



# Synthesis, characterization, and application of diester/diurethane tethered azo disperse dyes: A new strategy to improve dye's fastness properties



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## ABSTRACT

A series of new kinds of diester/diurethane tethered azo disperse dyes were synthesized through the reaction between the hydroxyl group in disperse dyes, such as C. I. Disperse Red 1 (**1a**), C. I. Disperse Red 13 (**1b**), and C. I. Disperse Blue 106 (**1c**), and terephthaloyl chloride or *p*-phenylene diisocyanate. Structures of these new dyes were fully characterized with NMR, MS, and FT-IR. Visible absorption measurement in DMF indicated that all new diester/diurethane tethered dyes exhibited a little shorter maximum absorption wavelength and much higher molar extinction coefficient than their prototypes. Moreover, the fastnesses to wash and sublimation of dyeing on polyurethane fibre were dramatically improved due to the dye's moderately increased molecular size. It is an attractive new strategy to synthesize a library of tethered dyes with improved fastness properties using various different tethering agents or disperse dyes.

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## 1. Introduction

Disperse dyes are commonly used for dyeing secondary cellulose acetate, nylon, and polyester fibres, among of which polyester has become more and more important in industrial production. Polyethylene terephthalate (PET), the most common polyester fibres, is quite crystalline and features a very impact internal structure, so that the disperse dyes with smaller molecular size are favourable for fibre interior access [1]. The chromophore of disperse dyes mainly includes the nonionic monoazo functional group and anthraquinone subunit. There are many thousands of azo disperse dyes, because of numerous substitution possibility in the diverse diazonium ion and coupling counterpart [2]. Recently, the heterocyclic amino based azo dyes have been widely applied for the brilliance of colour producing [3,4]. For the regular PET fibre, the current disperse dyes can satisfy well with the dyeing properties required by various end-use.

Polyurethane (PU) fibre has great significance on manufacture of faddish and comfortable apparel owing to its high elastic stretch and good shape retention. Its blending with polyester has been

mainly utilized in sportswear and outdoor apparel which have a larger market share in textile field. The application of disperse dyes is essential as a given depth of shade need to be imparted to elastane/polyester blends. The polyurethane component consists of hard and soft segments. Hard segment forms intermolecular hydrogen bonds which contribute to good tensile and chemical resistance; and soft segment, made of repeating aliphatic polyester or aliphatic polyether subunits, is responsible for good flexibility and stretch [5]. The PTMG based PU fibres feature low glass transition temperature, usually ranging from  $-60\text{ }^{\circ}\text{C}$  to  $-30\text{ }^{\circ}\text{C}$  [6]. The open internal structure in soft segment region allows dyes to easily penetrate into the fibres and migrate out to deposit on the surface of fibres. The relatively insoluble dyes on the surface of fibres become the nucleus for disperse dye crystal formation, so that a large number of dye particles can be observed on the surface of dyed PU fibres by scanning electron microscope [7]. Heavy stain on PU component leads to an inferior wet fastness [8–10]. Moreover, the degree of stain can dramatically increase along with the increase of concentration of dye used in bath.

One way to solve the dyeing problem described above with the PU/polyester blends is to minimize the degree of migration by enhancing the interaction between fibre and dye. It is well known that the size of disperse dye becomes larger, the van der Waals force

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of dye with fibre chain becomes stronger. Therefore, the development of disperse dyes with low degree of thermomigration by increasing molecular size is feasible and it is particularly suitable for PU fibres having much larger free volumes in soft region compared with other hydrophobic fibres.

Several strategies have been reported in literature to increase dye's molecular size: (a) introducing a bulkier group into dye molecule, such as substituting two acetoxy groups of C.I. Disperse Red 82 with two benzoxy groups [11]; (b) diazotizing a free primary amino group in dye, followed by coupling to form bisazo disperse dye. In this case, a different degree of bathochromic shift usually occurs because of the formation of larger conjugate system in dye molecules, resulting in producing duller colour [12,13]; and (c) polymerizing dyes. Although polymerizing is a good way to dramatically increase dye's molecular size, the molecule is too large to easily penetrate into regular fibre interior to reach a desirable colour depth [14–16].

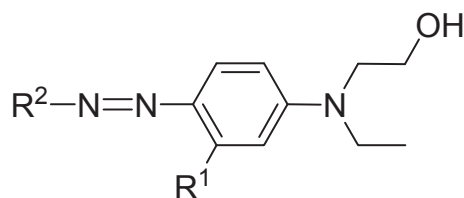
The present study attempted to develop a new strategy to obtain new kinds of azo disperse dyes with appropriate molecular weight and size and further enhance the interaction between dye and fibre. We envisaged that two monoazo disperse dyes might be coupled through selective reaction of a functional group in dye such as hydroxyl group with a difunctionalized compound such as terephthaloyl chloride or *p*-phenylene diisocyanate, resulting in diester/diurethane tethered azo disperse dyes respectively, with moderately increased dye size. We reported herein the synthesis, characterization, and application of diester/diurethane tethered C.I. Disperse Red 1 (**1a**), C.I. Disperse Red 13 (**1b**), and C.I. Disperse Blue 106 (**1c**). It was found that these new dyes exhibited highly improved colourfastness and sublimation fastness for polyurethane fibre.

## 2. Experimental

### 2.1. General

C.I. Disperse Red 1 (**1a**), C.I. Disperse Red 13 (**1b**), and C.I. Disperse Blue 106 (**1c**) were kindly provided as the form of press cake by the Zhejiang Wanfeng Chemical Co., Ltd (China) and purified through recrystallization in acetone before use. Their structures are shown in Fig. 1.

Bis-(5,5'-disulphonate)-naphthylmethane disodium salt (NNO) was provided by Zhejiang Longsheng Co., Ltd (China). *p*-Phenylene diisocyanate, terephthaloyl chloride, dichloromethane, triethylamine, acetone, *N,N*-dimethylformamide, toluene, sodium carbonate, and calcium hydroxide were purchased from Aladdin industrial corporation and used without further purification,



**1a:**  $R^1 = H$ ,  $R^2 = 4\text{-nitrophenyl}$

**1b:**  $R^1 = H$ ,  $R^2 = 2\text{-chloro-4-nitrophenyl}$

**1c:**  $R^1 = CH_3$ ,  $R^2 = 5\text{-nitrothiazol-2-yl}$

Fig. 1. Structures of C.I. Disperse red 1 (**1a**), C.I. Disperse red 13 (**1b**), and C.I. Disperse blue 106 (**1c**).

except that dichloromethane and triethylamine were dried with calcium hydride, followed by distillation before use. Other chemicals in the synthesis and characterization were of laboratory-reagent grade.

IR spectra were measured on Shimadzu prestige 21 FT-IR spectrophotometer. NMR spectra were recorded on Bruker AVANCE 400 MHz spectrometer, using TMS as an internal standard and  $CDCl_3$  or  $DMSO-d_6$  as solvent. Chemical shifts ( $\delta$ ) were measured in ppm and the coupling constants ( $J$ ) were measured in Hz. The MS analysis was performed on Agilent Technologies 1200 Series LC-MS system. Absorption spectra were measured in 1 cm quartz cells on a UV 2450 spectrophotometer (JPN, SHIMADZU).

### 2.2. Synthesis

Synthesis of diurethane tethered azo disperse dyes **2a-c** is depicted in Scheme 1. The method used is illustrated for synthesis of dye **2a** (Scheme 1). Triethylamine (1.01 g, 10 mmol) was slowly added to the solution of dye **1a** (3.14 g, 10 mmol) in dry dichloromethane (200 mL) at room temperature. *p*-Phenylene diisocyanate (0.88 g, 5.5 mmol) dissolved in dry dichloromethane (20–30 mL) was then slowly added within 0.5 h. After stirring at room temperature for 12 h, the reaction went into completion according to TLC analysis. The solvent was then removed with rotavapor under reduced pressure, and the residual solid was then washed with water and dried in oven at 100 °C. The crude dye was purified through recrystallization in DMF until a constant molar extinction coefficient and TLC purity were attained. The product **2a** was obtained in 87.5% yield (3.51 g). Employing the same method as dye **2a**, dyes **2b** and **2c** were obtained in 84.7% and 82.6% yields, respectively.

Synthesis of diester tethered azo disperse dyes **3a-c** is depicted in Scheme 2. The method used is illustrated for synthesis of dye **3a** (Scheme 2). Triethylamine (2.02 g, 20 mmol) was firstly slowly added to the solution of dye **1a** (3.14 g, 10 mmol) in dichloromethane (150 mL) at room temperature. After cooling to 0 °C with ice-water bath, terephthaloyl chloride (1.22 g, 6 mmol) in dichloromethane (15 mL) was then added dropwisely. The reaction went into completion according to TLC analysis after stirring at the same temperature for 2 h. The reaction mixture was neutralized with dilute hydrochloric acid solution and then extracted with EtOAc. After separating, the organic layer was concentrated with rotavapor under reduced pressure. The residual solid was washed with a sequence of aqueous sodium carbonate (10%) and water, and then dried in oven. The crude dye was purified through recrystallization in DMF until a constant molar extinction coefficient and TLC purity were attained. The product dye **3a** was obtained in 85.2% yield (3.71 g). Employing the same method as dye **3a**, dyes **3b** and **3c** were obtained in 82.5% and 80.6% yields, respectively.

### 2.3. Dyeing and fastness measurement

The PTMG based PU fibre, 44.4dtex, purchased from Zhejiang Kaipute Anlun Co., Ltd (China), was firstly cut into 2–3 cm length and scoured in a bath containing 2 g/L non-ionic surfactant at 85 °C for 30 min, then rinsed with water and dried at room temperature.

The purified dyes and disperse agent NNO (weight ratio 1:1) were milled to dye dispersions whose average particle size was smaller than 0.5  $\mu m$ . For each of new dyes, a set of dye baths containing different initial concentration of dye ranging from 1% to 4% owf and 1 g/L ammonium sulfate were prepared, respectively, and all the liquor ratio were 50:1. Dyeings were performed in an IR laboratory dyeing machine (RAPID, China). The temperature was raised from 40 °C to 120 °C at rate of 2 °C/min, maintained for

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