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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 **D_1–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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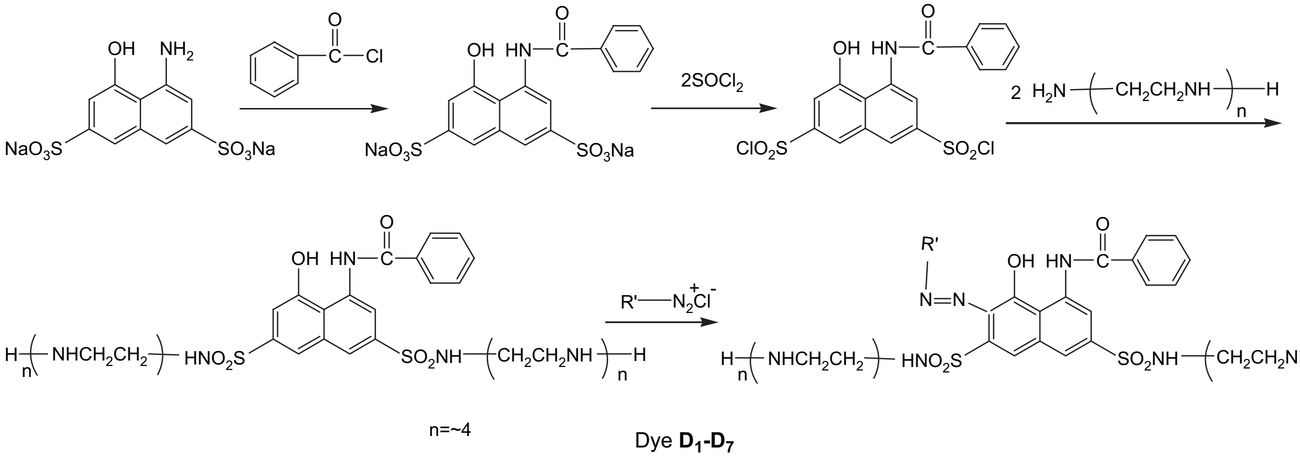


Scheme 1.

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$^+$).

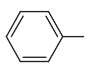
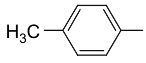
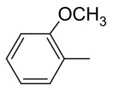
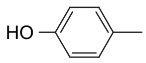
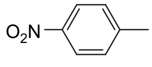
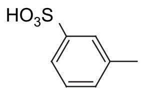
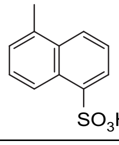
(3) The amination of chlorosulfonate benzoyl H-acid was carried out according to the following method. Tetraethylenepentamine (5 ml) was dissolved in acetone (20 ml) and stirred at room temperature. Slurry of chlorosulfonate benzoyl H-acid (6.1 g) and acetone (20 ml) was added dropwise to the stirred 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.

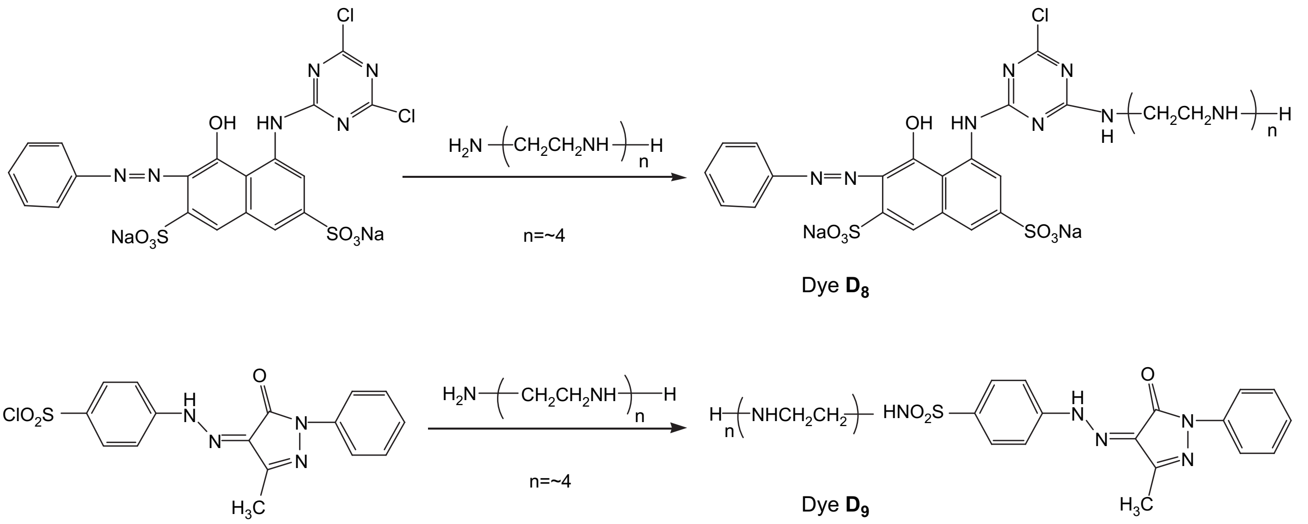
IR (KBr): 1155 cm^{-1} and 1390 cm^{-1} (SO_2^-), 1707 cm^{-1} (C=O), 2958 cm^{-1} (CH_2–), 3432 cm^{-1} and 1617 cm^{-1} (NH_2– and NH–).

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



Scheme 2.

The coupling: the diazo salt of aniline was added to a viscid solution of the product from the amination of chlorosulfonate benzoyl H-acid and hydrochloric acid (1 wt/wt%) was added to adjust the pH to 4–5. The mixture was stirred for 10 h at 0–5 °C, and the reaction was examined by a thin layer chromatography, using *n*-butanol:acetic acid:water (4:1:5 v:v:v). The R_f of the dye was 0.04. When the reaction was complete, sodium carbonate was added with stirring to adjust the pH to 10. The dye was filtered, washed and dried at room temperature under vacuum. The yield was 5.8 g (74.5%).

D_2–D_7 were synthesized by the similar procedure, as was **D_1**.

2.2.3. Synthesis of dye D_8

Tetraethylenepentamine (2.2 ml) and sodium carbonate (0.4 g) were dissolved in 10 ml water under stirring at room temperature. C.I. Reactive Red 2 (6.0 g) was then added, the mixture was kept at room temperature until the reaction was over. The reaction termination was determined by thin layer chromatography (*n*-propanol:ammonia, 3:1 v:v) (R_f of the red dye = 0; R_f of C.I. Reactive Red 2 = 0.65). When the reaction was complete, hydrochloric acid was added with stirring to adjust the pH to 8. The product was filtered, washed and dried at room temperature under vacuum. The yield of the dye was 6.2 g (86.1%) ($\lambda_{max} = 520$ nm).

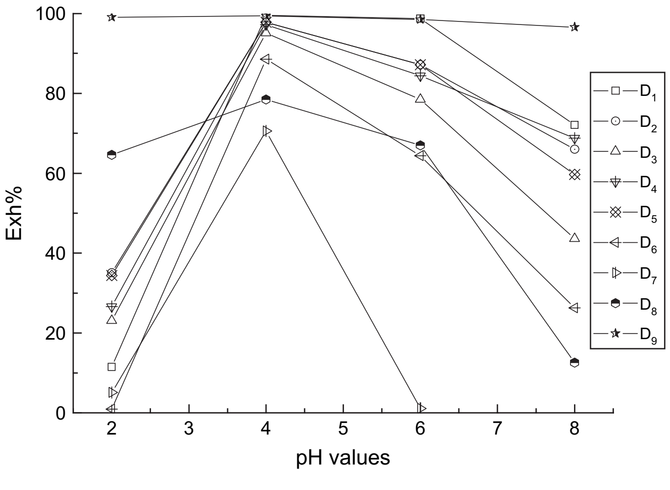


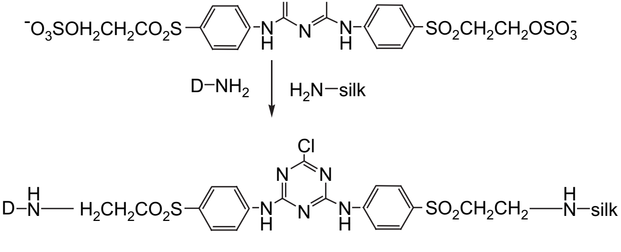
Fig. 1. Exhaustion % of the nine dyes versus different dye-bath pH values on silk.

IR (KBr): 2985 cm^{-1} (CH_2–), 3434 cm^{-1} and 1614 cm^{-1} (NH_2– and NH–).

2.2.4. Synthesis of dye D_9

(1) 4-(4-Chlorosulfonyl-phenylhydrazono)-3-methyl-1-phenyl-5-pyrazolone was synthesized by known methods [9]. Yield 95.1%; IR (KBr): 1172 cm^{-1} and 1375 cm^{-1} (SO_2^-), 1667 cm^{-1} (C=O). MS *m/z*: 376 (M^+).

(2) Tetraethylenepentamine (4.2 ml) was dissolved in chloroform (10 ml) and stirred at room temperature. A slurry of 4-(4-chlorosulfonyl-phenylhydrazono)-3-methyl-1-phenyl-5-pyrazolone (7.6 g) and chloroform (40 ml) was added dropwise to the stirred mixture from a hypodermic syringe for a 30 min period. The mixture was stirred for 4 h. Testing of reaction progress was conducted by diluting a small amount of the reaction mixture with hydrochloric acid (2 ml, 1 wt/wt%). Then the solution was spotted on thin layer chromatography and developed in an eluent containing *n*-butanol:acetic acid:water (4:1:5 v:v:v). The 4-(4-chlorosulfonyl-phenylhydrazono)-3-methyl-1-phenyl-5-pyrazolone ($R_f = 0.75$) was fully converted to the product ($R_f = 0$). When the reaction



Scheme 3.

Table 2
Comparison of fixation of red polyamine crosslinking dyes with the dyes uncrosslinked in exhaust dyeing

No	*E* (%)	Without DAST		DAST (2 wt/wt%)	
		M (%)	*A* (%)	*C* (%)	*F* (%)
$\mathbf{D_1}$	99.7	89.3	89.0	99.9	99.6
$\mathbf{D_2}$	97.8	92.4	90.4	99.4	97.2
$\mathbf{D_3}$	95.1	95.7	91.0	96.7	92.0
$\mathbf{D_4}$	97.3	92.2	89.7	98.7	95.9
$\mathbf{D_5}$	97.8	94.2	92.1	99.1	96.9
$\mathbf{D_6}$	88.6	73.7	65.3	95.9	84.9
$\mathbf{D_7}$	70.6	91.9	64.9	97.2	68.7
$\mathbf{D_8}$	78.5	85.6	67.2	99.5	78.1
$\mathbf{D_9}$	99.4	93.1	92.5	99.0	98.4

was over, the chloroform was removed under reduced pressure. The precipitate was washed twice with ethanol, followed by vacuum drying to yield the yellow dye product (9.8 g; 98.0%). Its wavelength of maximum absorption (λ_{max}) in water was 390 nm.

IR (KBr): $1153\ cm^{-1}$ and $1370\ cm^{-1}$ (SO_2^-), $2974\ cm^{-1}$ (CH_2–), $3395\ cm^{-1}$ and $1607\ cm^{-1}$ (NH_2– and NH–). MS *m/z*: 529 (M^+).

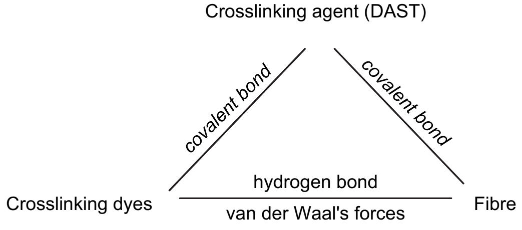


Fig. 2. Sketch of crosslinking dyeing.

2.3. Dyeing of silk

2.3.1. Exhaustion (*E*)

All dyeings were carried out using 2% o.m.f. dye. The dyeing of polyamine dyes was carried out in water using fabric (1 g) at a liquor ratio of 30:1. Fabric was immerged into water (30 ml) at room temperature. The dye-bath was heated to 90 °C within 60 min and the dyeing continued at 90 °C for further 60 min. The dyed fabric was removed from the dye-bath and dried at room temperature. The absorbance of the diluted dye solution was measured at the wavelength of maximum absorption (λ_{max}) of the dye using a UV–Visible spectrophotometer (HP-8453). The exhaustion *E* of the dyes on the silk was calculated according to Eq. (1):

$$E\% = (1 - A_1/A_0) \times 100 \tag{1}$$

wherein A_0 and A_1 are the absorbance values of the dye-bath before and after the dyeing process, respectively.

2.3.2. Fixation (*F*)

Crosslinking reaction: the dyed fabric was crosslinked with a fixative solution which consisted of 10 g/l crosslinking agent DAST by the use of dip-pad method two times at

Table 3
Exhaustion and fixation of three reactive dyes

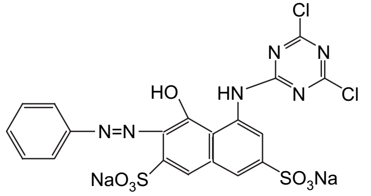
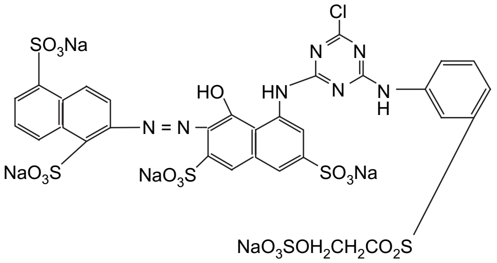
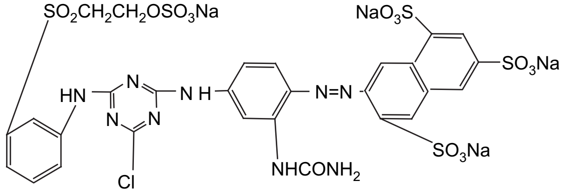
	Structure	Exhaustion (%)	Reaction (%)	Fixation (%)
C.I. Reactive Red 2		61.9	85.3	52.8
C.I. Reactive Red 195		71.4	87.0	62.1
C.I. Reactive Yellow 145		86.8	90.1	78.2

Table 4
Comparison of fixation of crosslinking polyamine dyes with the dyes uncroslinked in pad dyeing

No	F (%)	
	Without DAST	DAST (2 wt/wt%)
D_8	12	99
D_9	50	98

a liquor-to-goods ratio of 20:1, and dried at 50 °C for 10 min. The fabric was soaped-off using a weakly anionic detergent (2 g/l) at boil temperature for 10 min. The absorbance value A_2 of the liquor which consisted of fixative solution and detergent was measured as well as the reflectance values of the dried sample. Crosslinking reaction ratio C and the overall fixation efficiency F were calculated according to Eqs. (2) and (3), respectively:

$$C\% = (1 - A_2/(A_0 \times E\%)) \times 100 \quad (2)$$

$$F\% = E\% \times C\%/100 \quad (3)$$

The unfixed fabric was directly soaped-off using a weakly anionic detergent (2 g/l) at boil temperature for 10 min. The absorbance A_3 of detergent was measured at the wavelength of maximum absorption (λ_{max}) of the dye. Remainder of the crosslinking dye M and the overall remainder A were calculated according to Eqs. (4) and (5), respectively:

$$M\% = (1 - A_3/(A_0 \times E\%)) \times 100 \quad (4)$$

$$A\% = E\% \times M\%/100 \quad (5)$$

2.3.3. Fastness testing

The color fastness of the dyed fabric was tested according to Chinese standard methods including fastness to washing (GB/T 3921-97) and rubbing (GB/T 3920-97).

3. Results and discussion

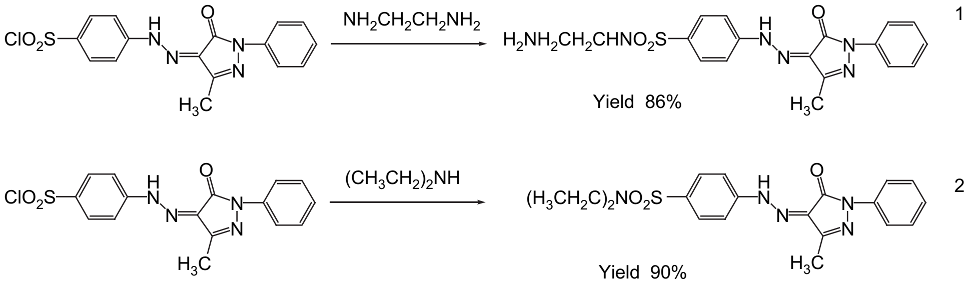
3.1. Synthesis and dyeing performance of crosslinking polyamine dyes

Seven dyes **D_1–D_7** containing tetraethylenepentamine were synthesized according to the routes shown in Scheme 1 and their structures are presented in Table 1. And two dyes **D_8** and **D_9** were synthesized following the routes shown in Scheme 2.

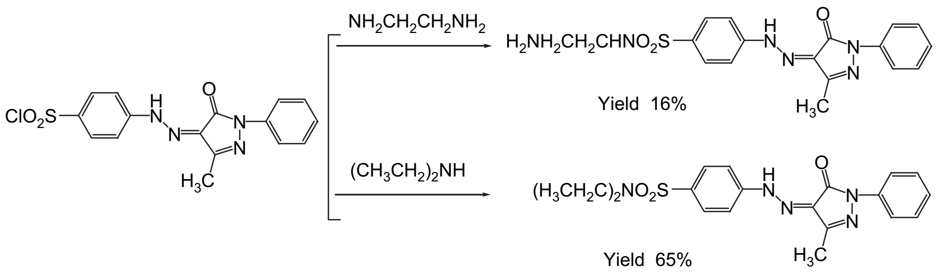
Primary or secondary amino groups in the crosslinking polyamine dyes were hydrophilic under acidic conditions. Generally, the stronger the hydrophobe of the dye matrix was, the better the dye affinity was. The maximum exhaustion ($E\%$) for the nine dyes was obtained from Fig. 1 when dyeing proceeded at pH 4. The isoelectric point of silk is pH 3.9–4.3 at room temperature. In exhaust dyeing at pH values below 4, protonation of the amino groups in both the polyamine dye and the silk fibre brought the repulsion from the same electric charge, and then the dye became much hydrophilic, and consequently lower dye exhaustion was observed. At the isoelectric point of silk, the positive charges and negative charges of the fibre kept balance, the fibre presented to be neutral. Amines in the crosslinking polyamine dye inclined to be dissociative amine as a result of the decreasing water-solubility of the dye. The repulsion in both the polyamine dye and the silk fibre was reduced. In these processes, there would be a further dye adsorption on the fibre to reach its highest exhaustion. If pH value was greater than 6, in spite of great dye affinity between the amino groups and fibre, dye uptake was low due to decreased dissolution of the polyamine dye.

From chemical structures of the dyes, it is seen that exhaustion of dyes **D_6** and **D_7** bearing sulfonate groups was lower than that of dyes **D_1–D_5** at different pHs. Dye **D_8** had two sulfonate groups, at pH values below 4, sulfonate groups in the dye could balance part of positive charges of the dye as a result of the declined water-solubility of dye **D_8**, and then dye–fibre exhaustion was higher than that of dyes **D_1–D_7**. When the pH values were higher than the isoelectric point of silk, the increasing water-solubility of dye **D_8** led to low dye uptake. Contrary to dyes **D_1–D_8**, **D_9** had different chemical structure to obtain good results in exhaustion of the dye, and its exhaustion was almost not influenced by dye-bath pH values.

The fabric dyed with exhaust method was crosslinked with crosslinking agent DAST, a simplified reaction scheme covering reaction among polyamine crosslinking dye, DAST and fibre nucleophile is illustrated in Scheme 3. Table 2 showed that fixation values were markedly increased by adding crosslinking agent DAST, compared to the fixation of the red crosslinking dyes on silk with and without crosslinking reaction of DAST. This indicated that covalent dye–fibre bond formation was achieved by the use of DAST, which acted as a crosslinking agent.



Scheme 4.



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Scheme 5.

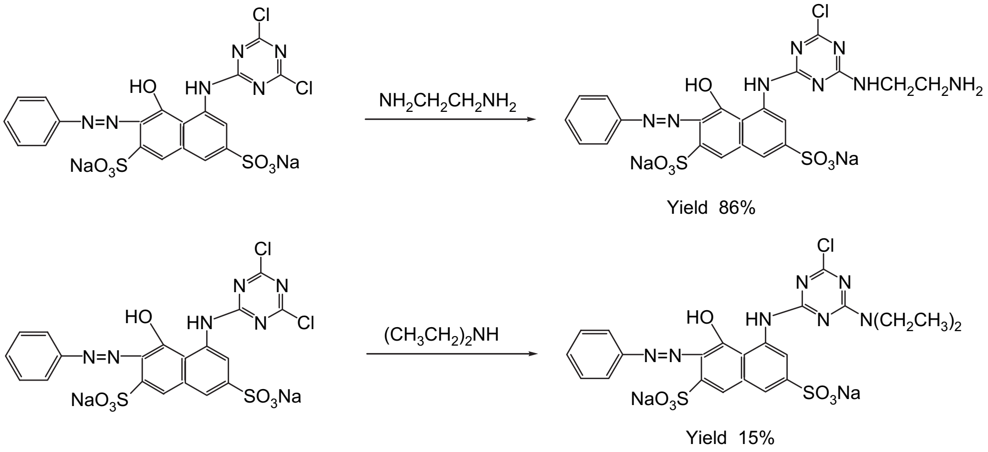
Generally, the reactive dye was linked to the fibre by covalent bonds, the fixation of monofunctional reactive dye was about 50–60%, and the fixation of difunctional reactive dye was about 80%. For example, for C.I. Reactive Red 2, C.I. Reactive Red 195 and C.I. Reactive Yellow 145, the exhaustion, reaction efficiency and fixation are shown in Table 3.

Comparison was made between data in Tables 2 and 3, if polyamine crosslinking dye in exhaust dyeing did not use the crosslinking agent, the crosslinking dye remained fixed to the fibre barely by hydrogen bonding and van der Waal's forces, the overall remainder of the crosslinking dye on the fabric was about 90% for the dye without anion water-solubility groups after the dyed fibre was soaped with a mild detergent. Crosslinking reaction ratio of the crosslinking dye with crosslinking agent DAST was up to 95.9%, and the overall fixation efficiency was more than 98% by the use of the crosslinking dye with high affinity (dyes $\mathbf{D_1}$ and $\mathbf{D_9}$). It had been reported that the crosslinking dyes were linked to the fibre through covalent bonding, hydrogen bonding and van der Waal's forces [4]. The sketch of crosslinking dyeing was as followed (Fig. 2).

The crosslinking effect of the crosslinking agent was more outstanding in pad dyeing when dyeing with this crosslinking dye. In our present study, pad dyeing with the crosslinking polyamine dye on silk was carried out by the use of '3-dip-3-nip' padding operation of dye and crosslinking agent at room temperature. And the dyed fibre was fixed at 50 °C for 10 min, the results are listed in Table 4. After the unfixed fabric was soaped-off, reservation of the crosslinking of dyes $\mathbf{D_8}$ and $\mathbf{D_9}$ on the fabric was only 12% and 50%. The fixation of the crosslinking dye was over 98% with the crosslinking reaction of DAST. This clearly indicated that during the crosslinking–fixing process the usage of the crosslinking agent must be the main factor affecting the fixation.

3.2. The activity of reaction and crosslinking of primary and secondary amines of crosslinking polyamine dye

Using tetraethylenepentamine as the crosslinking group, if two primary amines of it could react entirely with sulfonyl chlorides to form sulfonamides, did the crosslinking dye of secondary amines have crosslinking activity to the fibre? The Hinsberg test may be used to demonstrate whether an amine is primary, secondary, or tertiary. 4-(4-Chlorosulfonyl-phenylhydrazono)-3-methyl-1-phenyl-5-pyrazolone reacted, respectively, with ethylenediamine and diethylamine (molar ratio 1:1) in the non-polar aprotic solvent similar to the synthetic procedure of dye $\mathbf{D_9}$. The yield of the former product was 86%, and that of the latter was 90% (Scheme 4). When 4-(4-chlorosulfonyl-phenylhydrazono)-3-methyl-1-phenyl-5-pyrazolone was added to the mixture containing ethylenediamine and diethylamine (molar ratio 1:1:1) with the synthesis procedure similar to dye $\mathbf{D_9}$, each type of amine – primary or secondary – gave different visible results after the Hinsberg test, the total yield was about 81%, as shown in Scheme 5. The yield of diethylamine reaction with the sulfonyl chloride



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Scheme 6.

was high since the secondary amine was a more potent nucleophile compared to the primary amine in chloroform. When ethylenediamine and diethylamine reacted with C.I. Reactive Red 2, respectively, similar to the process of dye **D$_8$** in water, the yields of the reactions were 15% and 86%, respectively, in Scheme 6. In hydroxylic solvents, secondary amines having a high concentration of charge were usually strongly solvated by hydrogen bonding compared to primary amines.

That is to say, when polyethylene polyamine was used as the crosslinking group for preparing the crosslinking dye in different solvents, the reactivity of the primary amines or the secondary amines was different. According to the result of the crosslinking dyeing, the excessive amount of amine of the dye whether it was the primary amines or the secondary amines would be used as the crosslinking groups, so it couldn't influence the crosslinking reactivity of the dye.

3.3. Fastness properties of the dyes on silk

Fastness properties of the novel polyamine crosslinking dyes on silk are listed in Table 5. It can be seen that the wash fastness and rub fastness can reach 4 grade and 3 grade, respectively. This was attributed to the reason that the crosslinking dyes were fixed on silk by covalent bonds with the crosslinking agent – DAST, which acted as a bridge between the fibre and the dye molecule.

Table 5
Fastness properties of the seven red polyamine crosslinking dyes

No	Rub fastness		Wash fastness		
	Dry	Wet	Alteration	Staining	
				Silk	Cotton
D$_1$	3	3	4–5	4	4–5
D$_2$	3	3–4	4–5	4	4–5
D$_3$	4	4	4–5	4–5	4–5
D$_4$	4	3–4	4–5	4–5	4–5
D$_5$	3	3–4	3	4	4–5
D$_6$	3	3	4–5	4	4–5
D$_7$	3	3–4	4	4	4–5
D$_8$	3–4	3	3–4	3–4	4
D$_9$	4	4	4	4–5	4–5

4. Conclusions

Seven novel crosslinking dyes containing polyamine groups have been synthesized by the diazonium coupling reaction of seven different aromatic amines with the product of the amination of chlorosulfonate benzoyl H-acid. And 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. Their dyeing performances on silk were studied via exhaust dyeing process. The results showed that the crosslinking reactivity reached more than 95.9% when the pH value of the dye-bath was 4.

The crosslinking dye was linked to the fibre by covalent bonds with the crosslinking agent acting as a bridge between the fibre and the dye molecule. Only one amino group reacted with the dye substrate based on certain mole ratio of the reactants, no matter primary or secondary amine was used, so the residue amino groups (including primary and secondary ones) acted as crosslinkable groups and little difference of reactivity existed between the polyamine crosslinking dyes. The dyeing results of novel polyamine dyes showed that the dye had perfect exhaustion and fixation. The wash fastness and rub fastness reached 4 grade and 3 grade, respectively.

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