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Synthesis and application of novel crosslinking polyamine dyes with good dyeing performance

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Abstract

Novel crosslinking dyes were synthesized using tetraethylenepentamine. A series of novel red polyamine crosslinking dyes $\mathbf{D_1}$–$\mathbf{D_7}$ based on benzoyl H-acid sulfonamide were prepared via the reaction of it with diazo salts of aniline, *p*-toluidine, *o*-methoxyaniline, *p*-aminophenol, *p*-nitraniline, *m*-aminobenzene sulfonic acid, 1-aminonaphthalene-5-sulfonic acid, respectively. Two novel polyamine crosslinking dyes were synthesized via the reactions of tetraethylenepentamine with C.I. Reactive Red 2 and 4-(4-chlorosulfonyl-phenylhydrazono)-3-methyl-1-phenyl-5-pyrazolone, respectively. The silk dyed with these polyamine dyes was fixed via crosslinking agent 2-chloro-4,6-di(aminobenzene-4′-β-sulfatoethylsulfone)-1,3,5-*s*-triazine, which acted as a bridge between the fibre and the dye molecule. The crosslinking reaction ratio of these dyes reached more than 95%, and the overall fixation efficiency of the crosslinking dye of high affinity was more than 98%. The dyed samples exhibited good fastness to washing and rubbing.

Keywords: Crosslinking dyes; Crosslinking agent; Covalent bond; Fixation

1. Introduction

The most important distinguishing characteristic of reactive dyes is that they form covalent bonds with the substrate that is to be colored during the application process, which is attributed to specific functional groups in the dye molecule that can undergo addition or substitution reactions with the OH, SH, and NH_2 groups present in textile fibers. However, one of the most obvious disadvantages of reactive dyes is the hydrolysis of the reactive groups in the process of storage and application. It is estimated that between 20% and 50% of reactive dyes are lost during the dyeing process [1]. This is clearly uneconomical and can cause environmental problems. Dyeing nowadays should also have a good tinctorial yield and high reactivity, the objective being to provide especially dyeing having high degrees of fixing [2].

It has been known for many years that crosslinking dyes, i.e. basazol [3], indosol [4] and alkylamine crosslinking dyes [5] have excellent characteristics, for example simple procedures and excellent fixation. The dye is linked to the fibre through covalent bonding by the use of a crosslinking agent, so it has high fixation and good wet fastness. In the dyes' chemistry, crosslinking dye has been in the center of interest for many years.

This paper reports the synthesis and application of a series of novel crosslinking polyamine dyes. The simultaneous application of the specially prepared alkylamine dyes and a crosslinking agent 2-chloro-4,6-di(aminobenzene-4′-β-sulfatoethylsulfone)-1,3,5-*s*-triazine (DAST) [6] was evaluated as a means to achieve controlled covalent dye–fibre bonding, leading to improved levelness and good comparison with those of reactive dye wet fastness. The novel dyes should especially be distinguished by high fixation and high fibre–dye binding stability. The dyes should also yield good washing and rubbing fastness.

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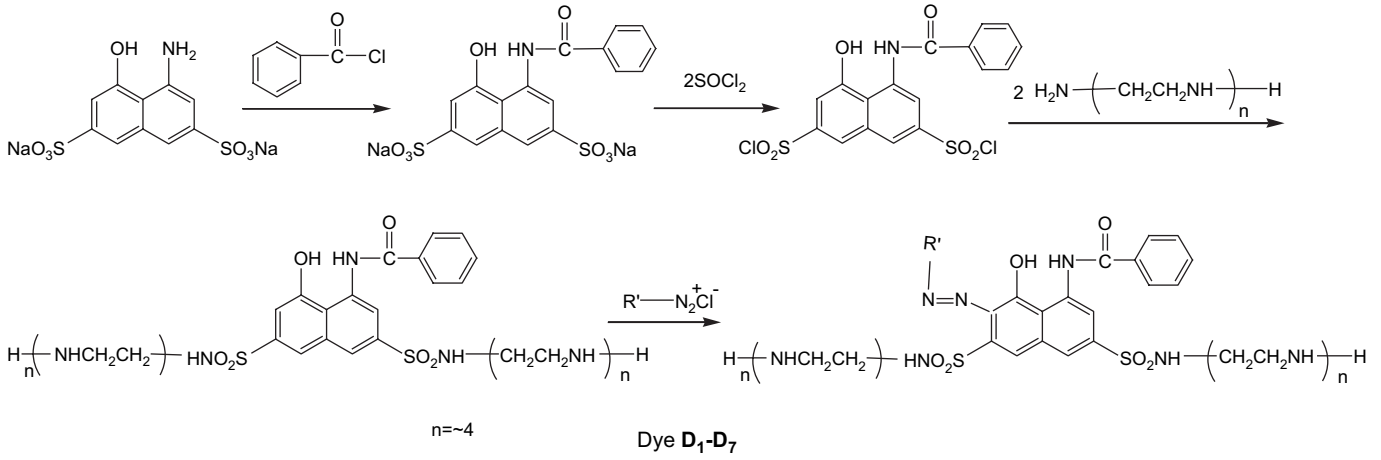


Scheme 1.

2. Experimental

2.1. Materials

02-Crepe de Chine silk (90 g/m^2) was obtained from Shanghai No. 1 Dyeing Factory. FT/IR 2430 spectrophotometer, HP1100 mass spectrometer, HP-8453 UV-100 spectrophotometer and routine organic synthesis instruments were used. The crosslinking agent, 2-chloro-4,6-di(aminobenzene-4′-β-sulfatoethylsulfone)-1,3,5-*s*-triazine (DAST) was prepared according to the method described by Tang et al. [6]. All other chemicals were of analytical grade quality and purchased from No. 1 Shenyang Chemical Reagent Factory (Liaoning, China).

2.2. Synthesis of crosslinking dyes

2.2.1. The amination of chlorosulfonate benzoyl H-acid

(1) Benzoyl H-acid was synthesized by known methods [7]. Yield 81.6%; IR (KBr): 1045 cm^{-1} and 1182 cm^{-1} (SO_2^-), 1288 cm^{-1} (C–N), 1562 cm^{-1} (N–H), 1630 cm^{-1} (C=O). MS *m/z*: 423 (M^+).

(2) Chlorosulfonate benzoyl H-acid was synthesized by known methods [8]. Yield 95.0%; IR (KBr): 1170 cm^{-1} and 1387 cm^{-1} (SO_2^-), 1284 cm^{-1} (C–N), 1542 cm^{-1} (N–H), 1630 cm^{-1} (C=O). MS *m/z*: 459 (M^+).

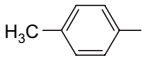
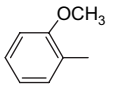
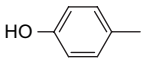
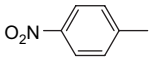
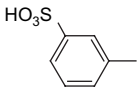
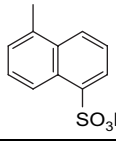
(3) The amination of chlorosulfonate benzoyl H-acid was carried out according to the following method. Tetraethylenepentamine (5 ml) was dissolved in acetone (20 ml) and stirred at room temperature. Slurry of chlorosulfonate benzoyl H-acid (6.1 g) and acetone (20 ml) was added dropwise to the stirred mixture from a hypodermic syringe for a 30 min period. The mixture was stirred until the reaction was over, and the reaction termination was determined by TLC (Silica GF254, *n*-butanol:acetic acid:water = 4:1:5 v:v:v). The R_f value of chlorosulfonate benzoyl H-acid is 0.89, and the R_f value of product is 0.34. Acetone was removed and the residue was dissolved in water to make a solution (pH = 10) for the synthesis of the dyes.

IR (KBr): 1155 cm^{-1} and 1390 cm^{-1} (SO_2^-), 1707 cm^{-1} (C=O), 2958 cm^{-1} (CH_2–), 3432 cm^{-1} and 1617 cm^{-1} (NH_2– and NH–).

2.2.2. Synthesis of dye D_1

Diazotization of aniline: hydrochloric acid (1.5 ml, 36 wt/wt%) and ice water (10 ml) were added to aniline (0.5 g) and the mixture was cooled to 0–5 °C, sodium nitrite (30 wt/wt%) was added with stirring until it was in excess. When diazotization was complete, the excess nitrous acid was decomposed by the use of urea.

Table 1
Structures of the polyamine crosslinking dyes synthesized

No	R′	λ_{max} (nm)	Yield (%)
D_1		518	74.5
D_2		525	82.1
D_3		541	96.6
D_4		535	76.3
D_5		524	93.3
D_6		519	82.4
D_7		558	85.7