# SYNTHESIS AND APPLICATION OF VINYLSULPHONE DISPERSE REACTIVE DYES DERIVED FROM PYRIDONE DERIVATIVES ON POLYESTER FABRIC

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***ABSTRACT***

*Vinylsulphone disperse reactive dyes were synthesized by diazotizing 2-methoxy-5-methyl-4-(sulfatoethylsulfonyl) aniline and coupling with substituted pyridone derivatives. The synthesized dyes were applied successfully on polyester without dispersing agent and the dyeing showed good leveling and build up with desired colour yield. The dyeing was dependent on the pH and the optimum pH was found to be 5, similar to that employed in conventional polyester dyeing. The fastness properties obtained are excellent and comparable with the conventional disperse dyes.*

**Keywords:** *Eco-friendly, effluent, vinylsulphone disperse reactive dyes, Dispersant-free disperse dyes.*

## 1. Introduction

Disperse dyes are used in aqueous dyebath in the form of fine dispersions, because their solubility in water is very low, even at high dyeing temperatures. During manufacture, dispersing agents are incorporated into the dye powders to improve the dyeing properties. One important aspects of dyeing with disperse dyes is the state of the dye in the dyebath during dyeing. Dye particles in the finely divided dispersion acts as a dye reservoir. The solubility of disperse dyes, though small, is also a very important factor. In addition, the stability of the dye dispersion, the equilibrium between dye dispersion and dye in true solution in the dyebath, and the rate of dyeing are all affected by the type and concentration of the disperse dyes. During dyeing, the kinetics of dye dissolution is more significant than those governing solubilisation. Equilibrium solubilisation of disperse dyes is attained in aqueous solutions of surfactants and dispersant agents at 130 $^{o}$C over a relatively long period (Monsoor, 2008).

In the conventional disperse dyeing of polyester, dispersing agents are usually added to increase the dispersion stability and solubility of disperse dyes. However, after the dyeing process is finished, they are not adsorbed onto polyester and they are discharged as effluents with the residual dyeing liquor, which increases the COD and BOD values of the effluents (Bradbent, 2001; Odbvarka and Schejbalova, 1994). One of the severe problem encountered in dyeing of polyester at high temperatures with disperse dyes is poor dispersion stability and its consequences i.e inadequate levelness and unacceptable reproducibility (Sigismund, 1981). The development of new disperse dyes must take into account the effect that dyeing effluent will have on the environment and therefore aim to minimize such pollution. These objectives are not mutually exclusive but interrelated, they must all be taken into account in any dye development programme (Jung *et al.,* 2005). In this work, we have synthesized vinylsuphone disperse reactive dyes using diazo component having vinylsulphone group with different substituted pyridone derivatives as coupler to produce mainly yellow dyes. The correlation between the dye structure and spectral properties of these dyes in dyebath during dyeing were undertaken and it was found that these dyes can be used as dispersant-free disperse dyes for polyester and their performance properties were also investigated.

## 2. Experimental

### 2.1 General Information

All the chemicals used in the synthesis of the dyes and intermediates were of analytical grade and were used without purification. Melting points were determined by the open capillary method. The visible absorption spectra were measured using HEX10SY UV-visible pectrophotometer. IR spectra were recorded on a Nicolet FTIR-100 Thermoelectron spectrophotometer and the Mass spectra were determined on an Agilent 6890 Mass spectrometer.

### 2.2 Synthesis of 1-ethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4a)

A mixture of ethylacetoacetate (11.3 g, 0.1 mol), ethyl cyanoacetate (13.0 g, 0.1 mol), ethanol (50 ml) and ethylamine (72 ml, 0.3 mol) was stirred and refluxed until the reaction was completed (about 7-8 h). During the reaction, the white product precipitated. The crude product was filtered, dried and recrystallised from ethanol to give white crystals (90%), m.p. 178 $^{o}$C ($P^{+}$ at *m/e* (177). 1-butyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4b) and 1-dedocyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4c) were obtained using butylamine and dedocylamine respectively to replace ethylamine (Sakoma *et al.,* 2012).

### 2.3 Diazotisation of 2-methoxy-5-methyl-4-(sulfatoethylsulfonyl) aniline (5)

2-Methoxy-5-methyl-4-(sulfatoethylsulfonyl) aniline (5), (0.02 mol) was suspended in water (30 ml) at room temperature. The pH of the suspension was raised to 5.5 by adding 2M sodium carbonate solution and the resulting solution was filtered. To the filtered solution, hydrochloric acid (36%, 0.02 mol) was added while placed in an ice bath to maintain the temperature at 0-5 $^{o}$C, a solution of sodium nitrite (0.021 mol) dissolved in water (10 ml) was then introduced in small portions over thirty minutes. After the addition of the sodium nitrite, the reaction was stirred under the above conditions for thirty minutes. Excess nitrous acid was destroyed by adding small amount of urea.

### 2.4 Coupling of diazotized Vinylsulphone (6) with pyridones (4)

The synthesized pyridones (4) (0.02 mol) was each dissolved in 5 mls of 4% solution of sodium hydroxide, 50 g of crushed ice was added to the solution. The diazonium salt (6) was added in portion into the solution with constant stirring in an ice bath at 0-5 °C for 30 minutes. The dyes produced were filtered out and dried to obtain dyes (7). The dyes were purified by recrystallisation from ethanol. Dye (8) was obtained similarly by coupling (6) with 2-naphthol and was similarly purified in the same way (scheme 1).

### 2.5 Dyeing of the Polyester

Polyester fabric was dyed in a Flexi dyer dyeing machine at L:R 1:20 and 2% shade on the w.o.f. The dyebaths were prepared with the synthesized dyes without using any dispersing agent and maintained at pH 4-5 by acetic acid. The dyebath temperature was raised at a rate of 1 °C/min to 130 °C, maintained at this temperature for 60 min, and rapidly cooled to 60 °C. The dyeings were rinsed and then reduction cleared in an aqueous solution of 2 g/l sodium hydroxide and 2 g/l sodium hydrosulphite at 80 °C for 30 min.

### 2.6 Exhaustion (%)

The exhaustion of dye on the polyester fabric was measured by DMF extraction method (30 min at 150 °C). The absorbance of the solution extracted was determined using HEX10SY UV-visible spectrophotometer. The percentage exhaustion was calculated using equation:

$$\text{Exhaustion (\%)} = [C_t/C_o] \times 100$$

where, $C_t$ is the amount of dye extracted from a dyed fabric at time t and $C_o$ is the amount of dye in the initial dyebath.

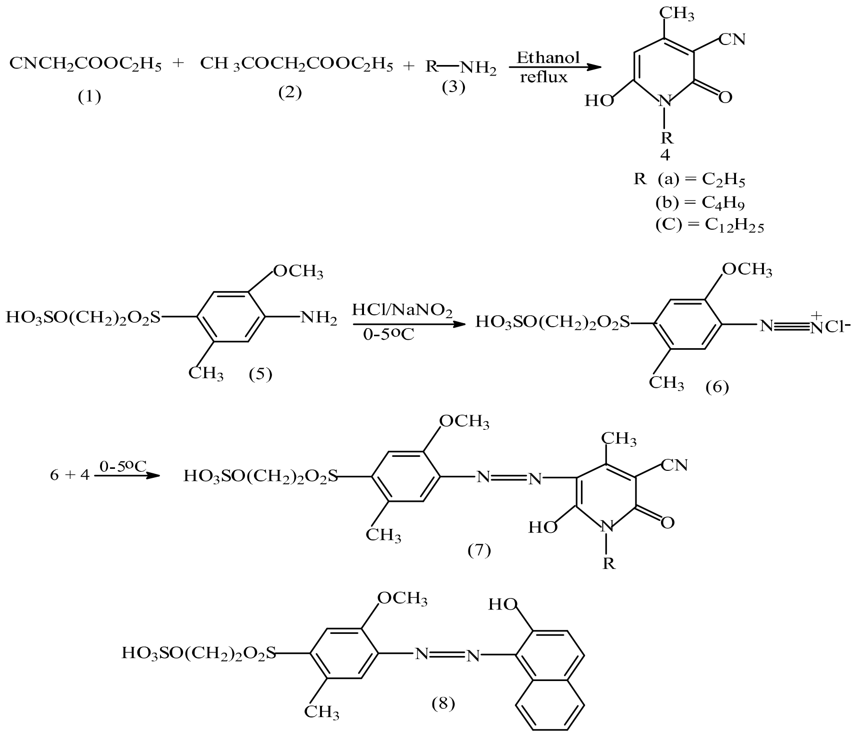
### 2.7 Fastness test

Rubbing fastness of the dyed samples was determined by using automatic Crockmeter using standard ISO 105 x 12 methods. The light fastness of the dyed samples was tested on Q-Sun Xenon Test Chamber using the AATCC 16-2004 method. Hot pressing fastness test was carried out according to the standard method (Josef, 1990). Washing fastness testing was done by the standard method ISO 2-105-C10:2006(E). The shade change, together with staining of adjacent fabrics was rated according to appropriate SDC grey scales.

## 3. Results and Discussion

### 3.1 Synthesis of Dyes and Intermediates

1-Substituted-2-hydroxy-4-methyl-5-cyano-6-pyridones (4a-4c) were prepared from a mixture of ethyl cyanoacetate (1), ethyl acetoacetate (2) and amines (3a-3c) in ethanol under reflux. 2-methoxy-5-methyl-4-(sulfatoethylsulfonyl)aniline was diazotised using hydrochloric acid and sodium nitrite at 0-5°C and the diazonium salts (6) was coupled with pyridone compounds (4a-4c) at pH 3-4 to give the 1-substituted 3-(p-substituted phenylazo)-6-pyridone dyes (7a-7c). Dye (8) was similarly obtained by coupling the diazonium salt (6) with 2-naphthol. The dyes were purified by recrystallisation from ethanol and their purity examined by thin-layer chromatography. The structures of the pyridones were confirmed by mass spectrometry and IR while the structures of the dyes were confirmed by IR. The physical characteristics of the dyes are summarized in Table 1.



Scheme 1: Synthetic Route for the Intermediates and Dyes

Table 1: Physical Characteristics of the Dyes

| Dye No | Molar Mass (g/mol) | M.Pt. (°C) | Yeild (%) | Colour of the Crystal |
|---|---|---|---|---|
| **(7a)** | 536 | 272-274 | 80 | Yellow |
| **(7b)** | 564 | 207-209 | 72 | Yellow |
| **(7c)** | 676 | 140-142 | 56 | Yellow |
| **(8)** | 502 | 274-276 | 50 | Orange |

As can be seen from physical characteristics of the dyes in Table 1, all the dyes have low molecular weight which is a good characteristic of disperse dyes for polyester fibres. They also have high melting points and the yield obtained are moderate, ranging from 50% to 80 %. The dyes obtained by coupling with substituted pyridones are mainly yellow in colour with the exception of dye (8) which was obtained by coupling with 2-naphthol which is orange in colour.

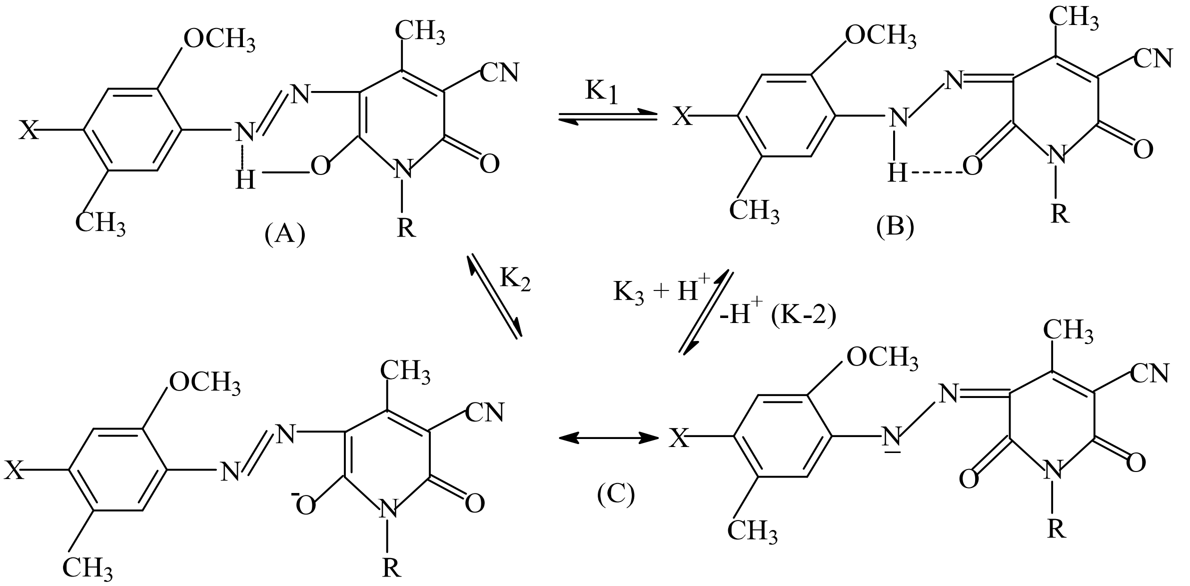
## 3.2 Infrared spectra of the Dyes

As can be seen from the infra-red spectra results in Table 2, all the dyes gave absorption peaks due to azo group, N=N stretching vibration at 1578-1510cm$^{-1}$; aromatic C-C stretching vibration bands appeared in the region of 1457-1419cm$^{-1}$; aromatic C-H bending vibration bands appeared in the region of 868 - 826cm$^{-1}$; C≡N stretching vibration bands appeared in the region of 2227-2222cm$^{-1}$; C=C stretching vibration band appeared in the region of 1048-1020cm$^{-1}$; C=O stretching vibration bands appeared in the region of 1630-1601cm$^{-1}$; N-H stretching vibration bands appeared in the region of 1516-1421cm$^{-1}$; O-H stretching vibration bands appeared in the region of 3884-3433cm$^{-1}$ and C-$SO_3H$ stretching vibration bands appeared at the peak of 669cm$^{-1}$ - 625cm$^{-1}$.

The infrared spectra of all the compounds (in **KBr**) showed two intense carbonyl bands at 1630 and 1601 cm$^{-1}$; intensities of the two bands were very similar, and the latter band is related to intramolecularly hydrogen-bonded carbonyl. It was therefore assigned to the diketohydrazone form **B**. In the infrared spectra of the compounds in $CHCl_3$, two carbonyl bands were also observed, with the 1601 cm$^{-1}$ band having lower intensity. This suggests that the dyes exits in the hydrazone form in the solid state and predominantly in the hydrazone form in $CHCl_3$. These conclusions are in accord with those of Ertan and Gurkan (1997) and Cheng *et al.,* (1986). The dyes may exist in two tautomeric forms, namely the azohydroxypyridone form **A** and the diketohydrazone form **B**. The deprotonation of the two tautomers leads to a common anion **C**, as shown in Scheme 2.

Table 2: Infra-Red Spectra of the Dyes

| Functional group | Azo N=N | Aromatic C-C | Aromatic C-H | CN | C=C | C=O | Aromatic 3°N-H | C-$SO_3$H | O-H |
|---|---|---|---|---|---|---|---|---|---|
| **Type of Vibration** | Stretching | Stretching | Bending | Stretching | Stretching | Stretching | Stretching | Stretching | Stretching |
| **Dye No** | | | | | | | | | |
| **(7a)** | 1578 | 1419 | 838 | 2226 | 1036 | 1630 | 1516 | 625 | 3433 |
| **(7b)** | 1560 | 1420 | 826 | 2222 | 1020 | 1629 | 1509 | 627 | 3444 |
| **(7c)** | 1510 | 1421 | 828 | 2227 | 1047 | 1601 | 1421 | 628 | 3884 |
| **(8)** | 1558 | 1457 | 868 | - | 1048 | - | - | 669 | 3648 |



Scheme 2: hydrazone-common anion equilibrium

### 3.3 Visible Absorption Spectra of the Dyes

Visible absorption maxima of the dyes in various solvents are given in Table 3. The visible absorption spectra of the dyes were found to exhibit a strong solvent dependence which did not show a regular variation with the dielectric constants of the solvent. It was observed that in DMF, ethanol and ethanol plus a drop of HCl, the absorption spectra of the dyes did not change significantly. $\lambda_{max}$ of the dyes shifted considerably in ethanol for example dye (7a), $\lambda_{max}$ is 449.0 nm in DMF and 480.0 nm in ethanol. The absorption maxima of most of the dyes also showed hypsochromic shifts when a small amount of HCl was added to dye solutions in ethanol. A typical example is (7c) with $\lambda_{max}$ of 505.00 nm in ethanol and 449 nm when a drop of HCl was added to the solution in ethanol.

Dye (7a) was obtained by diazotising 2-methoxy-5-methyl-4-(sulfatoethylsulfonyl)aniline and coupling to 1-ethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4a) absorbed at 447.0nm in methanol and when the ethyl group in pyridone was replaced by butyl group the dye (7b) absorbed at the same maximum absorption wavelength in the same solvent. Showing no effect on increasing the chain length of the substituent. Increasing the chain length further by replacing the butyl group by dedocyl group gave dye (7c) with $\lambda_{max}$ of 446 nm, an hypsochromic shift of 1 nm in the same solvent. This clearly showed that the dye showed negligible change with increase in the chain length of the substituents. Dyes (8) which was obtained by replacing the pyridone with 2- naphthol absorbed at 496 nm in methanol and this gave bathochromic shift of 49 nm compared with dyes (7a) and (7b) in the same solvent. The bathochromic shift obtained with dye (8) can be attributed to increase in the conjugation of the 2-naphthol compared with pyridone ring. The effects of solvent polarity on the visible absorption spectra was also studied and from the results summarized in Table 3, there is no specific pattern in the results. For example, dye (7a) absorbed at 449.0nm in DMF and gave $\lambda_{max}$ of 480.0nm in ethanol which is hypsochromic by 31 nm. Most of the dyes showed negative solvatochromism when the solvent was changed to more polar solvents. Similarly, the effects of few drops of HCl on ethanolic solution of the dyes showed positive and negative halochromism as can be seen in the results summarized in Table 3. This means that the dyes can be used as indicator in acid-base titration. The extinction coefficients of the dyes are very high, ranging from 2.0 x $10^4$ – 2.7 x $10^4$ lmol$^{-1}$cm$^{-1}$ which are very good for textile application.

Table 3: Visible Absorption Spectra of the Dyes

| Dye No | $\lambda_{max}$ MeOH/nm | $\lambda_{max}$ DMF/nm | $\lambda_{max}$ EtOH/nm | $\lambda_{max}$ EtOH + HC/nm | $\varepsilon_{max}$ in DMF/lmol$^{-1}$cm$^{-1}$ |
|---|---|---|---|---|---|
| **(7a)** | 447 | 449 | 480 | 449 | 2,5000 |
| **(7b)** | 447 | 446 | 466 | 454 | 2,6000 |
| **(7c)** | 446 | 448 | 505 | 449 | 2,0000 |
| **(8)** | 496 | 497 | 440 | 498 | 2,7000 |

### 3.4 Dyeing Properties of the Dyes

The exhaustion % at different pH of dyebath is given in Table 4 for dyes (7) and (8). The trend in exhaustion % remained same for all the dyes for polyester dyeing and good colour yields were obtained. The maximum colour yields was observed at pH 5 for all the dyes and was of the tune of 90%. The colour yields at pH 7 and 8 were lower than those at pH 5 and also the dyeing showed some unlevelness. Therefore, the optimum pH condition for dyeing was at pH 5. At pH 4, colour yield was low due to the low conversion rate of the soluble dye into the insoluble vinylsulphone form. The colour yield on the polyester fabric increased continuously throughout the whole dyeing procedure, implying gradual increase in the conversion of dye. The low dye uptake and poor leveling at pH 10 can be attributed to the rapid conversion of the dye causing a collapse in the dyebath dispersion stability. Thus the exhaustion of dyebath in terms of exhaustion % was highly dependent on the pH of the dyebath with maximum exhaustion of 90.7%; 89.8%; 91% and 91.2% respectively for dyes (7a), (7b), (7c) and (8) obtained at pH 5.

Table 4: Effect of pH on Exhaustion (%) of the Dyes on Polyester

| **pH** | **Exhaustion (%)** | | | |
|---|---|---|---|---|
| | Dye (7a) | Dye (7b) | Dye (7c) | Dye (8) |
| **4** | 78.1 | 77.1 | 78.5 | 79.5 |
| **5** | 90.7 | 89.8 | 91.0 | 91.2 |
| **6** | 88.3 | 87.0 | 88.4 | 88.1 |
| **7** | 79.0 | 78.6 | 77.9 | 79.1 |
| **8** | 74.5 | 75.0 | 74.8 | 75.2 |
| **9** | 67.7 | 68.5 | 66.7 | 69.2 |
| **10** | 61.5 | 60.3 | 59.8 | 61.7 |

### 3.5 Fastness Properties of the Dyes

The colour fastness tests were carried out for all the dyeings done at pH 5, which was obtained as the optimum pH of dyeing. The results of the fastness tests for the dyes on polyester are summarized in Table 5 and showed good to excellent wash fastness. The rubbing and hot pressing fastnesses were good and light fastness moderate to good on polyester fabric.

Table 5: Fastness Tests for the Dyes on Polyester

| **Dye No** | **Change in Colour** | **Staining on** | | | | | | **Rubbing** | | **Light** | **Hot pressing** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Acetate | Cotton | Nylon | Polyester | Acrylic | Wool | Wet | Dry | | |
| **(7a)** | 4-5 | 4-5 | 4-5 | 4 | 5 | 5 | 4-5 | 4-5 | 4-5 | 5 | 5 |
| **(7b)** | 5 | 4-5 | 4-5 | 4 | 4-5 | 5 | 4-5 | 4-5 | 4 | 4 | 4 |
| **(7c)** | 4-5 | 4-5 | 5 | 4-5 | 5 | 5 | 4-5 | 4 | 4-5 | 5 | 5 |
| **(8)** | 4-5 | 4-5 | 5 | 4-5 | 5 | 5 | 4-5 | 4-5 | 4-5 | 5 | 5 |

## 4. Conclusion

Polyester fabrics were successfully dyed with the synthesized dyes without using dispersing agent during dyeing. The colour yield on polyester was found to be dependent on the dyeing pH and the optimum result was obtained at pH 5 similar to that employed in commercial polyester dyeing. Therefore no modification of the dyeing process is needed for the application of the synthesized dyes and pollution of the water discharge into the environment by the dispersing agent is eliminated. The dyes gave yellow to orange hues on polyester and showed good build-up and leveling properties. The dyes exhibited good to excellent wash fastness while rubbing; hot pressing and light fastness results were good and moderate to good and mainly dependent on the structure of the dyes. This research clearly showed the use of vinylsulphone disperse reactive dyes as dispersant-free dyes for dyeing of polyester.

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