

Improved Fixation of Dyes on Polyamide Fibres. Part 3: Using 2-Chloro-4,6-di(aminobenzene-4'-vinylsulphone)-s- Triazine [XLC-VS] as an After-Treatment of Nucleophilic Aminoalkyl Dyes

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ABSTRACT

A mono-aminoalkyl-s-triazine polysulphonated dye was used as a model nucleophilic dye. When applied to nylon 6,6 this dye gave good uptake under mildly acidic conditions but, as expected, no covalent bonding was observed. When such dyeings were after-treated with anionic dispersions of the specially synthesised, fibre substantive, cross-linking agent, 2-chloro-4,6-di(aminobenzene-4'-vinylsulphone)-s-triazine [XLC-VS], a very significant degree of covalent bonding was achieved.

1 INTRODUCTION

The use of crosslinking agents to modify the reactive dyeing properties of nylon 6,6 was described by the present authors in Parts 1 and 2 of this series.^{1,2} Part 1 studied the use of triacroylamino-hexahydro-s-triazine (FAP) as the crosslinker and Part 2 employed a more substantive agent, 2-chloro-4,6-di(aminobenzene-4'- β -sulphatoethylsulphone)-s-triazine (XLC).

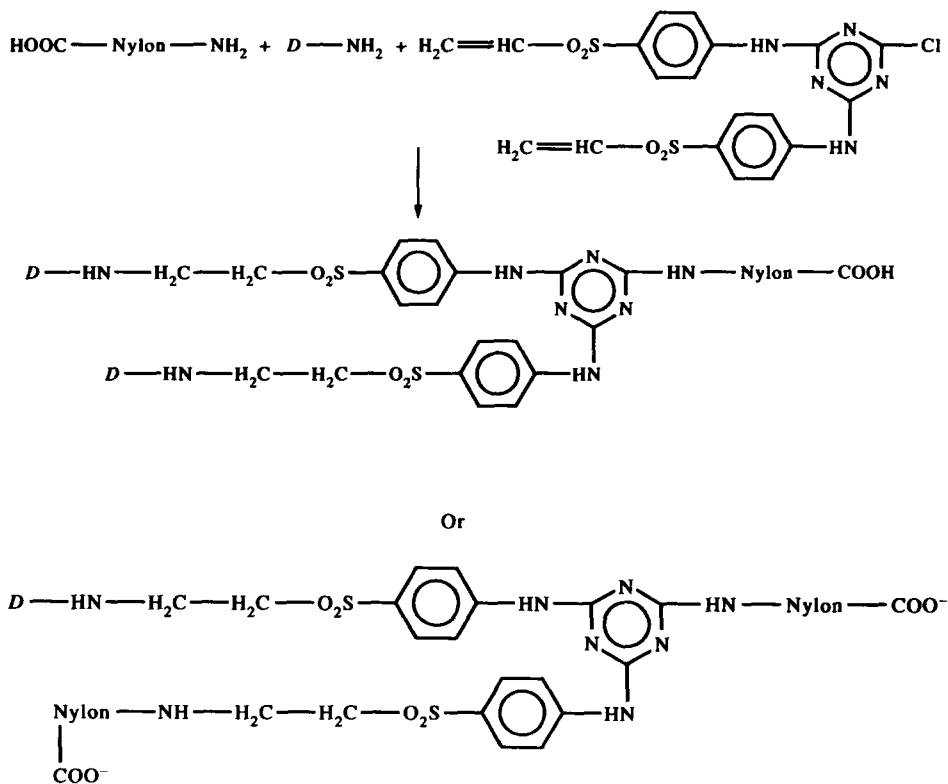
Part 2 of this series² showed that, as expected, nylon which had been pre-treated with XLC was hardly dyeable with a sulphonated reactive dye under pH 4, 5, and 6 conditions, showing poor exhaustion and fixation compared with untreated nylon. It was also demonstrated that XLC treatment of nylon produced a modified nylon which dyed well and underwent

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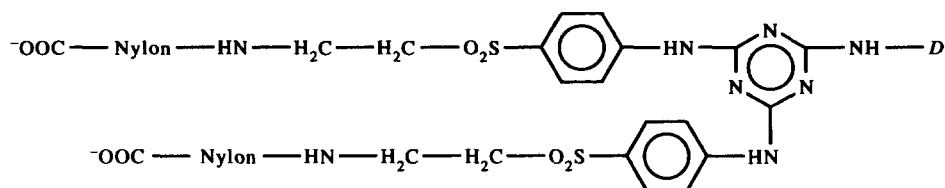
covalent fixation with an aminoethyl dye prepared from the reaction of ethylenediamine with CI Reactive Red 3. XLC treatment followed by an ammonia treatment gave a nylon which showed good exhaustion and fixation when dyed with unmodified CI Reactive Red 3. XLC is a masked vinylsulphone derivative which forms the free reactive vinylsulphone by β -elimination of the sulphato group; this reaction occurs in the presence of alkali or on boiling in neutral aqueous solutions.

In the present study the above amino-ethyl anionic dye was first dyed on nylon and then after-treated with a dispersion of the activated vinylsulphone form of XLC (XLC-VS).

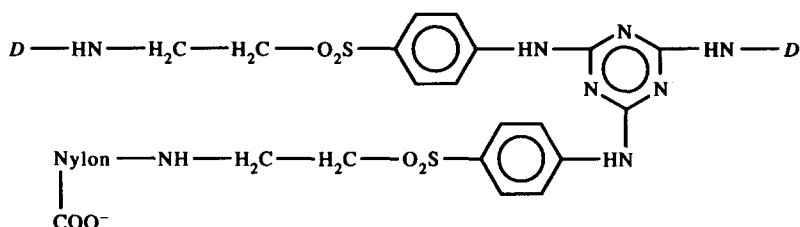
XLC-VS is a bifunctional vinylsulphonyl derivative; it contains two double bonds, activated by strongly electron-withdrawing sulphone groups, which are more reactive towards nucleophiles than the acrylamido residues in FAP.¹ Furthermore, XLC-VS also contains one mono-chloro-triazine reactive group which is less reactive than the vinylsulphonyl residue. The compound thus contains reactive groups of different reactivity. The desired products of reaction of XLC-VS with the aminoethyl anionic dye and nylon fibre may be summarised by the following scheme:



Or



Or



2 EXPERIMENTAL

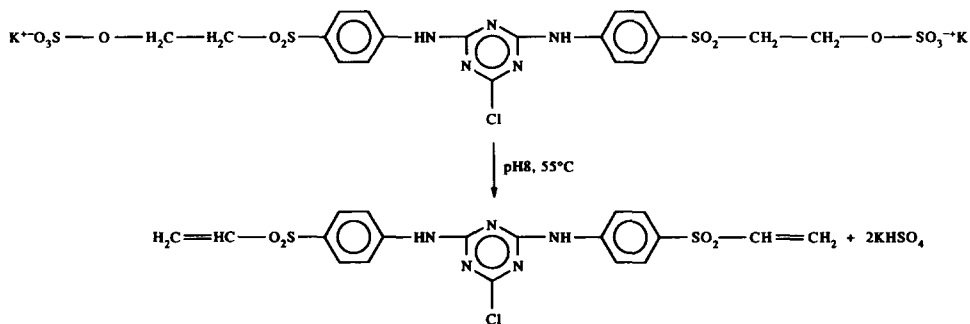
2.1 Dyes

The aminoethyl-amino triazinyl dye was prepared by the reaction of CI Reactive Red 3 (monochlorotriazine derivative) with ethylene diamine as described previously.¹

2.2 Synthesis of XLC-VS

XLC (2.5 g), prepared as previously described,² was dissolved in water (150 ml) and sodium carbonate was added to raise the pH value of the mixture to 8. The temperature of the mixture was then maintained at 55°C and further aqueous sodium carbonate (0.5N) was added portionwise until the pH value remained constant at 8. The solution was then stirred for a further 1 h and after cooling to room temperature, the white solid which precipitated was filtered and dried at 40°C (yield 2.16 g).

The reaction scheme may be written:



2.3 Preparation of dispersion of XLC-VS

XLC-VS (5 g), dispersing agent (Matexil DA-AC) (1 g), and water (94 ml) were added to a milling bottle which also contained milling balls. The bottle was then placed on the rollers of a laboratory milling machine and rotated for 2 h at 180 revs/min.

2.4 IR analysis

IR analyses of XLC and XLC-VS were carried out using the Perkin Elmer 1740 Fourier Transform Infrared Spectrometer. Samples were prepared by mixing 1 mg of the sample in 200 mg of potassium bromide (KBr).

2.5 HPLC analysis

XLC and XLC-VS were analysed using a Varian 5000 Liquid Chromatograph, separating on an Apex octadecyl (C18) column. The mobile phase used in this analysis was a mixture of water/methanol, which also contained 0.001 mole of tetrabutylammonium bromide as an ion-pairing reagent and 0.5 ml litre⁻¹ of 20% (w/w) acetic acid and 0.5 ml litre⁻¹ of 5% (w/w) of potassium hydroxide as a buffer.

Flow: 0.9 ml⁻¹ min; detector wavelength setting: 290 nm; eluent composition: water/methanol (gradient elution); temperature: 20°C.

T(min)	A% (water)	B% (methanol)
0.0	70	30
3.0	70	30
5.5	45	55
8.5	45	55
11.0	20	80
16.0	70	30

2.6 Measurements of dye exhaustion

The uptake of dye was measured by sampling the dyebath before and after the dyeing process. The absorbance of the diluted dye solution was measured at the wavelength of maximum absorption of the dye using a UV-visible spectrophotometer (KONTRON UVIKON 860). Dyebath exhaustion was calculated using the following equation:

$$\text{Exhaustion} = 100(1 - A_1/A_0)\%$$

A_0 , A_1 = Absorbance of dye solution before and after the process, respectively.

2.7 Measurement of dye fixation

Measurement of the extent of dye-fibre covalent bonding or dye fixation was carried out by stripping any unfixed dye from the dyed material using 25% (v/v) pyridine/water (100°C, LR=20:1). The dyed fabric sample was repeatedly extracted with fresh pyridine/water for 3 min until all the unfixed dye had been stripped (a colourless extract was obtained). The combined extracts were collected and diluted to 1000 ml and the solution absorbance then measured spectrophotometrically at λ_{\max} . Fixation (F) was expressed as the percentage of dye not removed from the dyed fibre by the extraction procedure.

An alternative meaning of the term 'fixation' is sometimes used, which refers to the amount of original dye taken which is covalently bonded. This overall fixation efficiency (T) is related to (F) (exhausted dye fixed) by the equation:

$$\%T = (\%F \times \%oE)/100.$$

3 RESULTS AND DISCUSSION

3.1 Analysis of XLC-VS

Figures 1 and 2 show the FTIR spectra of the parent XLC and XLC-VS. Comparing the two spectra, the disappearance of the XLC absorbance at 1247, 1050, and 1040 cm^{-1} indicates that the $-\text{O}-\text{SO}_3$ bond has been removed. The peaks at 1148 and 803 cm^{-1} are from the SO_2 and C-C1 absorption. The new peak in the XLC-VS spectrum at 988 cm^{-1} is attributed to the C=C bond.

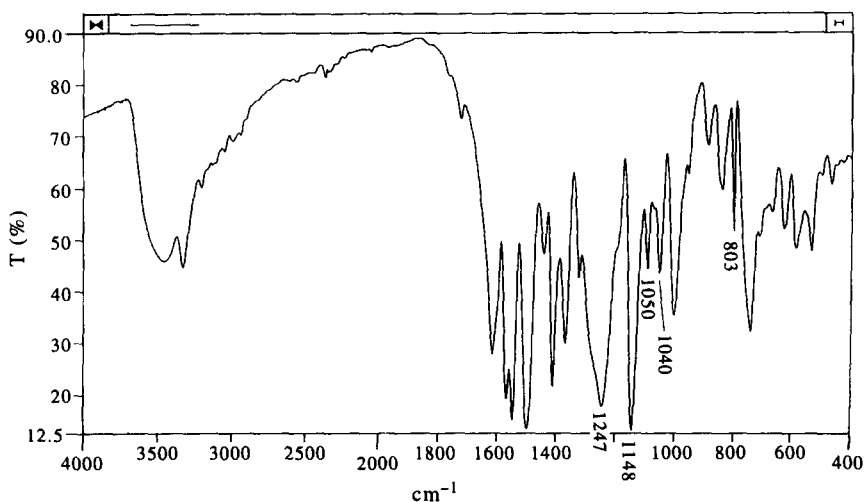


Fig. 1. FTIR spectrum of XLC (KBr disc).

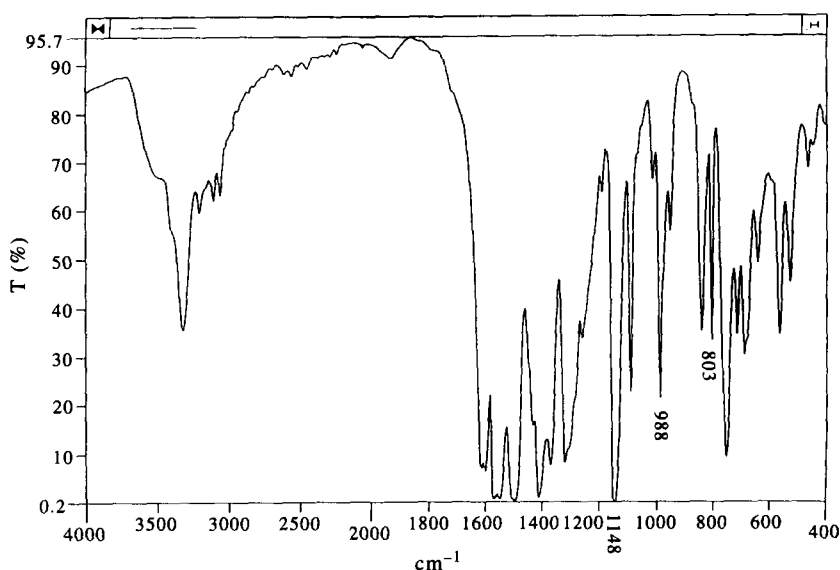


Fig. 2. FTIR spectrum of XLC-VS (KBr disc).

Figures 3 and 4 show the HPLC analysis printouts of the XLC-VS synthetic procedure, after pH 8 reaction at 55°C for 0, 20, 60 and 180 min. Peak 1 is attributable to XLC, peak 2 to XLC-mono-VS, and peak 3 to XLC-di-VS (XLC-VS).

Elemental analysis of XLC-VS gave the following result:

Found: C, 45.6%; N, 14.0%; H, 3.2%; S, 12.75%; Cl, 7.6%.
 Calc.: C, 46.7%; N, 14.7%; H, 3.4%; S, 13.20%; Cl, 7.4%.

3.2 Exhaustion of aminoethyl anionic dye on nylon followed by XLC and XLC-VS after-treatment

Dyeing was carried out at pH 4 and pH 5 for 1 h at the boil using a 20 : 1 liquor-to-goods ratio employing a 2% owf shade. Then, 3% owf of XLC or XLC-VS (dispersion) was added to the dyebath at the boil and the process was continued for a further 30 min (Scheme 1). Table 1 gives the results from this experiment.

From the results in Table 1, it can be seen that the dye exhaustion decreased significantly when XLC was added. Treatment with XLC for a further 30 min at the boil at either pH 4 or pH 5 did not produce appreciable amounts of the vinylsulphone form, and it was thus concluded that under these pH conditions the group most likely to be involved in reaction

Chemical reaction scheme showing the synthesis of a polymeric product. The starting material is a bis-phenol derivative with a central triazine ring substituted with a chlorine atom. This reacts with a diamine derivative (NH₂-CH₂-CH₂-NH-) and a triazine derivative (N-phenyl-1,3,5-triazine-2,4,6-triamine) in the presence of a base (D) and a sulfonate group (SO₃⁻). The product is a polymer chain where the central triazine ring is substituted with an amino group (-NH-CH₂-CH₂-NH-) and a phenyl group (-C₆H₅).

XLC-VS additions also had the effect of reducing dye exhaustion by 20–25%; this could be attributed to its reaction with amino sites in nylon, thus reducing the substantivity of the previously absorbed aminoethyl dye.

The effect of using different dyeing procedures was also investigated. Dyeing (2% dye owf) was carried out at different pH values for 1 h at the boil using a 20 : 1 liquor-to-goods ratio. Then, 3% owf of XLC-VS (dispersion) was added to the dyebath at the boil and dyeing was continued for various times up to 60 min without changing pH. Table 2 gives the results of this experiment.

3.4 Effect of the fixation pH on aminoethyl anionic dye fixation

Nylon was dyed with 2% owf aminoethyl anionic dye at pH 4 and pH 5 for 1 h at the boil using a 20 : 1 liquor-to-goods ratio. The dyeing profile shown in Scheme 2 was used and Table 3 gives the exhaustion/fixation results.

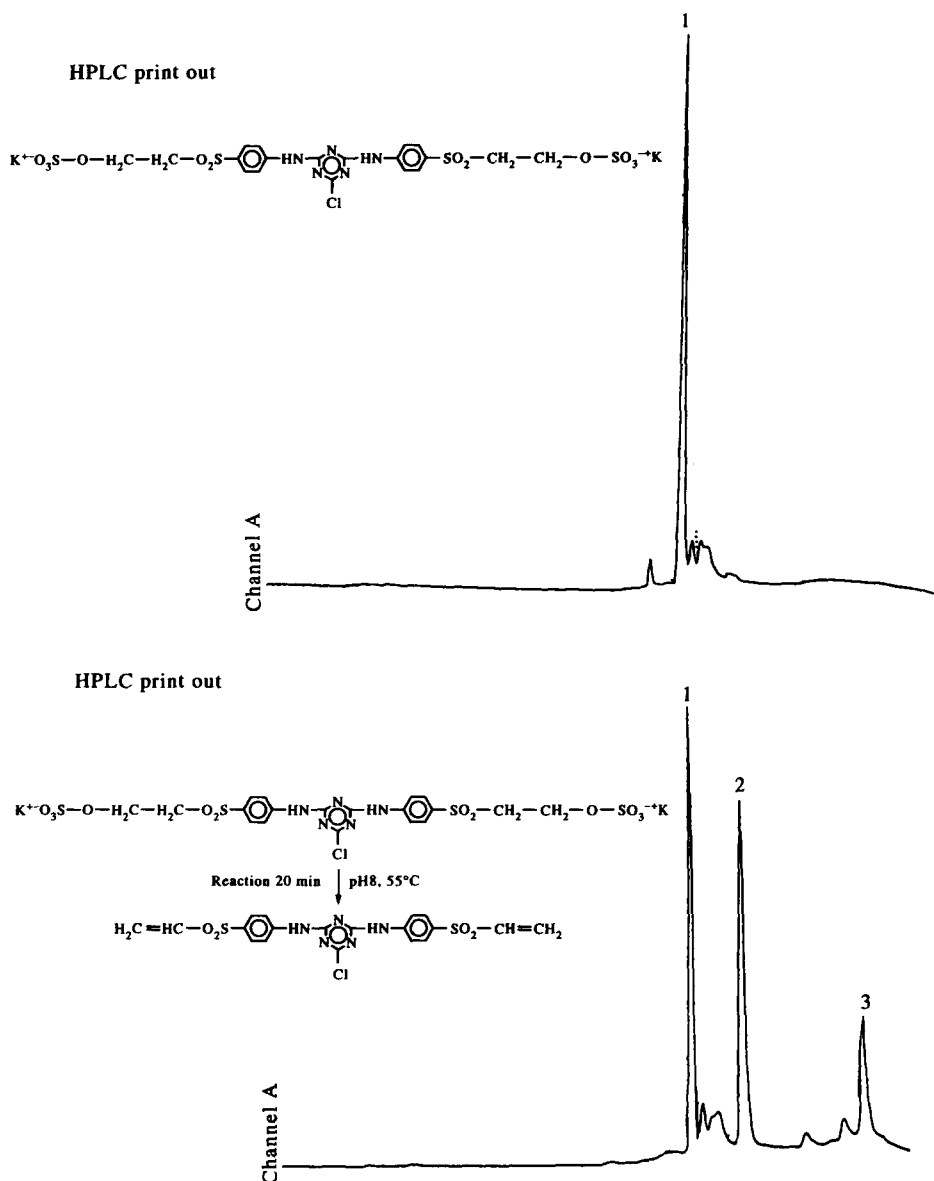


Fig. 3. Peak 1 is attributable to XLC, retention time is 11.11; peak 2 to XLC-mono-VS, retention time is 13.50; and peak 3 to XLC-di-VS (XLC-VS), retention time is 15.60.

The results shown in Table 3 indicate that good fixation values are achieved when using XLC-VS at pH 7 and higher. It should be noted that under weakly acidic to alkaline conditions XLC-VS has good substantivity for nylon² and this clearly is important in determining its effectiveness as a dye-fibre crosslinking agent. However, above pH 5 the substantivity of the

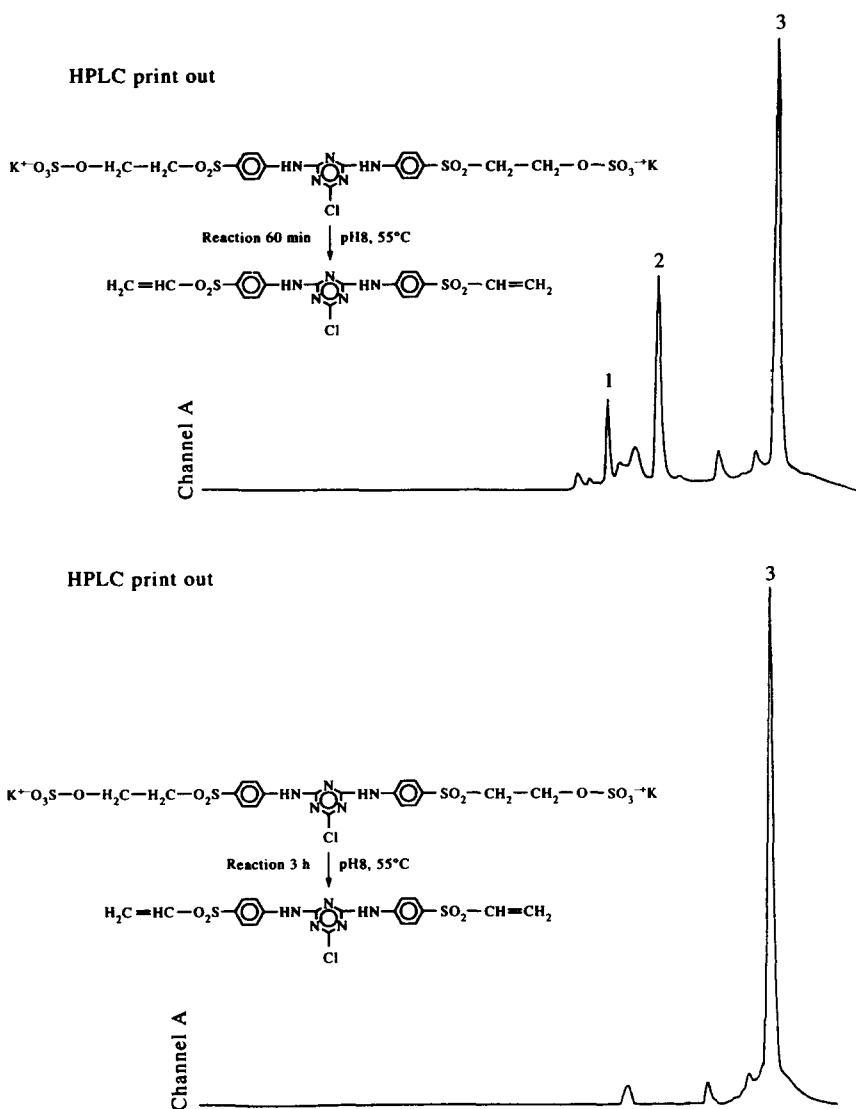
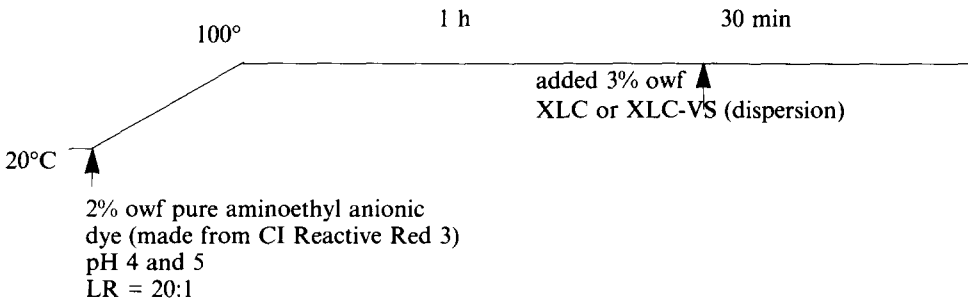


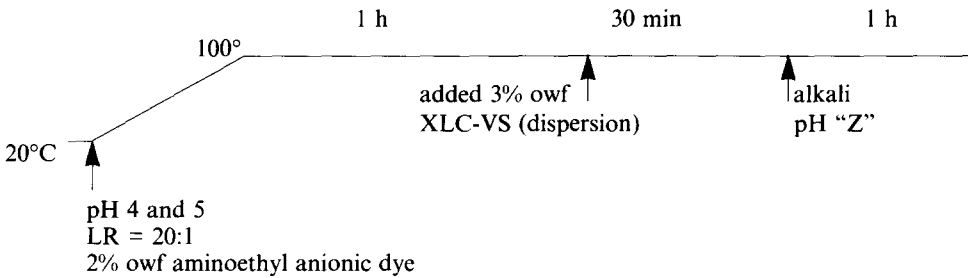
Fig. 4. Peak 1 is attributable to XLC, peak 2 to XLC-mono-VS, and peak 3 to XLC-di-VS(XLC-VS).

sulphonated aminoethyl anionic dye for nylon decreases greatly with increasing pH and, hence there are two opposing trends, viz.

- higher reactivity due to increased nucleophilicity of amino groups in the dye and the fibre at pH ≥ 7 ;
- reduced anionic dye substantivity at pH ≥ 5 leading to some dye desorption.



Scheme 1.



Scheme 2.

TABLE 1
Nucleophilic Dye Exhaustion and Fixation, With and Without Crosslinker Additions

<i>pH</i>	<i>No crosslinker</i>		<i>XLC addition</i>		<i>XLC-VS (dispersion) addition</i>	
	<i>E%</i>	<i>F%</i>	<i>E%</i>	<i>F%</i>	<i>E%</i>	<i>F%</i>
4	97.5	4.0	58.0	36.3	78.7	48.7
5	92.1	3.0	49.1	45.9	66.1	49.5

E = Exhaustion, *F* = Fixation.

TABLE 2
Effect of Bath pH and XLC-VS After-treatment Time on Exhaustion/Fixation Values of the Nucleophilic Dye

<i>pH</i>	<i>After-treatment time (min)</i>	<i>E%</i>	<i>F%</i>
4	30	78.7	48.7
4	60	76.4	44.9
5	30	66.1	49.5
5	60	61.6	46.8

TABLE 3

Effect of Dyebath pH and After-treatment pH on Exhaustion/Fixation Values of the Nucleophilic Dye

<i>Initial pH</i>	<i>Fixation pH value 'Z'</i>	<i>E%</i>	<i>F%</i>
4	6	73.3	90.9
4	7	71.9	94.7
4	8	64.6	94.5
5	6	64.4	90.2
5	7	61.2	95.8
5	8	55.6	94.9

3.5 Effect of XLC-VS fixation duration on dye fixation

The nylon fibre was dyed at pH 4 and pH 5 with 2% owf pure aminoethyl anionic dye and fixed using 3% owf XLC-VS. After the XLC-VS dispersion addition, the dyebath pH value was adjusted from 4 or 5 to 7 by the addition of NaHCO_3 and dyeing was continued for different lengths of time; the exhaustion/fixation results are given in Table 4.

From the results in Table 4, it can be seen that the dye exhaustion decreased and fixation increased slightly as the fixation time increased from 30 min to 60 min. Owing to the high reactivity of XLC-VS, 30 min is sufficient to complete the reaction at pH 7.

3.6 Effect of XLC-VS concentration on aminoethyl anionic dye fixation

Dyeing was carried out at pH 5 for 1 h at the boil; different XLC-VS concentrations were then added from dispersion to the dyebath and dyeing was continued for a further 30 min at the boil; the dyebath pH was then adjusted to 7 with NaHCO_3 and another 30 min at the boil completed the dyeing process; the experimental results are given in Figs 5 to 9. Figure 10 shows the

TABLE 4

Effect of XLC-VS After-treatment (Fixation) Time on Exhaustion/Fixation

<i>Initial pH</i>	<i>Fixation time at pH 7 (min)</i>	<i>E%</i>	<i>F%</i>
4	30	73.5	92.1
4	60	71.7	94.7
5	30	68.3	92.3
5	60	61.2	95.8

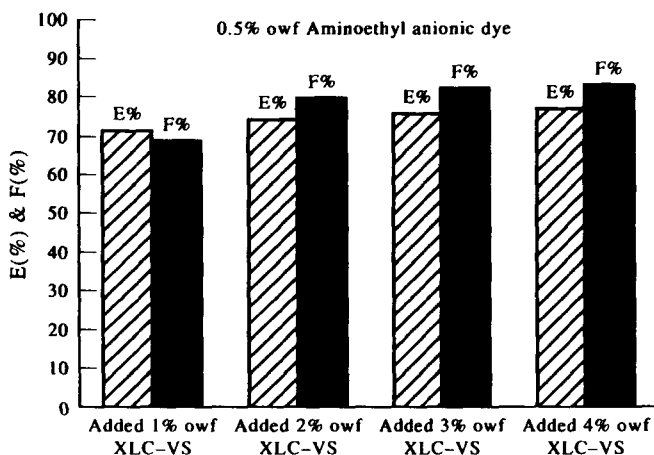


Fig. 5. Effect of dye and XLC-VS concentration on dye exhaustion (E%) and fixation (F%).

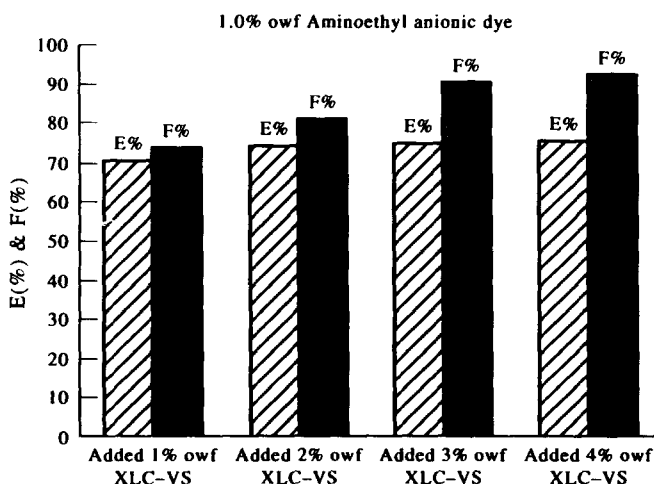


Fig. 6. Effect of dye and XLC-VS concentration on dye exhaustion (E%) and fixation (F%).

exhaustion and fixation values when no XLC-VS was added to the dyebath using the above conditions but without adjusting the pH to 7.0 (in the absence of crosslinker, raising the pH to 7.0 resulted in excessive dye desorption).

4 CONCLUSIONS

The substantive crosslinking agent, XLC-VS (dispersion), was prepared and used to covalently fix an aminoethyl anionic dye to nylon by an aftertreatment procedure. The optimised aminoethyl anionic dye plus XLC-VS

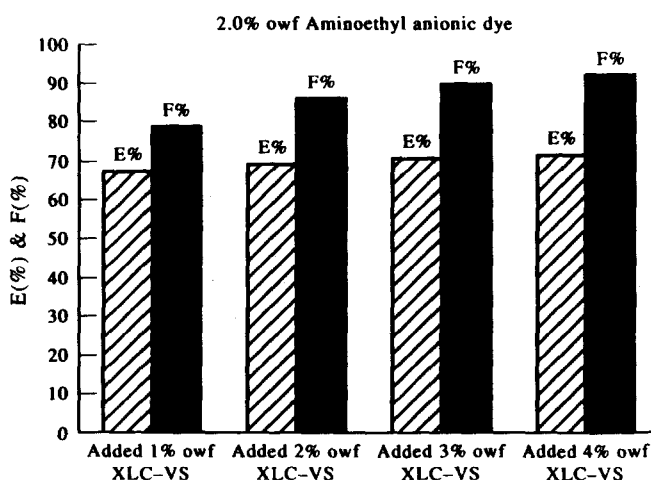


Fig. 7. Effect of dye and XLC-VS concentration on dye exhaustion (E^0) and fixation (F^0).

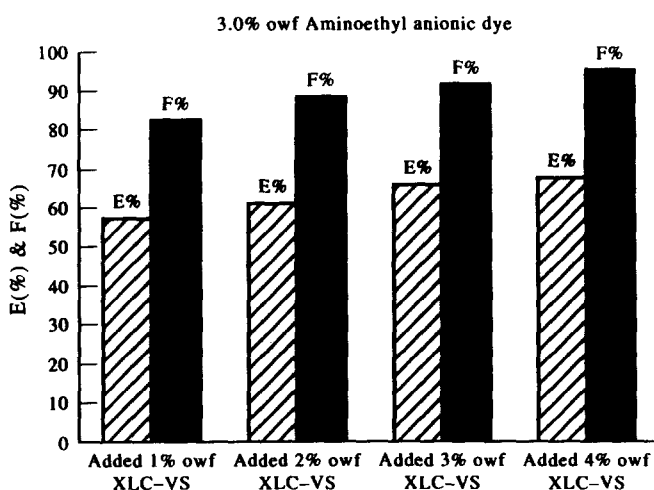


Fig. 8. Effect of dye and XLC-VS concentration on dye exhaustion (E^0) and fixation (F^0).

(dispersion) method involved an initial boiling application of the aminoethyl anionic dye at pH 5 followed by two separate steps of addition of (i) XLC-VS (dispersion) and (ii) alkali. Good fixation values were achieved when using XLC-VS (dispersion) at pH 7 and higher. It was shown that under weakly acidic to alkaline conditions, XLC-VS (dispersion) had good substantivity for nylon, and this clearly is important in determining its effectiveness as a dye-fibre crosslinking agent. However, the substantivity of the sulphonated aminoethyl anionic dye for nylon decreased greatly with increasing pH; hence there are two opposing trends: (i) higher reactivity due to increased

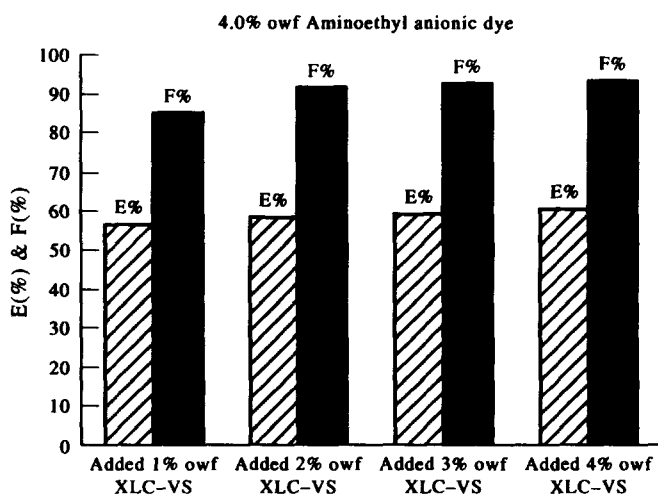


Fig. 9. Effect of dye and XLC-VS concentration on dye exhaustion (E%) and fixation (F%).

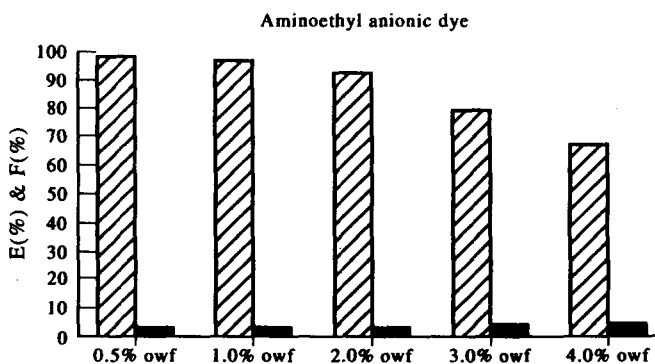


Fig. 10. Effect of aminoethyl anionic dye concentration on dye exhaustion (E%) and fixation (F%).

nucleophilicity of the amino groups in the dye and the fibre at $\text{pH} \geq 7$ and (ii) reduced anionic dye substantivity at $\text{pH} \geq 5$ leading to dye desorption and lower exhaustion values.

A solution to this problem would be to employ cationic aminoethyl dyes which would show increased substantivity on making the dyebath weakly alkaline; this approach will be the subject of Part 4 of this series.

REFERENCES

1. Ho, Y.-C. & Lewis, D. M., *Dyes and Pigments*, **26** (1995) 171.
2. Ho, Y.-C. & Lewis, D. M., *Dyes and Pigments*, **28** (1995) 237.