Dyes and Pigments, Vol. 31, No. 2, pp. 111–129, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0143-7208/96/$15.00+0.00
ELSEVIER 0143-7208(95)00099-2

Improved Fixation of Dyes on Polyamide Fibres—IV. The Use of a Nucleophilic Aminoethylsulphonyl Cationic Dye for Dyeing Nylon Followed by a Fixation Aftertreatment with 2-Chloro-4,6-di(aminobenzene-4′-sulphatoethylsulphone)-*s*-triazine [XLC]

D. M. Lewis* & Y. C. Ho

Department of Colour Chemistry and Dyeing, University of Leeds,
Leeds LS2 9JT, UK

(Received 20 September 1995; accepted 17 October 1995)

ABSTRACT

*A cationic aminoethylsulphonyl dye has been prepared by the reaction of ammonia with a vinylsulphonyl cationic dye. The result dyes nylon optimally from dyebaths set at pH > 10; addition of a substantive crosslinker, 2-chloro-4,6-di(aminobenzene-4′-sulphatoethylsulphone)-*s*-triazine [XLC], has been employed to covalently fix the dye to amine groups in the nylon fibre. Optimum exhaustion/fixation results have been achieved by dyeing at pH 10 for 1 h at the boil, adjusting the bath pH to 8, adding the crosslinker and continuing to boil for at least 1 h. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

In Parts 1–3 of this series [1–3] the authors described attempts to fix nucleophilic aminoethyl anionic dyes to nylon by crosslinking them after dyeing. The title crosslinking agent (XLC) and its bisvinylsulphone derivative (XLC-VS) were found to show high substantivity and crosslinking potential. However, the increasing desorption tendency of the anionic dye at pH values

---

* Corresponding author.

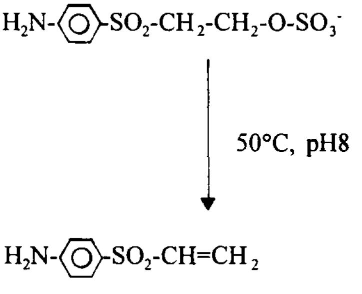
greater than 6 was seen as a clear disadvantage when using these crosslinking systems. The crosslinking systems employed (FAP, XLC and XLC-VS) showed high reactivity to amino nucleophiles only at $pH \geq 7$. It was thus decided to design nucleophilic dyes whose substantivity for nylon would increase with increasing pH; aminoalkyl dyes with pendant cationic groups were therefore targetted.

EXPERIMENTAL

Synthesis of 4-aminobenzene-vinylsulphone [4]

4-Aminobenzene-sulphatoethyl sulphone [PABSES] (0.05 mol, 14.05 g) was dissolved in water (100 ml) at room temperature with sufficient solid $NaHCO_3$ to adjust the pH to 5.5. The temperature of the mixture was then raised to 50°C, $NaHCO_3$ was added to raise the pH value of the mixture to 8, and further $NaHCO_3$ then added until the pH remained constant at 8. The mixture was stirred at 50°C for a further 30 min and, after cooling to room temperature, the solid which precipitated was collected, washed with water and dried in a desiccator under vacuum.

The reaction scheme is shown in Scheme 1.



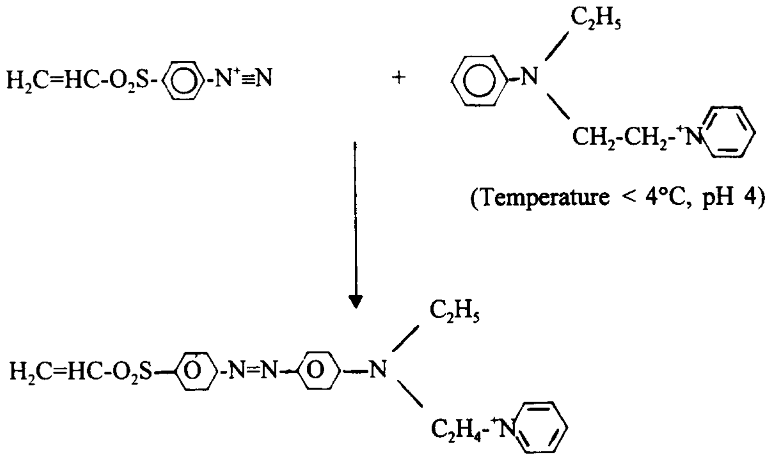
Scheme 1. Synthesis of 4-aminobenzene-vinylsulphone.

Synthesis of a cationic vinylsulphonyl dye [4,5]

4-Aminobenzene-vinylsulphone (0.05 mol, 9.15 g) was dissolved in 25 ml HCl (35%) at 0–4°C; a solution of sodium nitrite (0.05 mol) was added dropwise over 40 min. The temperature of the mixture was maintained below 4°C whilst stirring for another 30 min. Excess nitrous acid was then destroyed by addition of sulphamic acid.

N-Ethyl pyridine-*N*-ethylaniline hydrochloride (0.05 mol) was dissolved in water and cooled to 0–4°C and to this was added the above diazo solution over 30 min with stirring. The solution was stirred for another 30 min and the pH value of the solution was then raised to 4 by the addition of sodium acetate. The mixture temperature was kept below 4°C and its pH value maintained at 4. The solution was stirred for another 2 h and the dye isolated by the addition of 15 g of potassium chloride per 100 ml of solution; after being collected by filtration the dye was washed with a saturated solution of potassium chloride. The product was dried in a desiccator under vacuum.

The reaction scheme is as shown in Scheme 2.

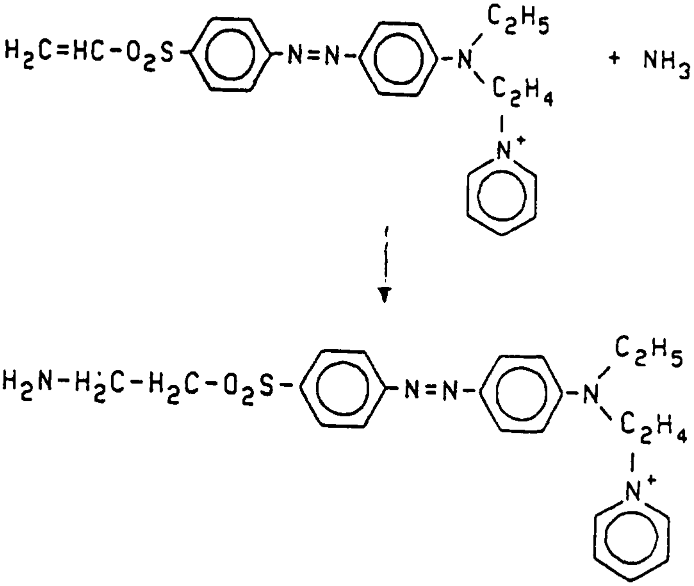


Scheme 2. Synthesis of vinylsulphone cationic dye.[4,5]

Synthesis of an aminoethylsulphonyl cationic dye

Fifty milligrams of 10 g/l ammonia ($d = 0.880$) aqueous solution was stirred and heated to 60°C; 50 ml of 5% (w/v) aqueous cationic orange vinylsulphone dye solution was added dropwise to this ammonia solution over 45 min. The mixture was then stirred for 2 h, then cooled to room temperature and the pH value of the mixture adjusted to 6 with hydrochloric acid (35%). The product was isolated by the addition of 15 g of potassium chloride per 100 ml of solution; it was then collected by filtration and washed with saturated potassium chloride solution. The product was dried at 30°C.

The reaction scheme is as shown in Scheme 3.



Scheme 3. Synthesis of aminoethyl cationic dye.

IR analysis

IR analyses of the aminoethyl cationic dye and its vinylsulphone precursor were carried out using a Perkin Elmer 1725 Fourier Transform Infrared Spectrometer. Samples were prepared by mixing 1 mg of the sample in 200 mg of potassium bromide (KBr).

HPLC analysis

XLC was analysed using a Varian 5000 Liquid Chromatograph using an Apex octadecyl C18 column as described previously [2].

Analysis by capillary electrophoresis

A Dionex Capillary Electrophoresis System 1 was used for the analysis of the aminoethyl cationic dye [6]. An uncoated silica capillary was used which had an internal diameter of 75 μm and was 58 cm in length. Samples were introduced into the capillary by gravity injection, the sample vial being elevated by 50 mm for 10 s. The buffer employed was 20 mmol/l citric acid at pH 4.5. Detection was by visible light absorbance at 450 nm. (λ_{max} of the dye).

Measurement 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 λ_{max} of the dye using a UV-visible spectrophotometer (Kontron Uvikon 860). Dyebath exhaustion was calculated using the following equation:

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

A_0 and A_1 are the absorbance of dye solution before and after the process, respectively.

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 then the solution absorbance 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 use of the term "fixation" is sometimes used which in fact refers to the amount of original dye taken which is covalently bonded. This overall fixation efficiency (T) is related to (F) (sorbed dye fixed) by the equation:

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

RESULTS AND DISCUSSION

Analysis of an aminoethyl cationic dye

Elemental analysis of the aminoethyl cationic dye, gave the following result (assuming $2Cl^-$ as the counter ions and $2H_2O$ as water of crystallization):Found: C, 49.95%; N, 11.65%; H, 6.01%.Calc.: C, 50.70%; N, 12.40%; H, 6.06%.

The CE analysis results are shown in Figs 1, 2, and 3. In CE the migration time is proportional to the mass:charge ratio. Clearly there is a big difference in migration time — the cationic orange vinylsulphone dye reaches the

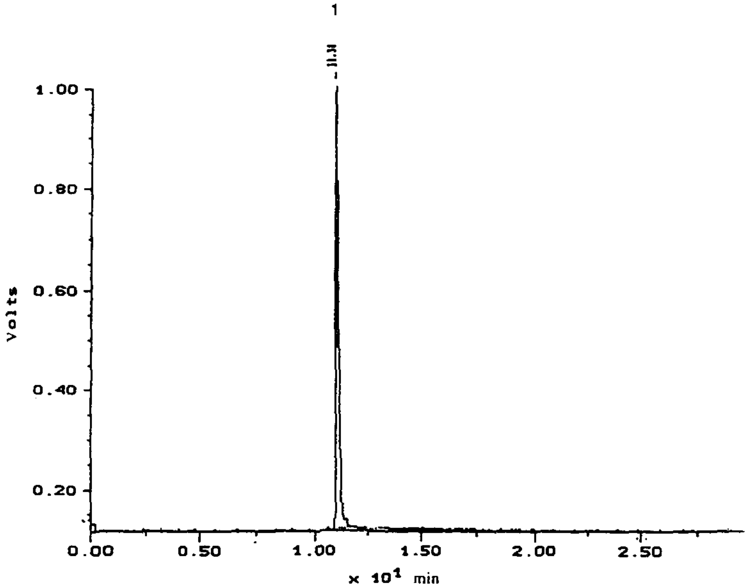


Fig. 1. CE analysis of cationic orange vinylsulphone dye (peak 1).

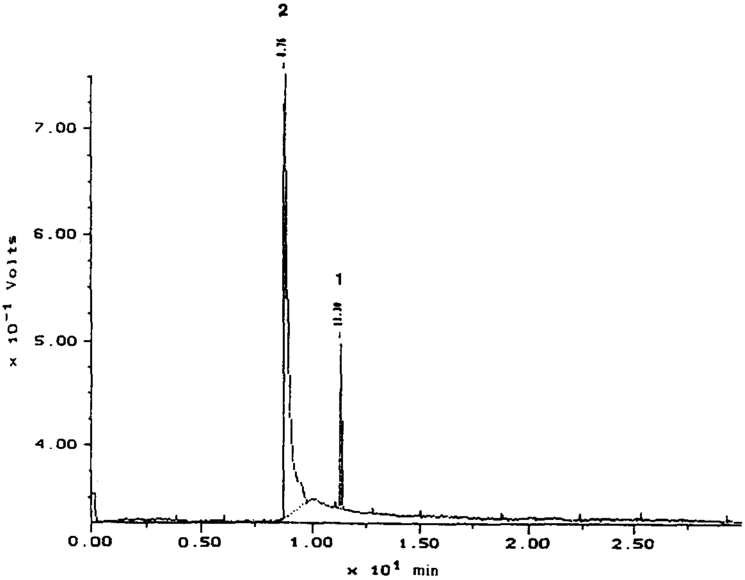


Fig. 2. CE analysis of cationic orange vinylsulphone dye (peak 1) and the aminoethyl derivative (peak 2).

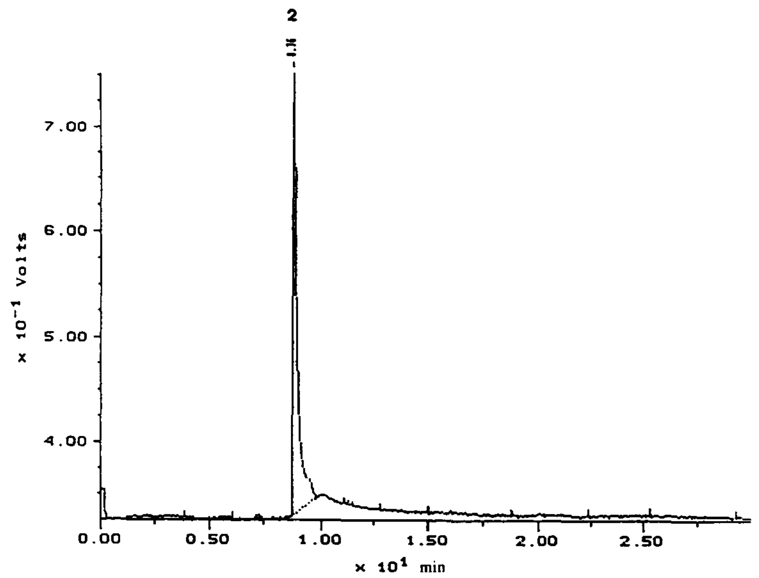
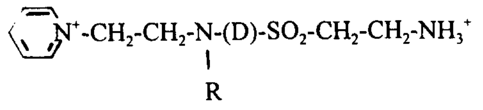
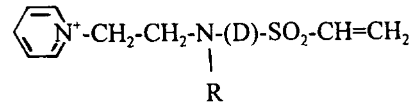


Fig. 3. CE analysis of cationic orange vinylsulphone aminoethyl derivative (peak 2).

detector in 11.38 min, whereas the aminoethyl derivative migrates in 8.76 min. This result confirms the presence, at the analysis pH of 4.5, of an additional cationic residue on the latter dye, viz.:



$$\text{N}^{+}\text{-CH}_2\text{-CH}_2\text{-}\underset{\text{R}}{\underset{|}{\text{N}}}\text{-(D)-SO}_2\text{-CH}_2\text{-CH}_2\text{-NH}_3^{+}$$



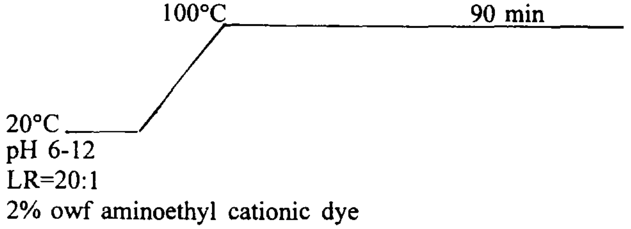
$$\text{N}^{+}\text{-CH}_2\text{-CH}_2\text{-}\underset{\text{R}}{\underset{|}{\text{N}}}\text{-(D)-SO}_2\text{-CH=CH}_2$$

[where (D) represents the chromophoric residue].

Figures 4 and 5 show the FTIR spectrum of the aminoethyl cationic dye and its parent vinylsulphone dye. The disppearance of the absorbance at 975 cm^{-1} indicates that the C=C bond has been removed. The new peak at 3047 cm^{-1} is the $-NH_3^+$ stretching vibration.

Uptake of the aminoethyl cationic dye on nylon

Dyeing was carried out at different pH values for 1 h at the boil using a 20:1 liquor to goods ratio employing a 2% owf shade (Scheme 4).



Scheme 4. Application profile for the aminoethyl cationic dye.

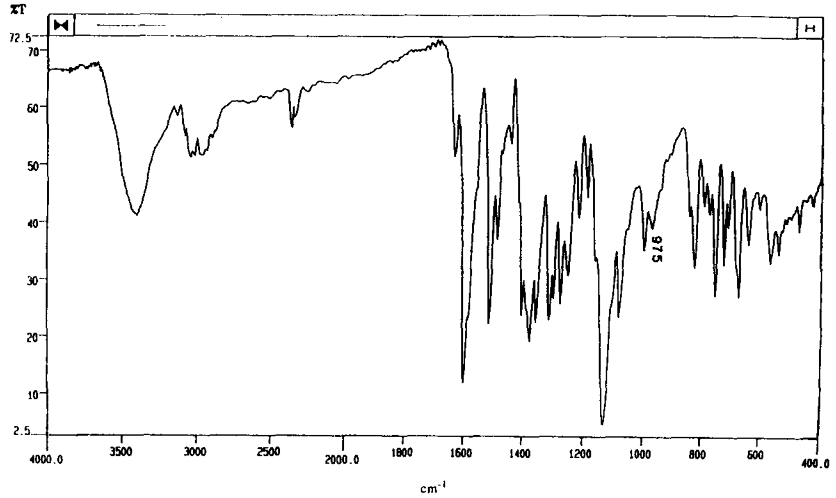


Fig. 4. FTIR spectrum of cationic orange vinylsulphone dye.

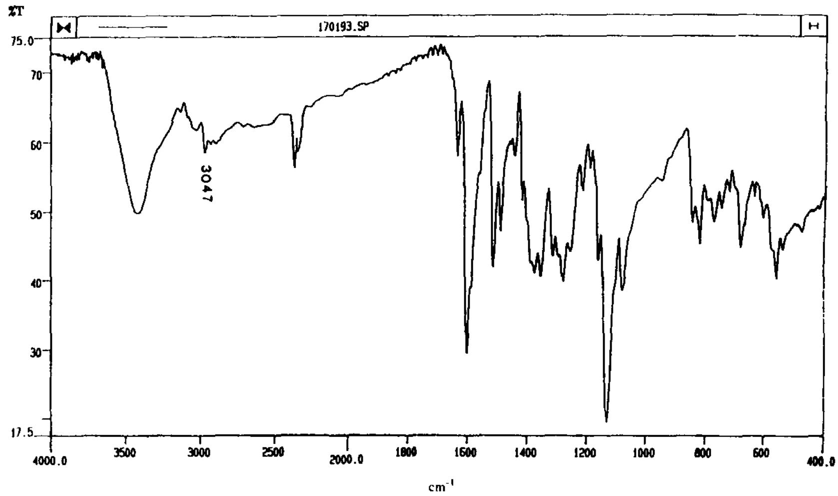


Fig. 5. FTIR spectrum of an aminoethyl cationic dye prepared from cationic orange vinylsulphone dye.

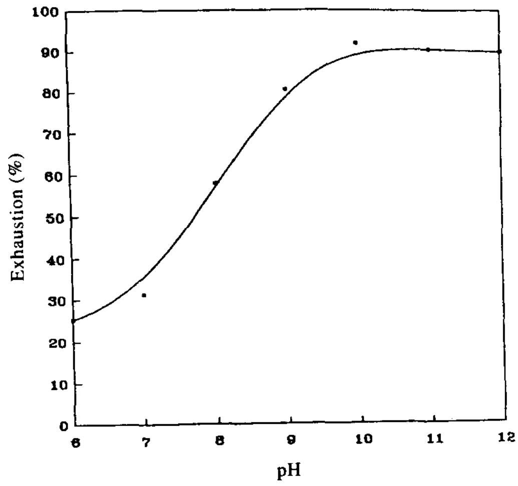
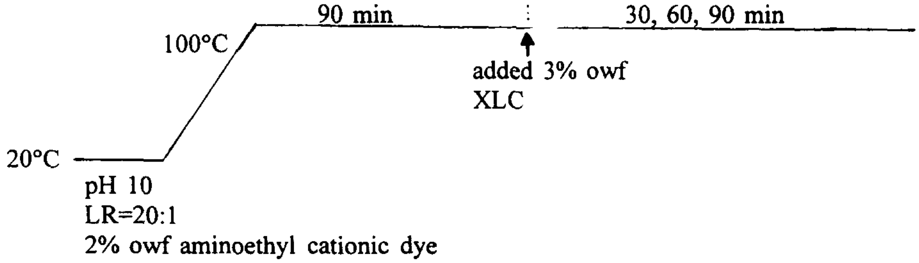


Fig. 6. Uptake of aminoethyl cationic dye (2% owf) on nylon.

Figure 6 shows the exhaustion values from these experiments. A study of this figure indicates high dye substantivity under alkaline conditions ($pH \geq 10$); in addition to the fully quaternized pyridinium group, the dye contains a tertiary amine and a primary amine residue that could be partly protonated even at these pH values. The nylon fibre surface is more negatively charged ($-COO^-$) under basic conditions and hence is more readily dyeable with cationic dyes under these conditions.

Effect of dyeing procedure on dye fixation

The effect of different dyeing procedures was also investigated. All dyeings were carried out at pH 10 for 90 min at the boil using a 20:1 liquor to goods ratio employing a 2% owf shade. After 90 min, 3% owf of XLC was added to the boiling dyebath and dyeing was continued for a further *X* min (Scheme 5).



Scheme 5. Dyeing profile for application of aminoethyl cationic dye and crosslinker.

TABLE 1

Effect of Time on Fixation Following the Addition of Crosslinker (pH 10)

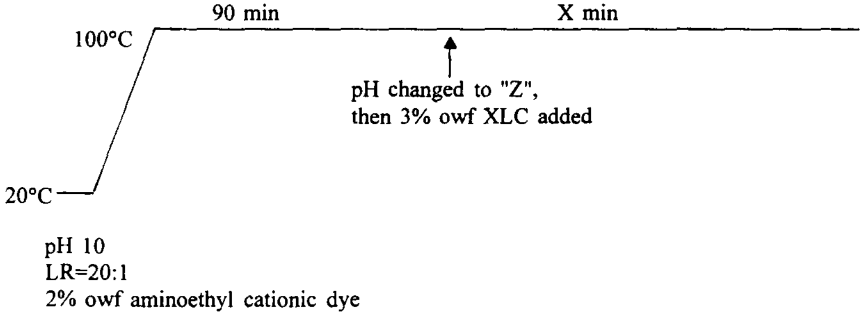
X (min)	*Exhaustion (E%)*	*Fixation (F%)*
30	93.0	45.3
60	93.2	45.0
90	93.2	45.1

The results are given in Table 1. Table 1 shows that the presence of XLC in the dyebath did not give outstanding dye fixation values when the dyebath pH remains unchanged at 10. However, exhaustion values remained high throughout due to the cationic character of the aminoethyl cationic dye. Under alkaline conditions the nylon fibre carries a negative charge (–COO$^-$) and thus strongly attracts the aminoethyl cationic dye. On the other hand, Fig. 7 shows that XLC is immediately converted to the water-insoluble di-vinylsulphone derivative (XLC-VS) at pH 10 and boiling; in the absence of dispersing agent this material will precipitate on the fibre surface and on the walls of the dyeing vessel and is thus less available for reactions with the dye and the fibre. However, XLC-VS is not easily hydrolysed under these strong alkaline (pH$\geq$10) conditions at the high temperature employed (Fig. 7), presumably because of its insolubility.

Effect of the fixation pH on dye fixation

Because of the above XLC-VS precipitation problem at pH 10, it was decided to reduce the fixation pH value to achieve improved fixation by crosslinking.

Nylon was dyed with 2% owf aminoethyl cationic dye at pH 10 for 90 min at the boil using a 20:1 liquor to goods ratio. After 3% owf of XLC was added to the dyebath at the boil, the dyebath pH value was changed from 10 to the value *Z* and dyeing was continued for a further *X* min (Scheme 6).



Scheme 6. Dye application scheme when varying the dyebath pH prior to crosslinker addition.

The results are shown in Table 2, it can be seen that pH 8 is the most suitable pH value for subsequent treatment with XLC. When the pH is lower than this value, the substantivity of the aminoethyl cationic dye is too low and desorption occurs, due to the nylon fibre decreasing in negative charge. When the XLC treatment pH is higher than 8, precipitation of XLC-VS becomes significant, thus reducing the crosslinking efficiency and the fixation values of the dyeings produced. Even though XLC-VS is formed rapidly at

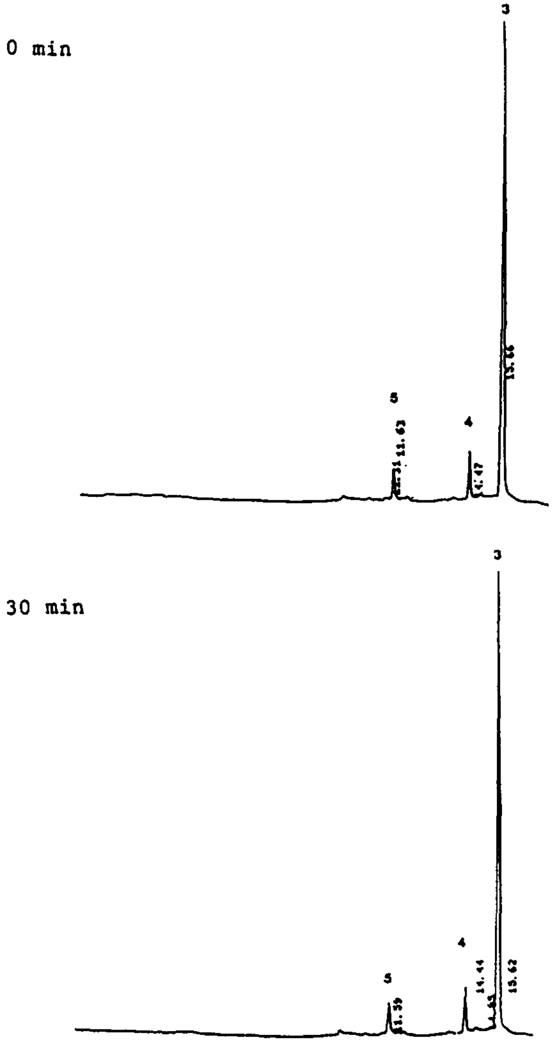


Fig. 7. HPLC printouts for the rate of conversion of XLC to its hydrolysed form at pH 10 and the boil. Peak 3 is attributable to XLC-VS, peak 4 to XLC-mono-OH, and peak 5 to XLC-di-OH.

pH 8 at the boil (Fig. 8) there is probably sufficient XLC-mono-VS (monosulphatoethylsulphone) present to act as a dispersing agent for XLC-VS, ensuring its even uptake on the dyed nylon.

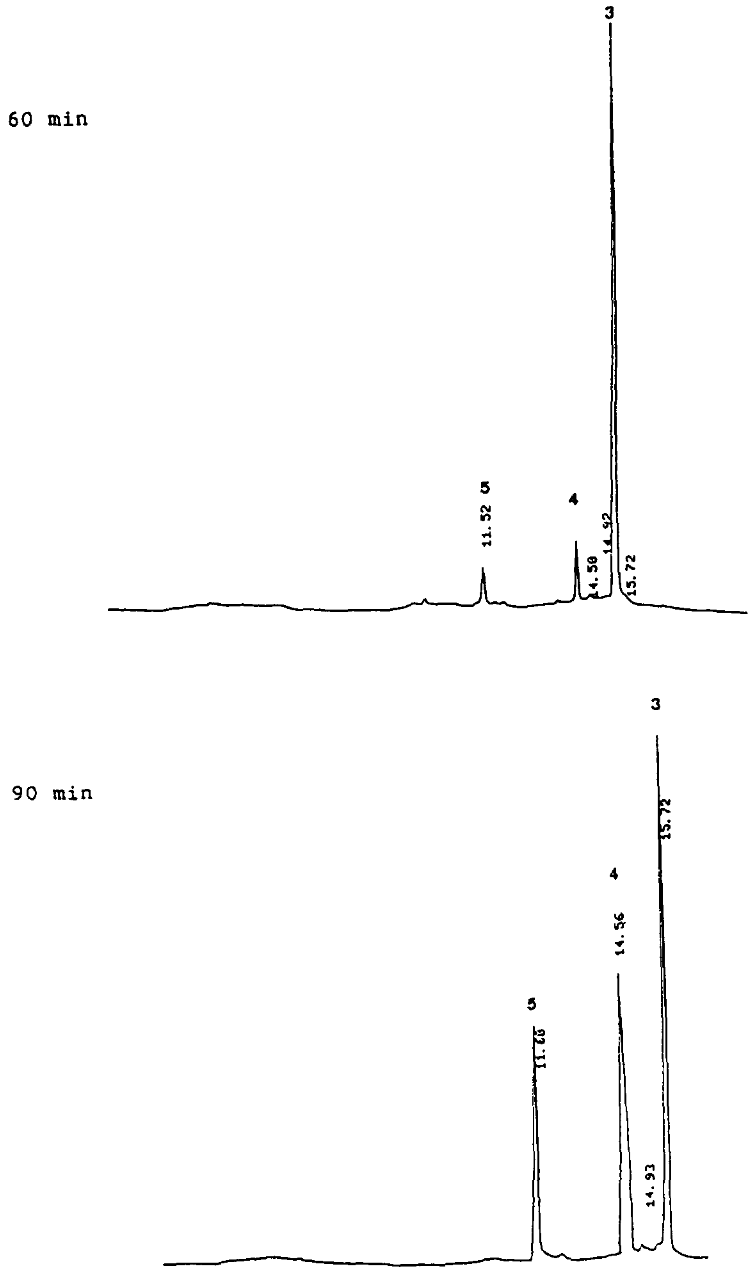


Fig. 7—*continued*

TABLE 2
Effect of Crosslinking pH on Exhaustion/Fixation

pH Z	*X(min)*	*E%*	*F%*	*T%*
7	30	80.4	74.5	59.9
7	60	78.5	83.8	65.8
8	30	84.9	81.9	69.5
8	60	83.9	88.1	73.9
9	30	91.3	66.6	60.8
9	60	91.2	66.8	60.9

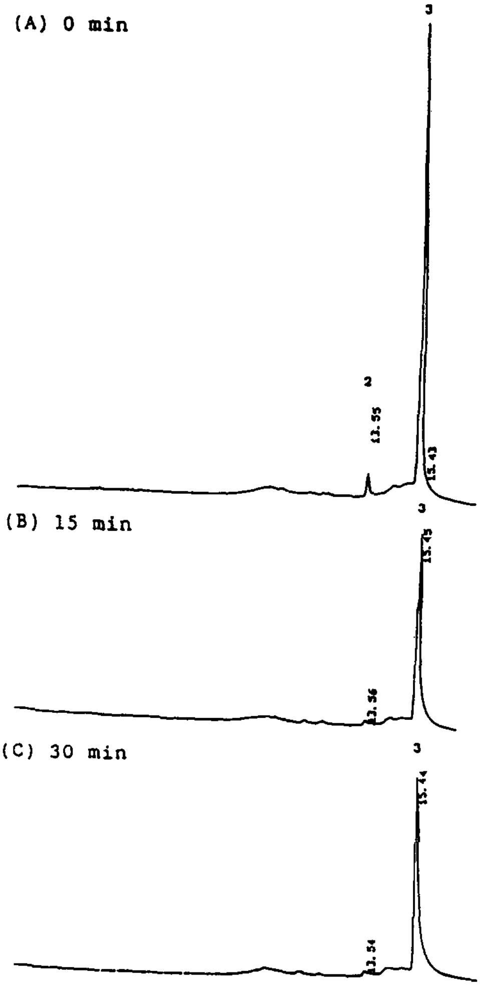


Fig. 8. HPLC printouts for the rate of conversion of XLC to the reactive vinylsulphone form at pH 8 and the boil. Peak 2 is attributable to XLC-mono-VS; and peak 3 to XLC-di-VS (XLC-VS).

At a treatment pH of 8 the dye exhaustion decreased slightly; however, at pH 8 fixation increased as the fixation time increased from 30 to 60 min. Due to the high reactivity of XLC, 60 min is sufficient to complete the reaction at

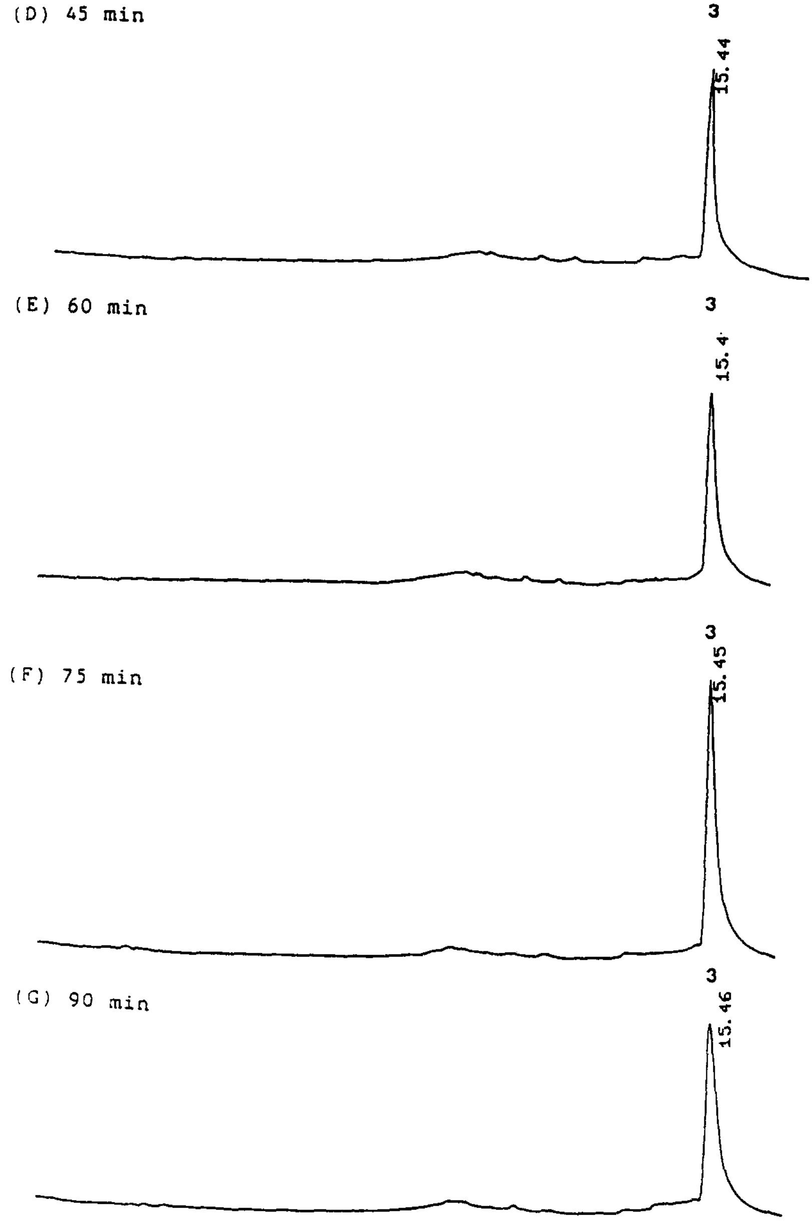
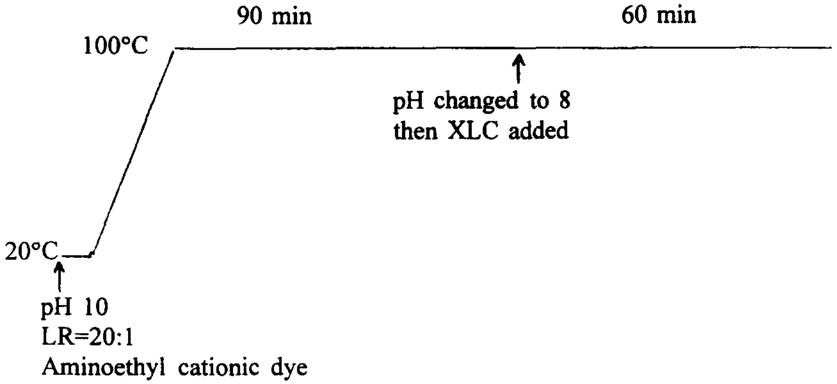


Fig. 8—*continued*

pH 8 (Fig. 8 shows the HPLC printouts for the rate of conversion of XLC to the reactive vinylsulphone form at pH 8 and 100°C).

Effect of XLC concentration on dye fixation

Dyeing was carried out at pH 10 for 90 min at the boil, after which the dyebath pH was adjusted to 8 and then different XLC concentrations were added to the dyebath and another 60 min at the boil completed the dyeing process (Scheme 7).



Scheme 7. Dye application scheme to study the effect of changing dye and crosslinker concentration.

The experimental results are given in Figs 9, 10, 11, 12 and 13. Figure 14 shows exhaustion and fixation values when no XLC was added to the dyebath.

CONCLUSIONS

A model orange aminoethylsulphonyl cationic dye was successfully synthesized and showed excellent substantivity for nylon at pH values >9. If the crosslinking agent, XLC, was added at pH 10 to fix covalently the nucleophilic dye to nucleophilic amino sites in the fibre, dye desorption did not occur but fixation values achieved were only modest. It was reasoned that this effect was due to a too rapid precipitation of the insoluble bis-vinylsulphone form of the crosslinker (XLC-VS) and this postulate was confirmed by reducing the pH to 8 prior to XLC addition; at this pH a slower rate of elimination to form the reactive divinylsulphone form (XLC-VS) was achieved and promising fixation results (80–90%) were measured.

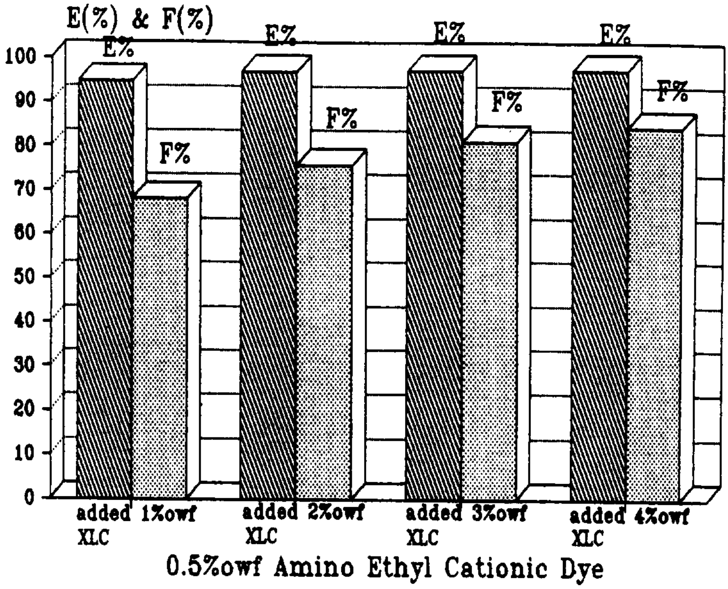


Fig. 9. Effect of dye and XLC concentration on dye exhaustion (*E*%) and fixation (*F*%).

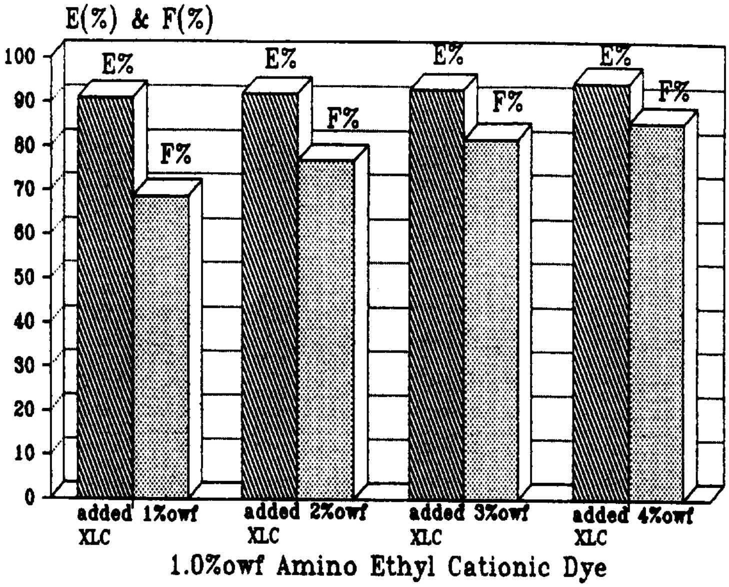


Fig. 10. Effect of dye and XLC concentration on dye exhaustion (*E*%) and fixation (*F*%).

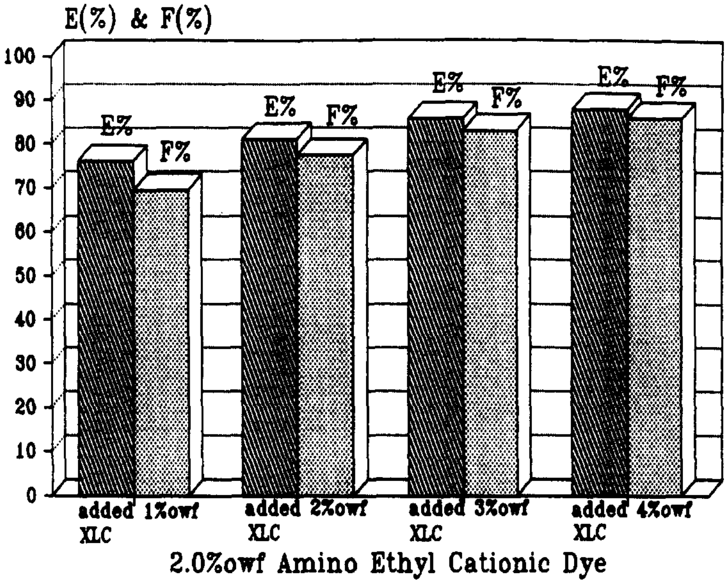


Fig. 11. Effect of dye and XLC concentration on dye exhaustion (*E*%) and fixation (*F*%).

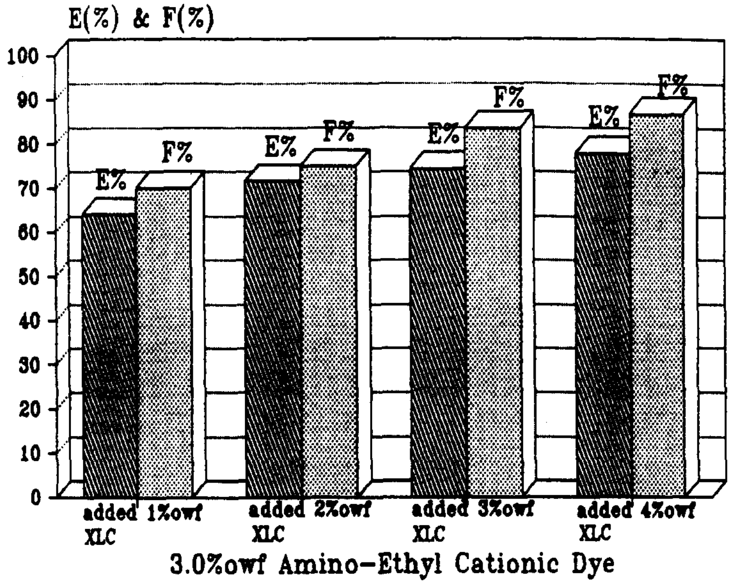


Fig. 12. Effect of dye and XLC concentration on dye exhaustion (*E*%) and fixation (*F*%).

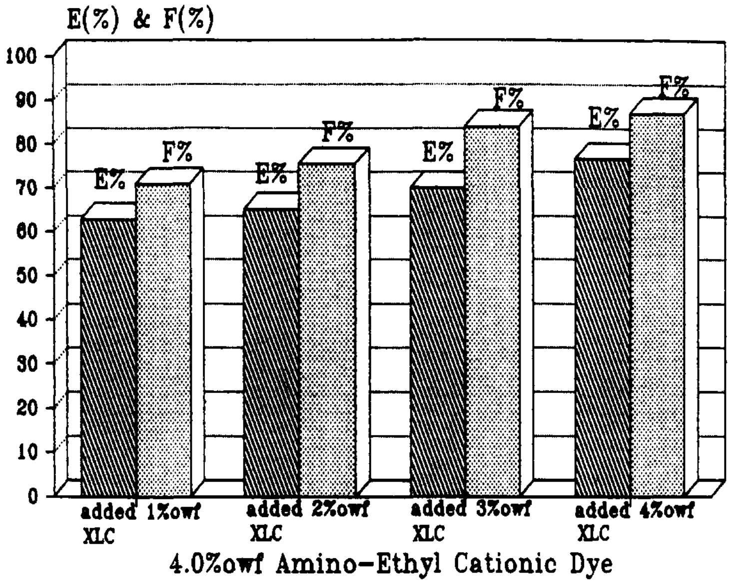


Fig. 13. Effect of dye and XLC concentration on dye exhaustion (*E*%) and fixation (*F*%).

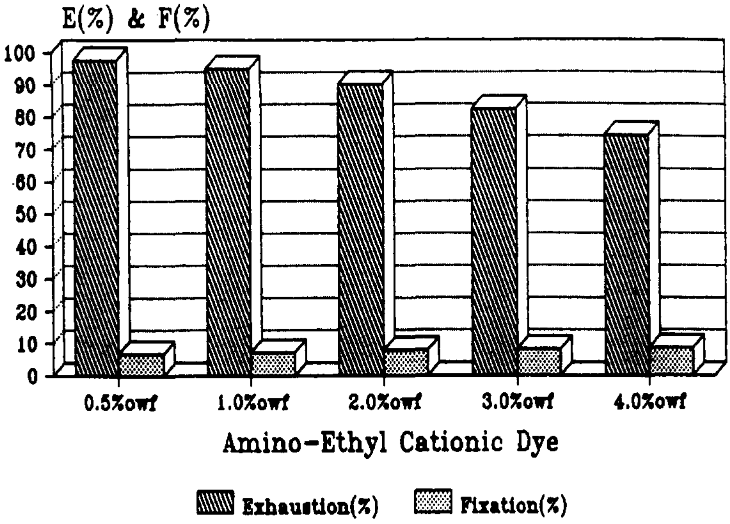


Fig. 14. Effect of amino-ethyl cationic dye concentration on dye exhaustion (%) and fixation (%).

REFERENCES

1. Lewis, D. M. & Ho, Y. C., *Dyes and Pigments*, **28** (1995) 171.
2. Lewis, D. M. & Ho, Y. C., *Dyes and Pigments*, **28** (1995) 237.
3. Lewis, D. M. & Ho, Y. C., *Dyes and Pigments*, **30** (1996) 301.
4. Hinks, D., PhD Thesis, Leeds University (1994).
5. Baumann, W., van Diest, J., Eichenberger H. & Oppliger, M., Sandoz, USP, 4820806 (1989).
6. Hinks, D. & Lewis, D. M., *Chromatogr. and Analysis*, **Aug/Sept** (1993) 9.