresponding to signals from $CH_2$, C=C and C-Cl,

respectively. Similarly, for dye $I_{13}$, 60, 63, 44, 133, 134 ppm peaks were seen which attributed to signals for $CH_2$, $CH_2$, C-Cl, C=C thiophene, C=C aromatic carbon, respectively.

### 3.2. Dyeing of Nylon 6.6. Fabric

The synthesized polyfunctional reactive disperse dyes were successfully applied for dyeing Nylon 6.6 fabric. Initially, the dyeing conditions such as pH, time and temperature were optimized. In addition, the dye fixation and fastness were also investigated.

#### 3.2.1. Effect of pH

The effect of pH on the exhaustion and fixation of the polyfunctional reactive disperse dyes on Nylon 6.6 fabric was studied using 2% o.w.f dye concentration. For this purpose, a series of dyeing were carried out by varying the dye bath pH from 2 to 12. (Fig. 1).

The results given clearly show that the exhaustion values and the total fixation yield significantly increased to a maximum value at pH of 8, this reflects the advantages of the combination of three reactive groups having different reactive levels, because the three reactive groups being complement each other for variations in dyeing

**Table 8**. Fastness to perspiration

| Dye code | Acidic | | | Alkaline | | |
|----------|--------|-----|-----|----------|-----|-----|
| | CC | SC | SN | CC | SC | SN |
| $I_{13}$ | 4-5 | 4-5 | 4 | 4-5 | 4-5 | 5 |
| $I_{14}$ | 4 | 4 | 4 | 3 | 5 | 3 |
| $I_{15}$ | 4 | 4 | 4 | 4 | 3 | 4-5 |
| $I_{16}$ | 4 | 4 | 4 | 4 | 4 | 4 |
| $I_{17}$ | 4 | 4 | 4 | 4 | 4 | 4-5 |
| $I_{18}$ | 4 | 4 | 4 | 4-5 | 4-5 | 4-5 |

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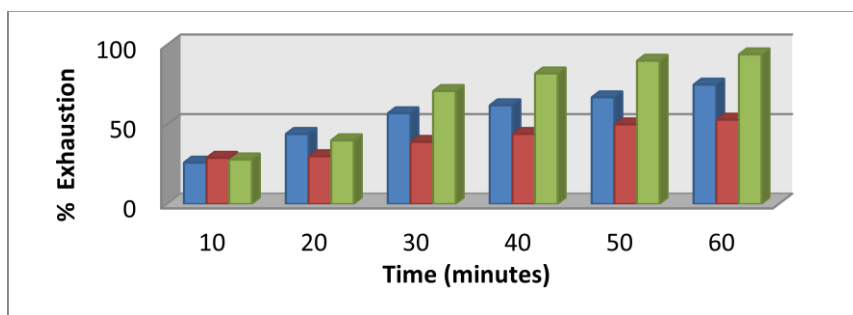*Chem. Sci. Eng. Res., (2020) 2(4), 18-25.*

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**Fig. 2.** Effect of Time on exhaustion on nylon 6.6 using dyes **I₁₃** (blue), **I₁₅** (red) and **I₁₈** (green).

**Table 9.** Fastness to washing

| Code | Change in colour | Staining on wool | Staining on nylon |
|------|------------------|------------------|-------------------|
| I₁₃ | 4 | 4 | 4 |
| I₁₄ | 3-4 | 4 | 3-4 |
| I₁₅ | 4 | 4 | 4 |
| I₁₆ | 4 | 4 | 4 |
| I₁₇ | 4 | 3 | 3 |
| I₁₈ | 4 | 4 | 4 |

conditions. 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.

*3.2.2. Effect of dyeing time*

The extent of exhaustion and total fixation yield was investigated at different dyeing time and at 100 °C using 2% o.w.f dye concentration. The results are given in Fig. 2 clearly show that the dye displays good build up and exhibits high rate of exhaustion fabric then equilibrate at dyeing time (60 min) for nylon fabrics, probably due to its high substantively.

It is also clear that the total fixation of the dyes increase as the dyeing proceeds (Fig. 3). This may be due to that the hydrophobic character of the nonionic bis(vinylsulphone)/ MCT reactive system in the dye, generated from elimination reaction of the temporarily anionic bis(SES) groups, not only imparts high substantively under the alkaline dyeing but also effectively exhibits high fixation efficiency.

The results show that the dyed nylon 6.6 samples in alkaline and acidic solution had good fastness properties to perspiration based on ratings between 4 and 4-5, with little and moderate staining on the adjacent fabric (Table 8). Generally, factors that affect colour fastness of textiles are internal and external factors. Internal factors include the dye and the fibre type while external factors are products imposed by external forces or conditions. Wash fastness properties of the synthesized dyes were generally moderate to good on nylon 6.6 of values between 3 to 4 for $I_{14}$, and mostly values of 4 for dyes $I_{13}$, $I_{15}$, $I_{16}$, $I_{17}$, and $I_{18}$ (Table 9). This is because the dyes containing vinylsulphone groups are compatible with the fibre and were covalently bonded with the nucleophilic sites in the fibre.

## 4. Conclusions

A new disazo polyfunctional reactive disperse dye, containing two temporarily anionic SES and MCT reactive groups, has been synthesized. The dyes found to have good dyeing performance on Nylon 6.6 fabrics. Optimum exhaustion and fixation on dyed 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–fiber interaction and improving the fixation on both silk and nylon 6 fabrics. The dyes have good fastness properties to light, washing and perspiration.
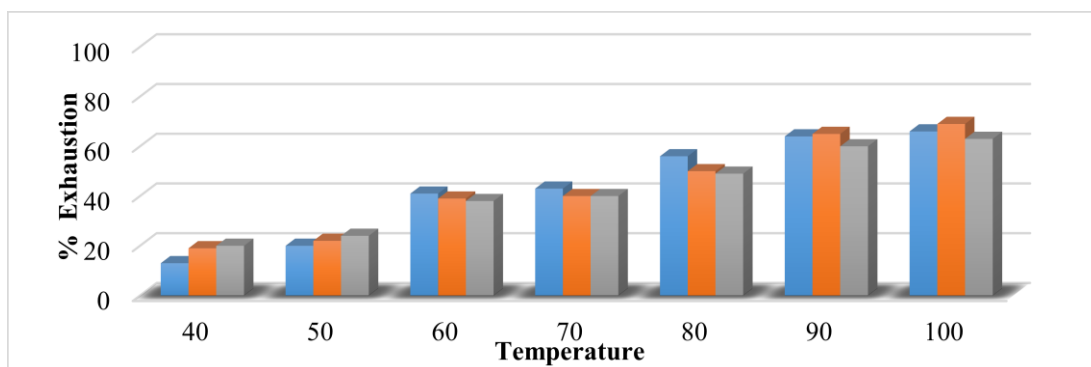


**Fig. 3.** Effect of temperature on dye exhaustion on Nylon 6.6 using dyes **I₁₃** (blue), **I₁₅** (red) and **I₁₈** (green).

## Conflicts of Interest

The authors declare no conflict of interest.

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