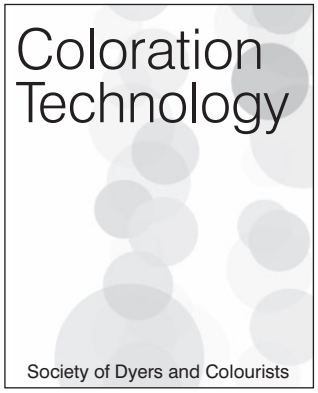
doi: 10.1111/j.1478-4408.2006.00005.x

Fixation of a tetraethylene pentamine dye on cotton and silk by bifunctional crosslinkers



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Received: 18 August 2005; Accepted: 16 November 2005

Four crosslinkers were synthesised by the reaction of 1,3,5-trichloro-2,4,6-triazine and polyethylene glycol. Their structures were confirmed by Fourier transform infrared spectra and mass spectra. A tetraethylene pentamine dye was crosslinked to cotton and silk via covalent bonds by the crosslinking dyeing process. The effects of pH, temperature, concentration and the chain length of the crosslinkers on the dye fixation were investigated in detail. The fixation of the dye using the crosslinkers on cotton and silk was >97%, and the infrared spectra of cotton, the dyed cotton and the crosslinked dyed one were compared with each other, which indicated that a covalent bond had been formed between the crosslinking dyes and fibres through the crosslinkers.

Introduction

Crosslinking dyes, such as basazol [1], indosol [2] and alkylamine crosslinking dyes [3], have been studied for about 40 years. The common characteristics of crosslinking dyes is that they have one or more suitable nucleophilic groups such as amino, sulphydrols, hydroxy groups, which can react with a crosslinker to form a covalent bond. Thus, crosslinking dyes are activated to be 'reactive dyes', bonding to the fibre indirectly; in the same way, the fibre can also be activated to react easily with crosslinking dyes through crosslinkers.

A number of readily available crosslinkers include aldehydes, multifunctional epoxides, isocyanates, acrylamides and various reactive polymers [4]. However, there are many practical, environmental and cost problems associated with their use with crosslinking dyes. So special crosslinkers especially with water solubility are badly needed and a few nonionic and anionic water soluble crosslinkers of good performance for crosslinking dyes have been developed [5,6].

Among many reactive groups, 1,3,5-trichloro-2,4,6-triazine is a common and cheap reactive group that has been used in reactive dyes and it can also be employed as a reactive group in crosslinkers. Polyethylene glycol (PEG) is a cheap and readily available polymer that exhibits many excellent properties such as being water soluble and non-toxic. Therefore, the resultant crosslinker from the reaction of 1,3,5-trichloro-2,4,6-triazine and PEG may have the advantages of both.

In our previous study, a yellow crosslinking polymeric dye was synthesised and crosslinked to fibre by 2-chloro-4,6-di(aminobenzene-4-sulphatoethylsulphone)-*S*-triazine (XLC) [7]. In this study a polyethylene polyamine crosslinking dye was used to dye cotton and silk by crosslinkers **3a**, **3b**, **3c** and **3d** prepared by the reaction of 1,3,5-trichloro-2,4,6-triazine with PEG200 (**2a**), PEG400 (**2b**), PEG600 (**2c**) and PEG1000 (**2d**), respectively. Dye fixation was >97%. Evidence for the covalent bond between the crosslinking dye and the fibre by the crosslinker was given by Fourier transform infrared spectra (FTIR) and extraction with DMF/water (1:1).

Experimental

Materials

Desized, scoured and bleached 100% cotton (120 g/m^2) and crepe de Chine silk (90 g/m^2) were used throughout the study. 1,3,5-Trichloro-2,4,6-triazine was an industrial product purified by sublimation. PEG200, PEG400, PEG600 and PEG1000 were dehydrated by the method of azeotropic distillation with 2-butanone. All other chemicals were analytical grade quality (Shenyang Chemical Reagent Factory, Liaoning, China).

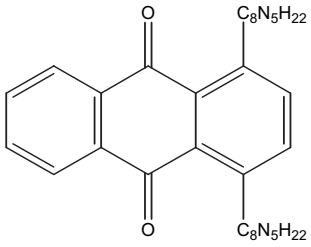
FTIR were measured with NEXUS FTIR spectrophotometer (Nexus, Nicolet, USA). Mass spectra (MS) were determined using a HP1100 system of high-performance liquid chromatography/MS with the atmospheric pressure chemical ionisation (APCI) technique.

Dye

The polyethylene polyamine dye ($\lambda_{max} = 602$ nm in water) was prepared by the reaction of tetraethylene pentamine with 1,4-dihydroxyanthraquinone as described by Murdock [8]. The structure of the blue polyethylene polyamine dye is shown as structure **1**.

Synthesis of crosslinkers

A 500 ml three-necked flask was charged with 1,3,5-trichloro-2,4,6-triazine (31.0 g, 0.168 mol), PEG200 (**2a**; 16.0 g, 0.080 mol), sodium carbonate (8.5 g, 0.08 mol), anhydrous sodium sulphate (5.0 g, 0.035 mol) and 250 ml tetrahydrofuran (Scheme 1). The temperature was kept at 10 °C. The reaction termination was determined



1

by thin layer chromatography (Silica G; acetone–water, 1:1 v/v; R_f of **a** = 0.51; R_f of PEG200 = 0.72). When the reaction was completed, the resulting slurry was filtered, and tetrahydrofuran was removed by vacuum. The resultant filtrate was filtered again to give **3a** (38.1 g) in 96.0% yield. Compounds **3b**, **3c** and **3d** were prepared in the same way in 93.7%, 90.4% and 80.0% yield, respectively.

Crosslinking dyeing process

Dyeing with the blue tetraethylene pentamine dye on cotton and silk was carried out by use of a 'two-dip-two-nip' operation at room temperature. The fibre was dipped in the dyebath containing 3% (w/w) blue polyamine dye at a liquor-to-goods ratio of 20:1 for 3 mins and nipped with 70% wet pick-up. After the dyed fibre had been dried at room temperature, it was dipped into the crosslinking bath for another 3 min and nipped once with approximately 70% wet pick-up. Then the fibre was heated in an oven for 10 min and then soaped using 2 g/l anionic detergent (sodium dodecyl benzene sulphonate; 10 min, 100 °C), washed and air-dried. Finally, the soaped fibre was treated with DMF/water (1:1) at the boiling temperature to prove the formation of the dye–crosslinker–fibre bond.

Measurement of dye fixation

The fixation of the blue polyamine dye was calculated first by determining the reflectance (R) of the dyed samples at the wavelength of maximum absorption on a Pye-Unicam SP8400 spectrophotometer (Pye-Unican, Cambridge, UK). The colour yield (K/S) was calculated according to the Kubelka–Munk equation (Eqn 1). K/S values were measured twice: before soaping [$(K/S)_b$] and after the soaping treatment [$(K/S)_a$]. Percentage fixation (F) of the dye was calculated using Eqn 2.

$$K/S = (1 - R)^2/2R \quad (1)$$

$$F(\%) = [(K/S)_a/(K/S)_b] \times 100 \quad (2)$$

Fastness testing

The colour fastness of the dyed fabrics was tested according to Chinese standard methods including fastness to washing [GB/T 3921-97] and rubbing [GB/T 3920-97].

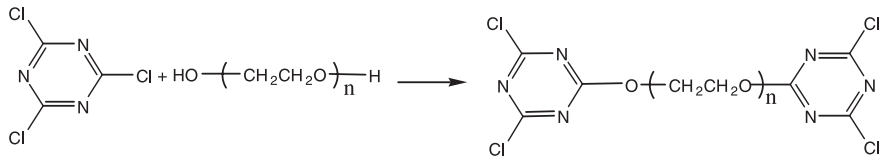
Results and Discussion

Structure confirmation of a, b, c and d

Infrared spectra of **3a**, **3b**, **3c** and **3d** exhibit the typical bands of $\nu_{C=N}$ at 1545 and 1510 cm^{-1}, ν_{C-Cl} at 806 cm^{-1} in the 1,3,5-trichloro-2,4,6-triazine ring, and stretching bands of ν_{C-O-C} for etheric group at 1105 and 1053 cm^{-1}. The disappearance of the band above 3000 cm^{-1} indicates that there is no hydroxy group in the crosslinkers molecules. MS (APCI) spectrum of **3a**, as an example, gives a correct series of quasimolecular ion peaks ($M + H^+$) at m/z 357, 401, 445, 489, 533, 577, 621, which obey the rule of $[(312 + 44 \times n) + 1]$. Therefore, the structure of the kind of crosslinker was confirmed.

Dye–crosslinker–fibre covalent bond

The crosslinking dye was attached to the fibre by non-covalent interaction such as hydrogen bond, salt bridge and van der Waal's forces before the crosslinking dyeing process, which are not strong enough to fix the dye to the fibre. As illustrated in Figures 1 and 2, the fixation on cotton and silk was only about 20% with zero crosslinker usage, moreover when the concentration was 2%, the fixation was >99%. The dyed–cured fibre was soaped for 10 min (100 °C) and subsequently treated with DMF without bleeding. The FTIR spectrum of the dyed cotton show a weak peak at about 1600 cm^{-1}, which is the typical band of the anthraquinone ring in the dye; the spectrum of the crosslinking dyed cotton exhibits a weak peak at 1559 cm^{-1} assigned to the typical band of s-triazine ring. Their weakness might result from the fact that the amount of the dye and crosslinker is relatively small in comparison with the amount of glucose residues in cellulose. Also, for the same reason, the peaks of the covalent bonds between the crosslinker and the amino groups of the dye or the hydroxy groups of cellulose



a PEG200
b PEG400
c PEG600
d PEG1000

2a–d **3a–d**

Scheme 1

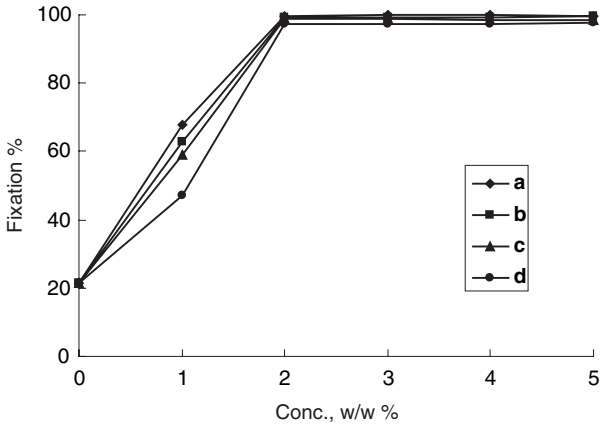


Figure 1 Effect of concentrations of crosslinking agents **3a–d** on fixation on cotton; crosslinking bath, pH 8.0, the fabric was cured at 60 °C/10 min

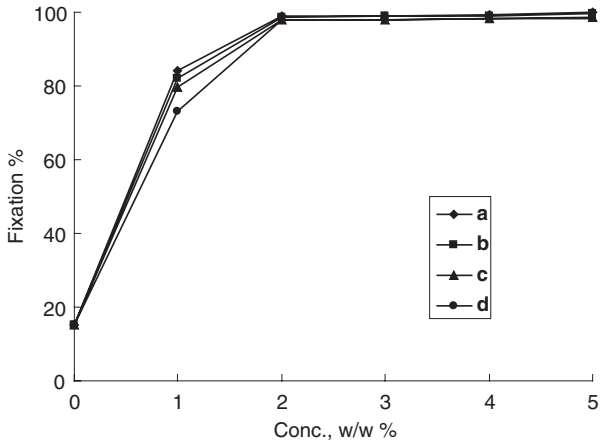


Figure 2 Effect of concentrations of crosslinking agents **3a–d** on fixation on silk; crosslinking bath, pH 8.0, the fabric was cured at 60 °C/10 min

could not be observed in the spectra. Although the spectra could not directly prove the covalent bond the dye, crosslinker and fibre, the existence of the typical band of an s-triazine ring in the crosslinker after bleeding with DMF/water gives evidence indirectly that a covalent bond formed between the tetraethylene pentamine crosslinking dye and fibre after the crosslinking dyeing process.

Effect of chain length of PEG on fixation

The effect of the chain length of PEG on fixation is shown in Table 1. The results indicate that the fixation decreased slightly with an increase in the chain length of PEG. This may be due to two main reasons: one is that with the increase of chain length of PEG, the formula weight of the crosslinker also increases, which results in a decrease in molecular numbers of crosslinker of a certain weight. The other reason is that the variety of PEG results in a difference in the water solubility of different crosslinkers because the hydrophilic chain length of PEG can increase the water solubility, which can be indicated by the hydrophilic–lipophilic balance (HLB) values (Table 1), i.e. **3a** did not have good water solubility, but **3b**, **3c** and **3d** possessed good water solubility. Although water solubility increased with increasing chain length of PEG, the yield of preparation and dye fixation decreased slightly. Compared with the others, **3b** showed excellent water solubility, yield and dye fixation. Therefore, some crosslinking dyeing factors were investigated using **3b** as an example.

Table 1 Fixation, hydrophilic–lipophilic balance (HLB) values and yields of the crosslinkers **3a–d**

Crosslinker	Cotton (*F* %)	Silk (*F* %)	HLB value	Yield
3a	99.3	99.5	8.0	96.0
3b	99.1	99.4	11.4	93.7
3c	98.3	98.8	13.3	90.4
3d	97.1	98.2	15.4	80.0

Effect of concentration of crosslinker on fixation

The results obtained for the effect of the concentrations of crosslinker on cotton and silk are illustrated in Figures 1 and 2, which shows that the concentration of crosslinker has a large effect on the fixation of the dye. High fixation was obtained when the concentrations were greater than 2% (w/w). At concentrations less than 2% (w/w), the amount of crosslinker molecules was not enough to complete the crosslinking reaction between the dye and the fibre, therefore the fixation was lower than 97%. At concentrations over 2% (w/w), the amount of crosslinker molecules was enough to fully complete the crosslinking reaction, so high fixation levels were obtained.

Effect of cure temperature on fixation

The results of the dye fixation with varying cure temperature using **3b** as an example are shown in Table 2. The results show that fixation is over 99% when a cure temperature of 60 °C was used. This might be attributed to the reactivity of the crosslinker, because the reaction temperature of the second chloro group of 1,3,5-trichloro-2,4,6-triazine ring is about 50 °C. At lower temperature, the crosslinker might react with the amino group in the dye, but could not react with the hydroxy group in the fibre, which led to lower fixation. On the contrary, when the cured temperature was above 50 °C, the second chloro group would react fully, even a part of the third chloro group would be activated to react with the dye and the fibre, thereby higher fixation was obtained.

Table 2 Effect of cured temperature of **3b** on fixation[a]

Cure temperature (°C)	Cotton (*F* %)	Silk (*F* %)
20	55.6	67.2
40	94.9	96.0
60	99.1	99.4
80	99.3	99.4
100	99.3	99.5

a Crosslinking bath contained 3% (w/w) **3b**, pH 8.0, the fabric was cured for 10 min

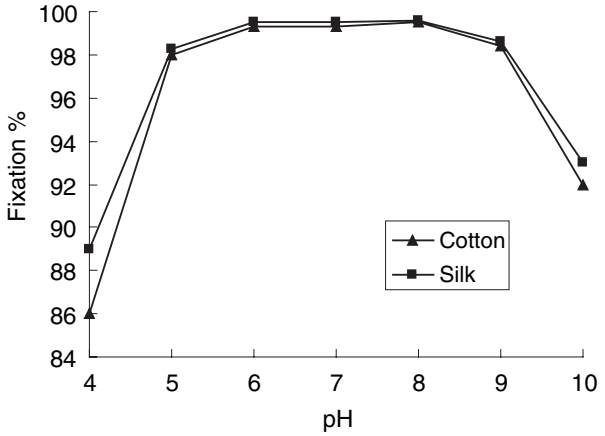


Figure 3 Effect of pH value of **3b** on fixation

Effect of pH of crosslinker bath on fixation

The effect of the pH of the crosslinker bath, using crosslinker **3b**, on fixation is illustrated in Figure 3. The results show that the fixation on cotton and silk is greatest from a neutral or nearly-neutral solution, while acidic and basic conditions hinder the crosslinking reaction and result in lower levels of fixation. The amino groups of tetraethylene pentamine could form ammonium groups in acidic condition, so electrophilic reaction could not take place between the dye and the crosslinker. In addition, ammonium groups give the dye excellent water solubility making it difficult to absorb on the fabric; although alkaline conditions could promote the nucleophilic substitution of the crosslinker with the dye and fibre, it could also accelerate the hydrolysis of crosslinker molecules.

Fastness properties

The fastness to washing and rubbing was evaluated for the crosslinked dyed samples. The results in Table 3 indicate that all the samples show excellent fastness to washing and their rubbing fastness is also as good as that achieved by conventional reactive dyeing. However, there was a trend that the fastness became slightly worse with an increase in the chain length of the crosslinker.

Conclusions

Crosslinkers were prepared by the reaction of 1,3,5-trichloro-2,4,6-triazine with PEG. Their structures were confirmed by FTIR and MS.

Table 3 Fastness properties of the tetraethylene pentamine dye

Crosslinker	**3a**		**3b**		**3c**		**3d**	
Fibre:	Cotton	Silk	Cotton	Silk	Cotton	Silk	Cotton	Silk
Washing fastness								
Change	5	5	4–5	5	4–5	5	4–5	4–5
Stain	4–5	5	5	4–5	5	4–5	4–5	5
Rubbing fastness								
Dry	5	5	4–5	4	4	4	3–4	3
Wet	4	4	3	3–4	3	3–4	3	3–4

The crosslinkers linked a tetraethylene pentamine crosslinking dye to cotton and silk in a crosslinking dyeing process. It was found that, under the optimum conditions (pH 8.0, conc. 2% and cure temperature 60 °C) the dye fixation reached, 99.8%, 99.5%, 98.6% and 97.8% on cotton and 99.9%, 99.6%, 98.7% and 98.3% on silk for crosslinkers **3a**, **3b**, **3c** and **3d**, respectively. The wash fastness of the crosslinked dyed samples was excellent and the rub fastness was also satisfactory. All the data demonstrated that this kind of crosslinker, especially **3b**, can be employed for crosslinking dyeing.

The fact that the crosslinking dyed fibre was fast to DMF/water (1:1) extraction, and the FTIR spectra indicated that a covalent bond formed between the dye and the fibre by the crosslinker.

Acknowledgement

The authors are grateful to the National Natural Science Foundation of China for financial support (No. 20276009).

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