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Improved Fixation of Dyes on Polyamide Fibres. Part 2: Use of the Reactive Crosslinking Agent, 2-Chloro-4,6-Di(Aminobenzene-4'-Sulphatoethylsulphone)-*s*-Triazine (XLC)

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ABSTRACT

*A reactive crosslinker (XLC) containing two sulphatoethylsulphone and one chloro-*s*-triazine residue has been synthesised and applied to nylon. The pretreated nylon shows reduced substantivity and reactivity towards a model reactive dye, CI Reactive Red 3. If these pretreated fibres are reacted with ammonia, they then show enhanced dye uptake and fixation when dyed with this dye. Opposite effects are achieved if the above reactive dye is converted to a nucleophilic aminoalkyl-*s*-triazine dye by reaction with ethylene diamine; the nucleophilic dye exhibits a high degree of covalent bonding only on the XLC treated nylon.*

1 INTRODUCTION

Owing to a paucity of nucleophilic amino sites in commercially available nylon fibres (nylon-6 and nylon-6,6), incomplete fixation of reactive dyes on nylon is a major problem for dyers, especially in moderate to deep shades when excellent wet fastness properties are desired. This necessitates the use of alkaline extraction procedures to remove hydrolysed and unreacted reactive dye. However, it should be possible to obtain a high degree of

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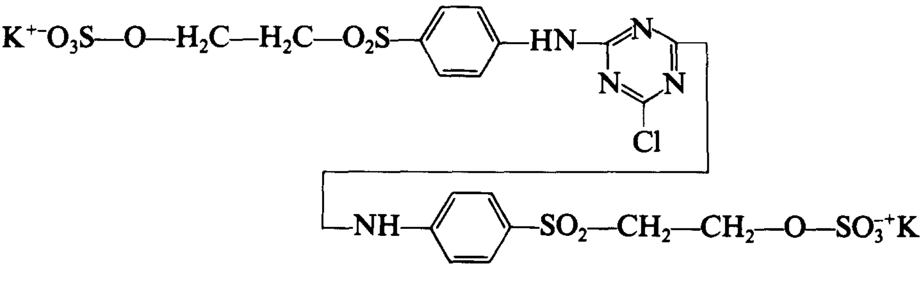
dye–fibre covalent fixation, even in deep shades, by the use of specially prepared amino ethyl dyes and a trifunctional crosslinking agent which would form a bridge between fibre amino nucleophiles and pendant amino nucleophiles on the dyes.

An alternative approach is to increase the number of amino nucleophiles in the fibre by pretreatment with the crosslinker and then add amino groups to unreacted sites by a subsequent reaction of the pretreated nylon with ammonia. This method should produce a nylon with a significantly greater number of free amino residues which should show enhanced dyeability with existing reactive dyes.

Part 1 of this series[1] described the use of triacroylamino-hexahydro-*s*-triazine as a crosslinker to improve the dyeing of nylon; it was shown that this crosslinker lacked fibre substantivity and hence gave only moderately interesting results. To improve substantivity, a trifunctional agent of greater molecular size and complexity has been investigated.

The water soluble trifunctional crosslinking agent, 2-chloro-4,6-di(aminobenzene-4'-sulphatoethylsulphone)-*s*-triazine potassium salt (XLC) was synthesised; its constitution is shown below:



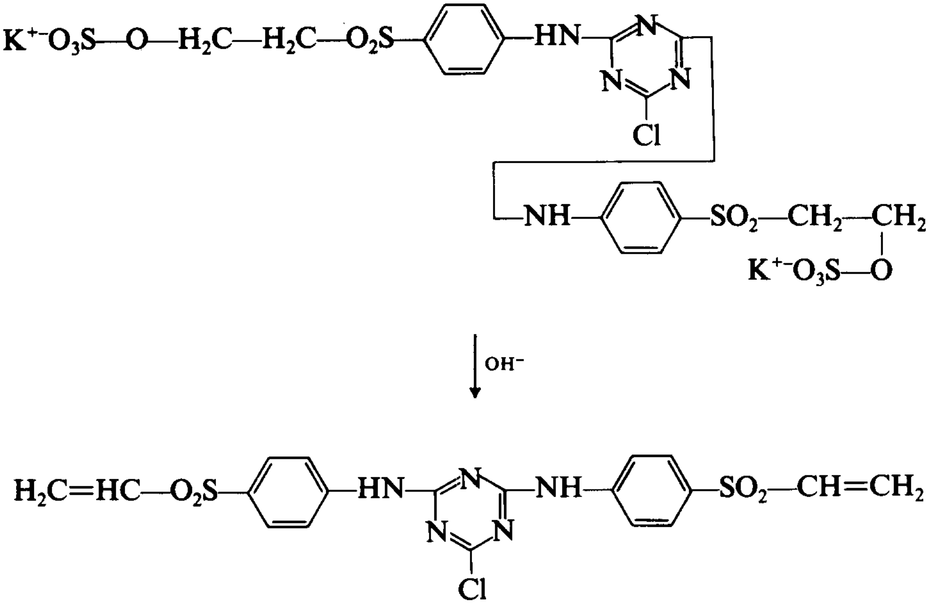
XLC

XLC has previously been studied as a wool fibre protective agent which inhibits fibre damage during dyeing;[2] its substantivity for wool and the efficiency of crosslinking on the substrate have also been described.[3,4] The amino groups in nylon will also serve as nucleophilic sites in reactions with XLC.

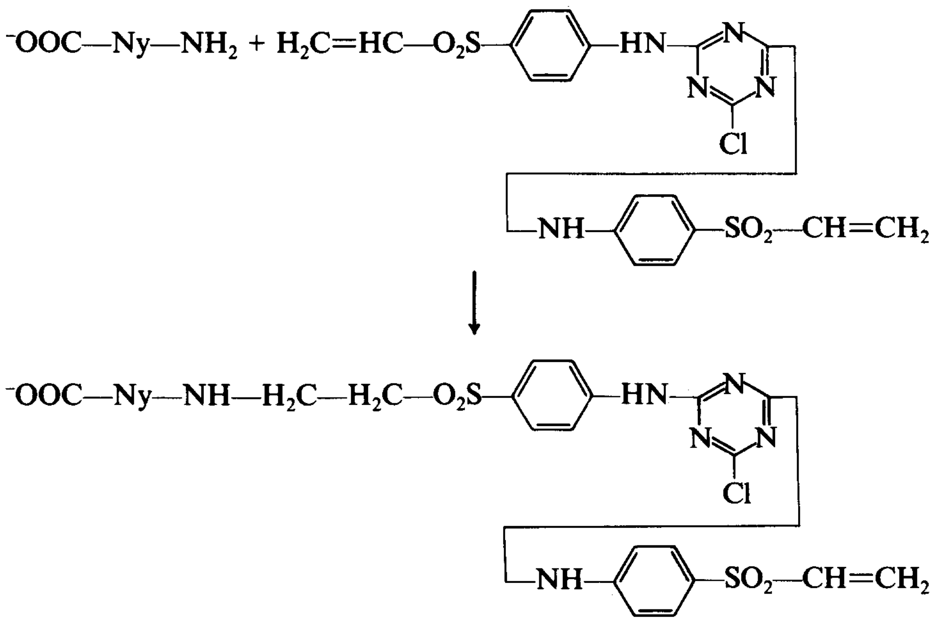
This study has thus investigated optimum conditions for effecting uptake and covalent reaction of XLC on nylon. Additionally, XLC treated nylon can be further reacted with ammonia to increase the nucleophilic character of the modified nylon and hence improve its reactive dyeing properties.

The crosslinking agent, XLC, may react with nylon as follows:

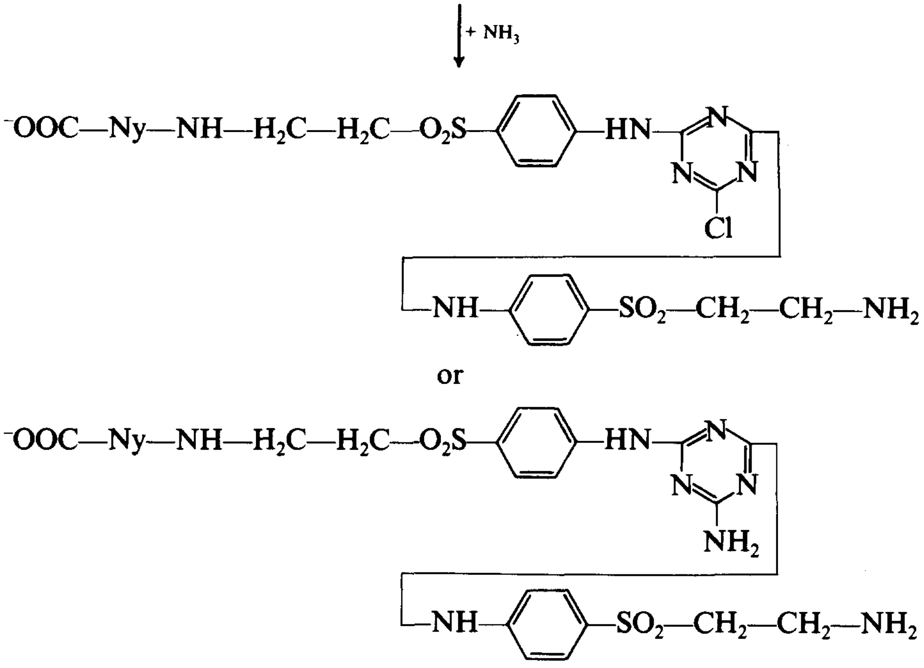
Step 1: Activation to the reactive vinylsulphone form



Step 2: Reaction with nylon



Step 3: Reaction with ammonia



Where ⁻OOC—Ny—NH_2 represents the nylon fibre.

2 EXPERIMENTAL

2.1 Synthesis of the dipotassium salt of 2-chloro-4,6-di(aminobenzene-4'-sulphatoethylsulphone)-*s*-triazine (XLC)[2]

p-Aminobenzene-sulphatoethylsulphone (PABSES) (7·025 g, 0·025 mole) was dissolved in water (100 cm^3) at room temperature with $KHCO_3$ to adjust the pH to 5·5–5·7. Acetone was then added to this solution to give a water : acetone ratio of 70 : 30 (v/v) and the solution cooled to 5°C. Cyanuric chloride (4·61 g, 0·025 mole) dissolved in acetone was then slowly dripped into this solution with continuous stirring, whilst maintaining the pH near 5·5 by addition of aq. $KHCO_3$; ice additions were also made to keep the temperature around 5°C. The mixture was stirred for a further 40 min at 5°C and then allowed to warm to room temperature. A further 0·025 mole (7·025 g) of PABSES was dissolved in water (100 cm^3) at room temperature with $KHCO_3$ to adjust the pH to 5·5–5·7 and this was then added to the above stirred solution. The temperature was raised slowly to 50°C, with continuous stirring, while maintaining the pH at 5·5–5·7 by the addition of $KHCO_3$; when the pH value remained at 5·5, the reaction was stopped and cooled to room temperature. The product was isolated by addition of 10 g of potassium chloride per 100 cm^3 of solution; after filtration, it was dried at 40°C in a vacuum drying oven; yield 17 g (91%).

2.2 Dyes

Two dyes were employed, CI Reactive Red 3 (monochloro-triazine type) and its aminoethylamino-triazine derivative; the preparation of these dyes was fully described in Part 1 of this series.[1]

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

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

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

2.4 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 a 25% (v/v) pyridine/water solution (100°C, LR = 20 : 1). The dyed fabric sample was repeatedly extracted with fresh pyridine/water solution 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 cm^3 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 definition of the term 'fixation' is sometimes used, which in fact refers to the amount of original dye taken that is covalently bonded. This overall fixation efficiency (T) is related to F (exhausted dye fixed) by the equation: $\%T = (\%F \times \%E)/100$.

2.5 Dyeing method

All dyeings were carried out in 100 cm^3 sealed stainless steel dyepots housed in a Rotadyer (John Jeffreys) laboratory dyeing machine, at a liquor to goods ratio of 20 : 1. The dyebath was set at the required pH value. Dyeing commenced at 20°C, the temperature was raised to the boil over 40 min (2°C min^{-1}) and dyeing was continued at the boil for the required length of time.

2.6 XLC treated nylon

All treatments of nylon fibre with XLC were carried out in 100 cm^3 sealed stainless steel dyepots housed in a Rotadyer machine at a liquor to goods ratio of 20 : 1. The treatment bath, which contained XLC and water, was set at the required pH value (pH 2–9). Treatment commenced at 20°C, the temperature was raised to the boil (2°C min^{-1}) and treatment continued at the boil for 1 h. The uptake of XLC on nylon was determined spectrophotometrically at 290 nm by the usual method.

2.7 XLC/NH_3 treated nylon

XLC treated nylon was modified in a solution containing 50 g l^{-1} of ammonia (d = 0·880). The treatment was carried out at the boil for 1 h in 100 cm^3 sealed stainless steel dyepots housed in a Rotadyer machine at a liquor to goods ratio of 20 : 1. The sample was then rinsed thoroughly in tap water and air dried.

2.8 Infrared (IR) analysis

2.8.1 IR/attenuated total internal reflectance (ATR) analysis of fabric materials

IR analyses of nylon fabric was carried out with the Perkin Elmer 1725 Infrared Fourier Transform Spectrometer using a vertical ATR pressure cell attachment.

2.8.2 Solids

IR analyses of XLC were carried out with the Perkin Elmer 1725 Fourier Transform Infrared Spectrometer. Samples were prepared by mixing 1 mg of the sample in 200 mg of potassium bromide (KBr) and pressing into discs.

2.9 HPLC analysis

XLC was analysed with a Varian 5000 Liquid Chromatograph using 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 cm^3 l^{-1} of 20% (w/w) acetic acid and 0·5 cm^3 l^{-1} of 5% (w/w) of potassium hydroxide as a buffer. Flow 0·9 cm^3 min^{-1}; detector wavelength setting 290 nm; eluent composition water/methanol = gradient elution.

Gradient elution conditions

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

3 RESULTS AND DISCUSSION

3.1 Analysis of XLC

Figure 1 shows the FT-IR spectrum of XLC; the peaks at 1247, 1050, and 1040 cm^{-1} are from the —O—SO$_3^-$ absorption and the peak at 1148 cm^{-1} is from the —SO$_2$— absorption. The absorption at 803 cm^{-1} is due to the presence of the C—Cl bond.

Using HPLC it was possible to accurately follow the progress of the reactions involved in the XLC synthesis. Typical printouts are reproduced in Fig. 2; stage 1 is from an analysis after reaction of 1 mole of PABSES with cyanuric chloride; stage 2 is representative of the reaction composi-

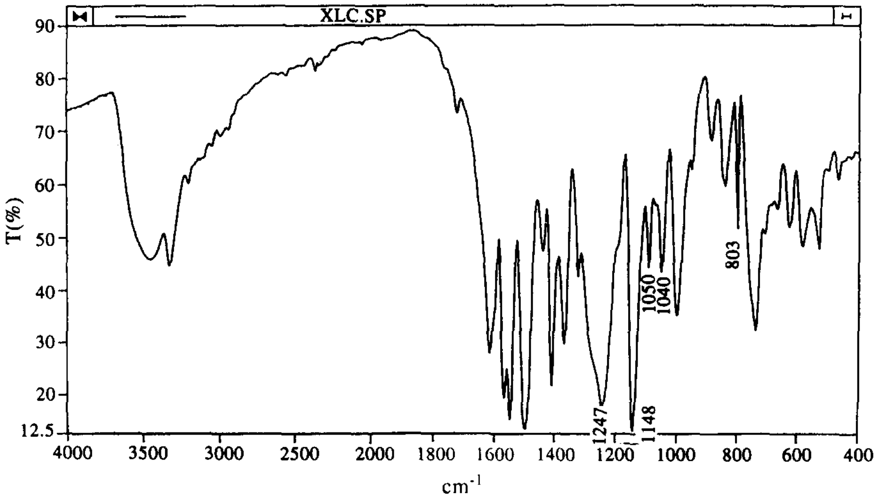


Fig. 1. FT-IR spectrum of XLC (KBr disc).

tion on addition of the second mole of PABSES and raising the reaction mixture to 50°C; stage 3 shows the reaction progression after 2 h at 50°C; and stage 4 shows the almost complete conversion to the desired XLC after 4 h at 50°C.

Elemental analysis of XLC: found C 28·2%, N 8·85%, H 2·65%, S 15·55%; calculated C 29·0%, N 8·87%, H 2·89%, S 16·32%.

3.2 Effect of pH on uptake of XLC

All the treatments of nylon fabric with XLC are described in the experimental section. At the end of the treatment procedure, samples were

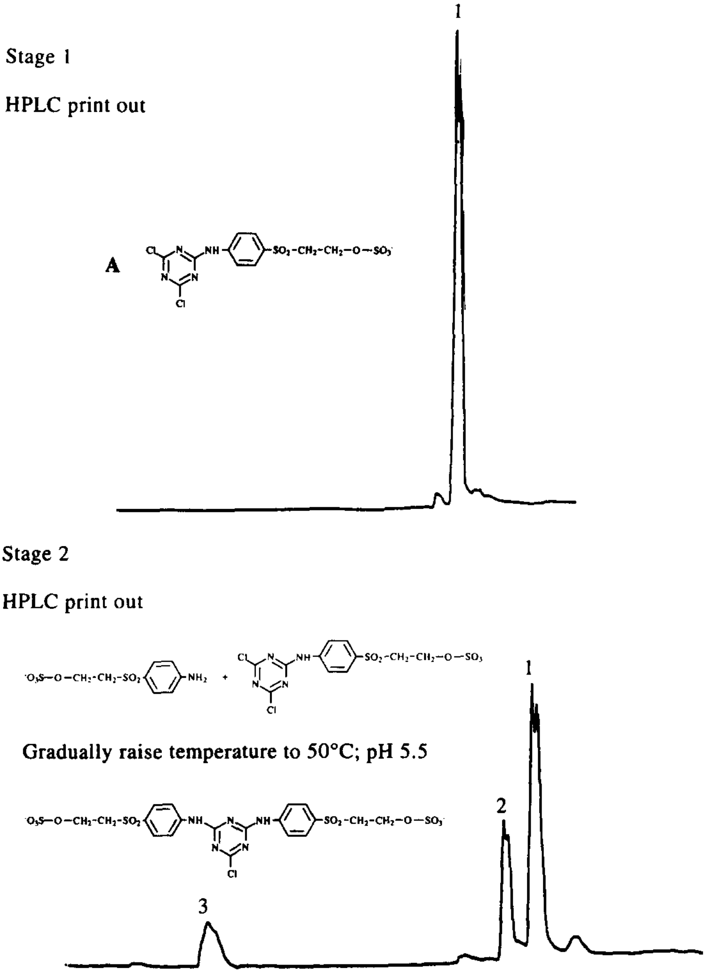
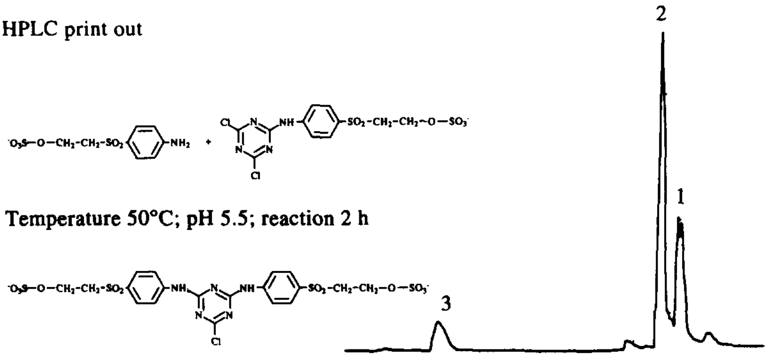


Fig. 2. Typical HPLC printouts. Peak 1 is attributable to compound A, retention time 11·90; peak 2 to XLC, retention time 11·11; and peak 3 to PABSES, retention time 4·13.

Stage 3

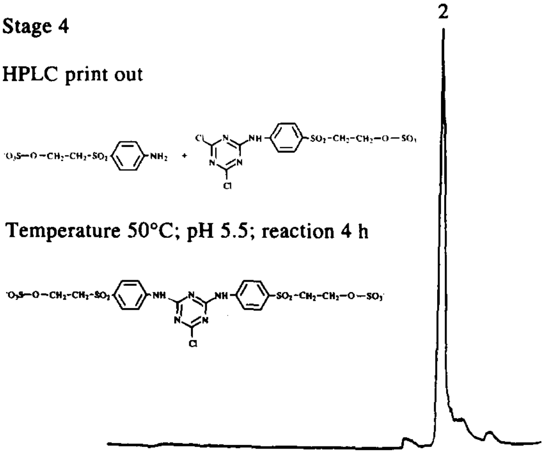
HPLC print out



Temperature 50°C; pH 5.5; reaction 2 h

Stage 4

HPLC print out



Temperature 50°C; pH 5.5; reaction 4 h

Fig. 2.—*contd.*

TABLE 1
Effect of Bath pH on the Uptake of XLC (3% owf) at 100°C

Bath pH	*Exhaustion (%)*
2	90·5
3	87·3
4	80·6
5	67·2
6	92·4
7	97·8
8	98·1
9	96·2

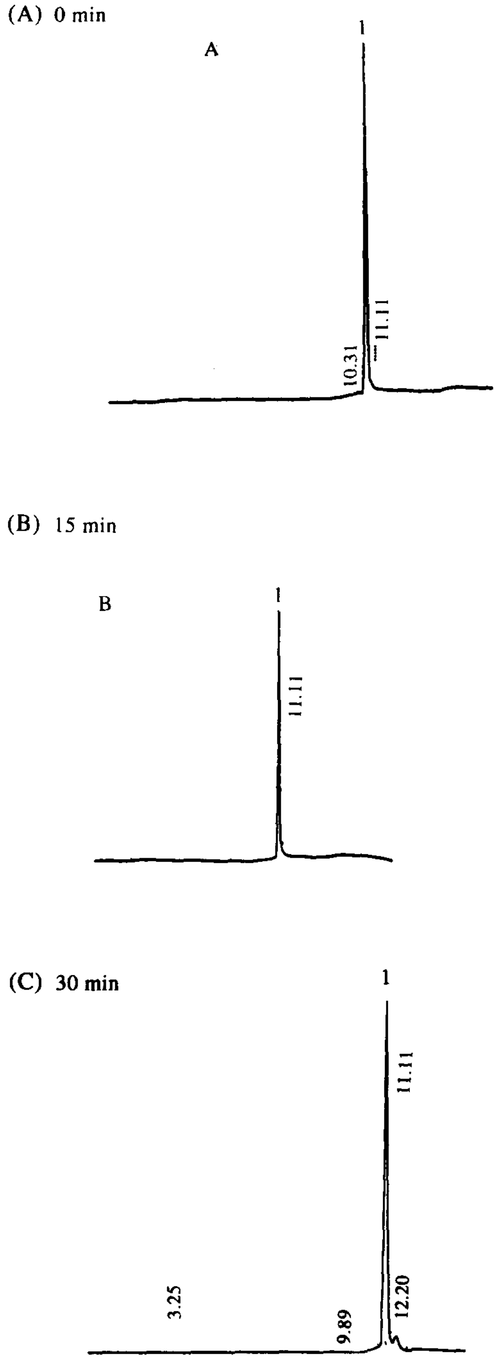


Fig. 3. HPLC printouts showing the rate of conversion of XLC to the reactive vinylsulphone form at pH 4 and the boil. Peak 1 is attributable to XLC; peak 2 to XLC-mono-VS; and peak 3 to XLC-di-VS (XLC-VS).

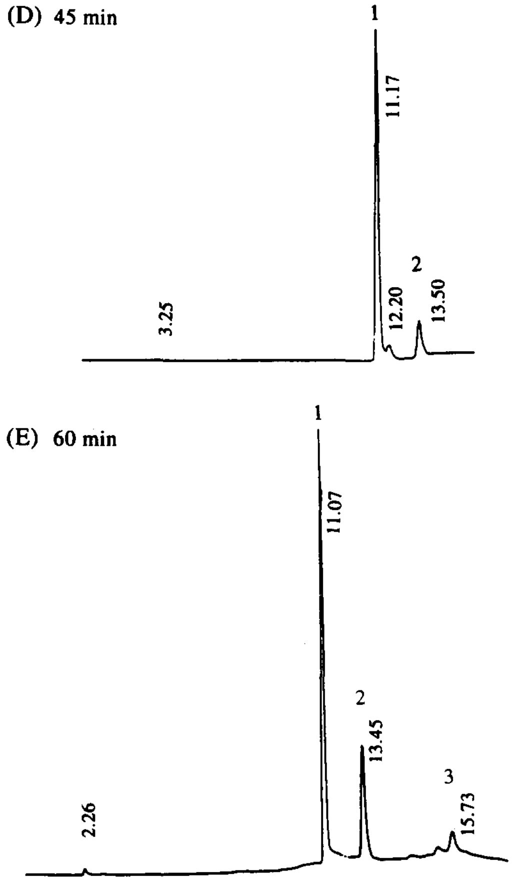


Fig. 3.—*contd.*

removed from the bath and UV absorbance measurements made on the residual solutions at 290 nm. The uptake of XLC expressed in terms of percentage bath exhaustion is shown in Table 1.

From the results it can be seen that pH 7 and 8 appear to be the most suitable values for maximum uptake of XLC. XLC is a bifunctional 'blocked' vinylsulphonyl derivative which would β-eliminate to give two activated double bonds when boiled at bath pH values of 6, 7 or 8. This latter aspect was further evaluated; Figs 3–7 show the HPLC printouts for the rate of conversion of XLC to the reactive vinylsulphone form at pH 4, 5, 6, 7 and 8 and at the boil. Due to the presence of two strongly electron withdrawing sulphonyl groups, the double bonds are more reactive than those in FAP. Additionally, XLC shows higher substantivity for nylon than FAP, presumably due to its increased molecular size, increased hydrophobicity (XLC-VS form only) and higher reactivity.

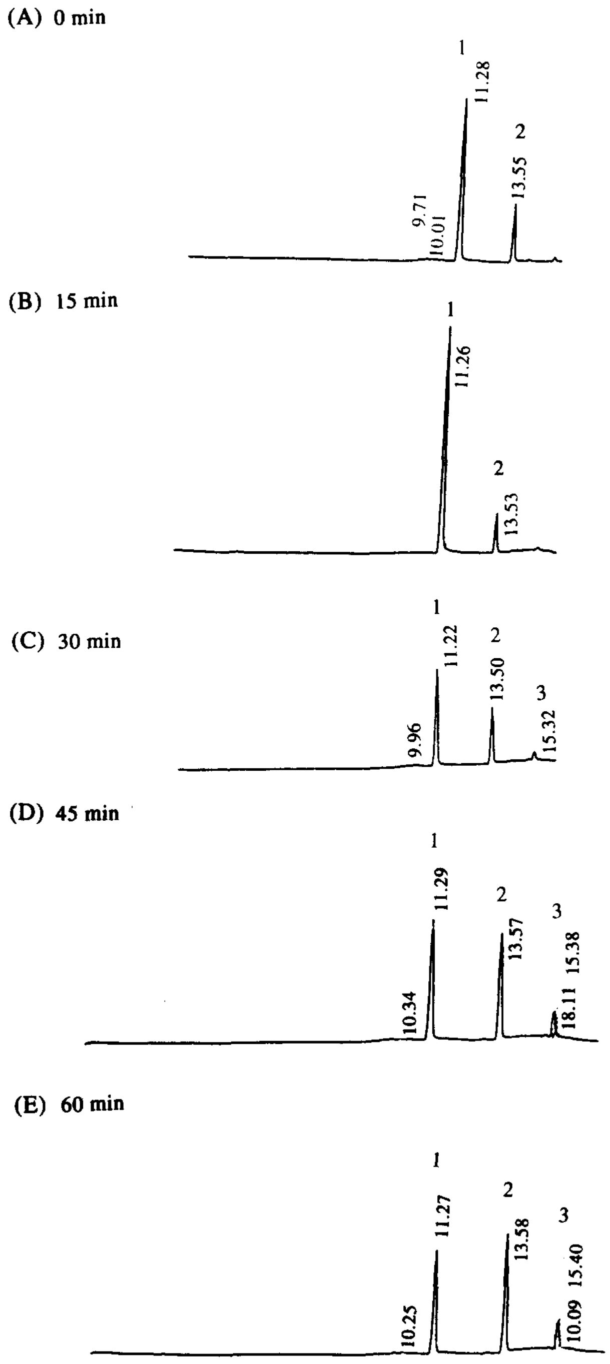


Fig. 4. HPLC printouts showing the rate of conversion of XLC to the reactive vinylsulphone form at pH 5 and the boil. Peak 1 is attributable to XLC; peak 2 to XLC-mono-VS; and peak 3 to XLC-di-VS (XLC-VS).

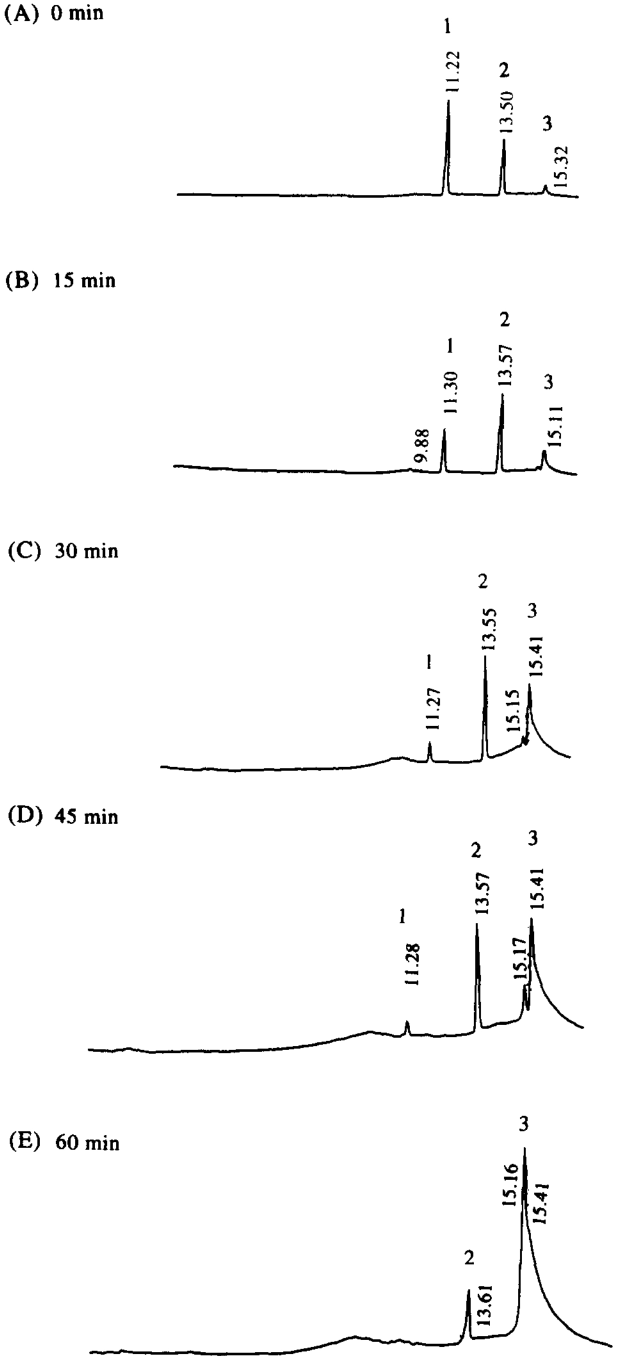


Fig. 5. HPLC printouts showing the rate of conversion of XLC to the reactive vinylsulphone form at pH 6 and the boil. Peak 1 is attributable to XLC; peak 2 to XLC-mono-VS; and peak 3 to XLC-di-VS (XLC-VS).

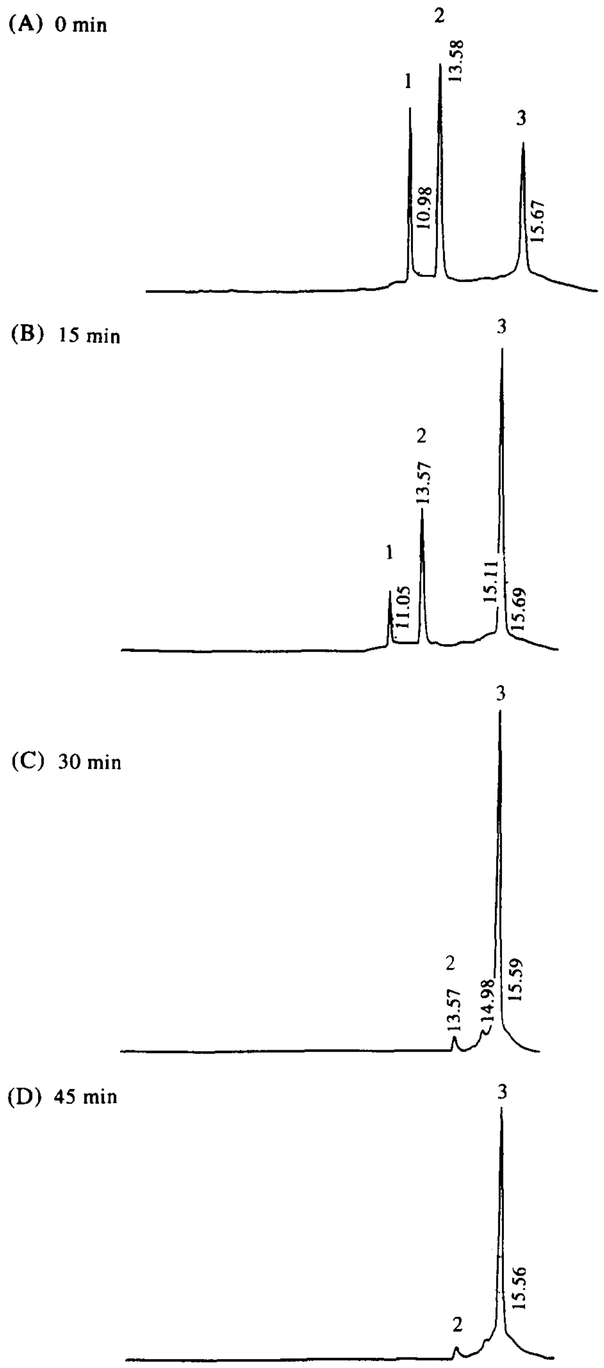


Fig. 6. HPLC printouts showing the rate of conversion of XLC to the reactive vinylsulphone form at pH 7 and the boil. Peak 1 is attributable to XLC; peak 2 to XLC-mono-VS; and peak 3 to XLC-di-VS (XLC-VS).

Fig. 6.—*contd.*

3.3 IR study of treated and untreated nylon fabric

Figures 8, 10 and 12 show the FT-IR spectra of XLC treated nylons from which the spectrum of untreated nylon has been computer subtracted. Of special note is the disappearance of the absorbances at 1247, 1050, and 1040 cm^{-1} (—O—SO_3^-). A new absorbance appears at 1675 cm^{-1}, possibly

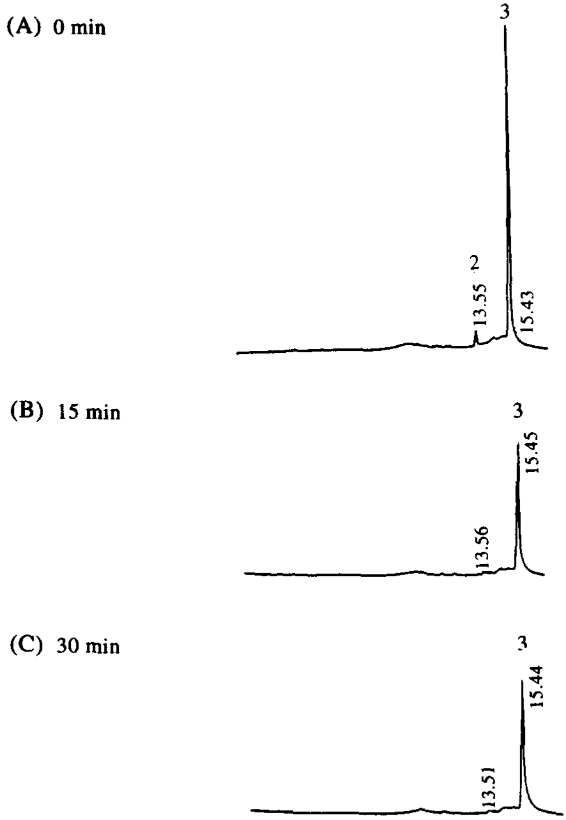


Fig. 7. HPLC printouts showing the rate of conversion of XLC to the reactive vinyl-sulphone form at pH 8 and the boil. Peak 2 is attributable to XLC-mono-VS; and peak 3 to XLC-di-VS (XLC-VS).

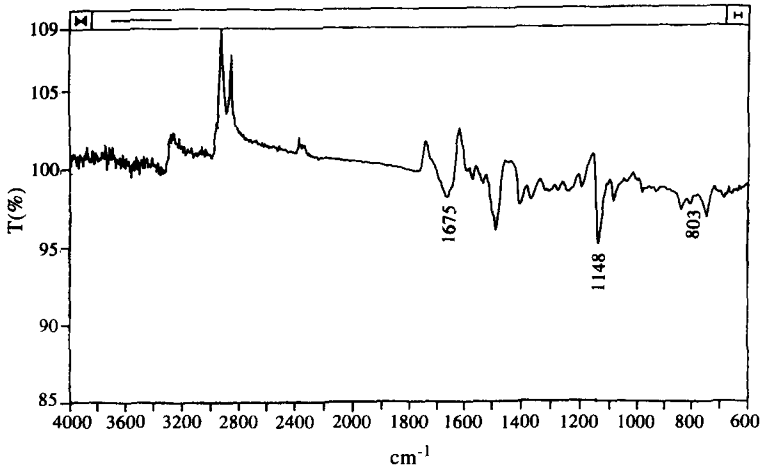


Fig. 8. FT-IR spectrum obtained by subtracting the IR spectrum of nylon from the XLC treated nylon IR spectrum. All treatments of nylon with XLC carried out at pH 6 for 60 min at 100°C.

due to the C=C bonds. The absorptions at 1148 and 803 cm^{-1} may be due to the presence of —SO_2— and C—Cl bonds in the attached XLC.

Figures 9, 11 and 13 show the spectra obtained from the corresponding XLC/NH_3 treated nylons from which the spectrum of untreated nylon has been subtracted. The disappearance of the

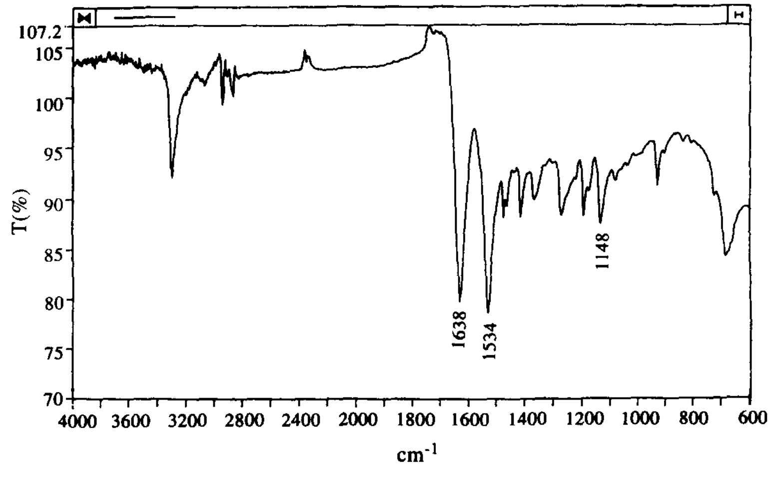


Fig. 9. FT-IR spectrum obtained by subtracting the nylon IR spectrum from the XLC/NH_3 treated nylon IR spectrum. All treatments of nylon with XLC carried out at pH 6 for 60 min at 100°C.

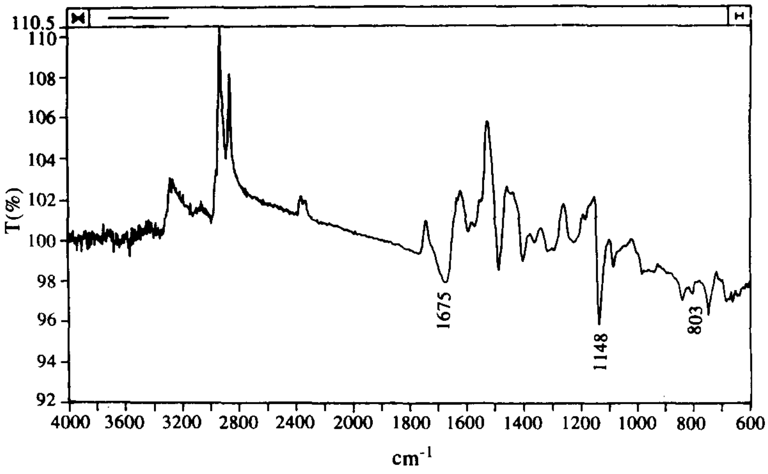


Fig. 10. FT-IR spectrum obtained by subtracting the nylon IR spectrum from the XLC treated nylon IR spectrum. All treatments of nylon with XLC carried out at pH 7 for 60 min at 100°C.

absorbances at 1675 cm^{-1} and 803 cm^{-1} indicates that ammonia adds to the double bond and the C—Cl bond. The two new absorbances in the XLC/NH$_3$ treated products, which appear at 1638 and 1534 cm^{-1}, are possibly due to —NH$_2$. The absorption at 1148 cm^{-1} may be due to the presence of —SO$_2$— bonds in the covalently attached XLC.

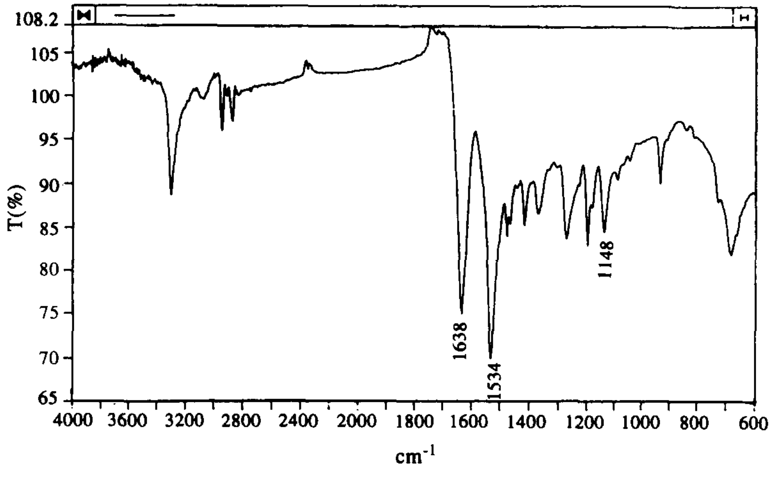


Fig. 11. FT-IR spectrum obtained by subtracting the nylon IR spectrum from the XLC/NH$_3$ treated nylon IR spectrum. All treatments of nylon with XLC carried out at pH 7 for 60 min at 100°C.

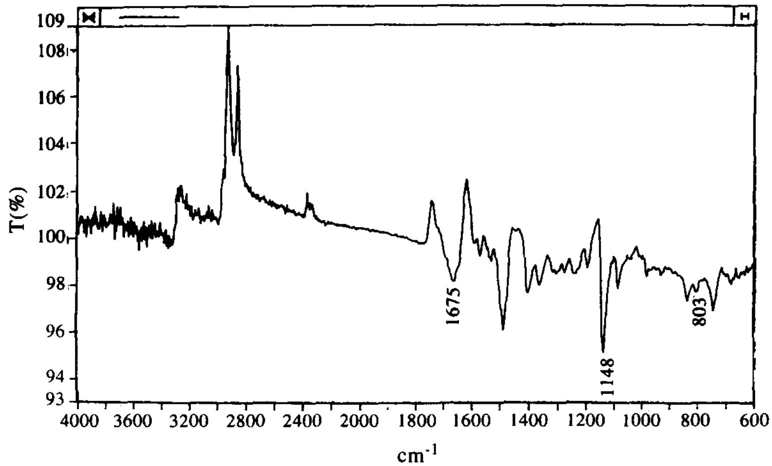


Fig. 12. FT-IR spectrum obtained by subtracting the nylon IR spectrum from the XLC treated nylon IR spectrum. All treatments of nylon with XLC carried out at pH 8 for 60 min at 100°C.

3.4 Exhaustion and fixation of CI Reactive Red 3 dyeings on treated and untreated nylon

Figures 14, 15 and 16 show the exhaustion (*E*) and fixation (*F*) values of CI Reactive Red 3 (12% owf) on dyed treated and untreated nylon. The pH of the nylon XLC pretreatments was 6, 7 and 8. Dyeing was carried

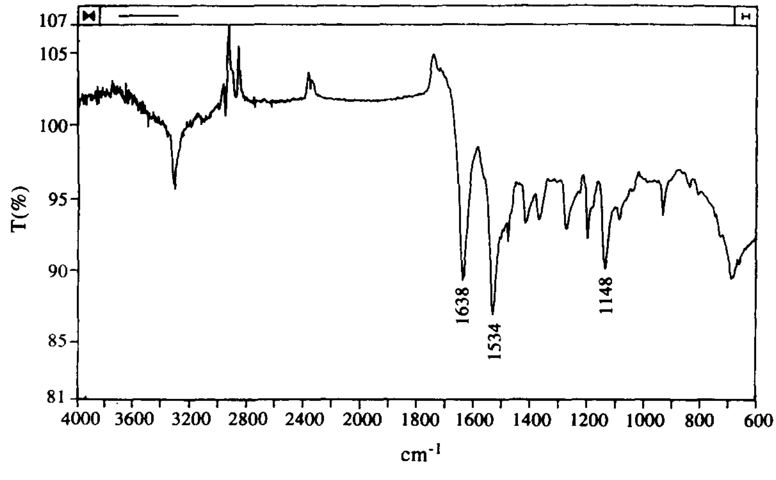


Fig. 13. FT-IR spectrum obtained by subtracting the nylon IR spectrum from the XLC/NH_3 treated nylon IR spectrum. All treatments of nylon with XLC carried out at pH 8 for 60 min at 100°C.

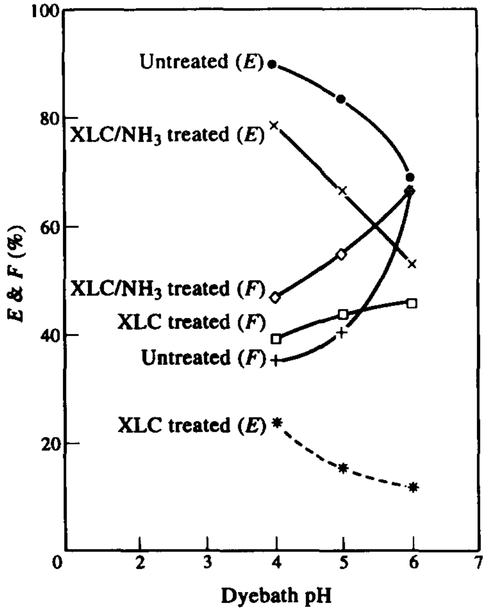


Fig. 14. Exhaustion (*E*) and fixation (*F*) of CI Reactive Red 3 (2% owf) on treated and untreated nylon. All pretreatments of nylon fabric with XLC carried out in a pH 6 bath, the bath being raised to 100°C and treatment continued at 100°C for 1 h.

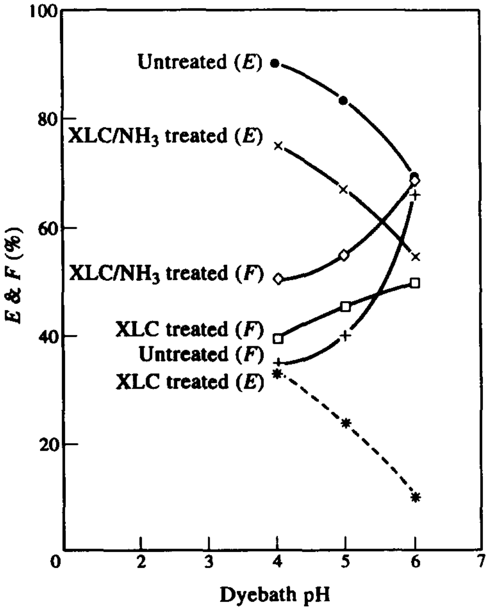


Fig. 15. Exhaustion (*E*) and fixation (*F*) of CI Reactive Red 3 (2% owf) on treated and untreated nylon. All pretreatments of nylon fabric with XLC carried out in a pH 7 bath, the bath being raised to 100°C and treatment continued at 100°C for 1 h.

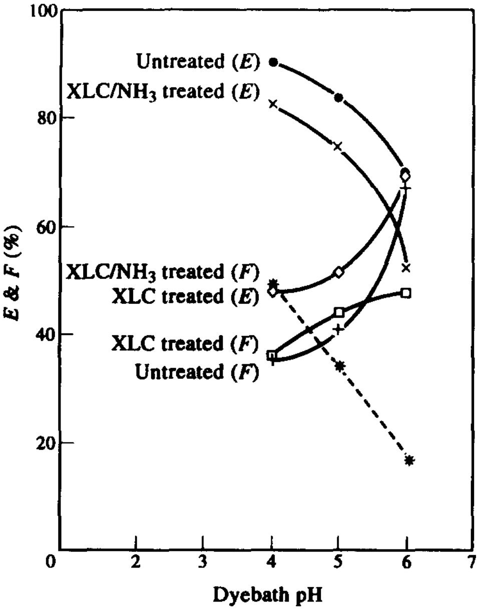


Fig. 16. Exhaustion (*E*) and fixation (*F*) of CI Reactive Red 3 (2% owf) on treated and untreated nylon. All pretreatments of nylon fabric with XLC carried out in a pH 8 bath, the bath being raised to 100°C and treatment continued at 100°C for 1 h.

out at different pH values for 1 h at the boil using a 20 : 1 liquor to goods ratio. It can be seen clearly that, no matter whether the substrate is untreated nylon or treated nylon, the dye exhaustion values decrease with increasing pH value and the dye fixation values increase with increasing pH value. However, it is noticeable that exhaustion values on 'XLC only' treated nylon are at least 50% lower than on untreated or XLC/NH_3 treated nylon.

Due to covalent bond formation between the amino end groups of nylon and the activated double bond in XLC, the number of available amino end groups in nylon decreases. Coupled with the introduction of C=C bonds into the nylon fibre, XLC reacts with the primary amino sites to give secondary or tertiary amino residues, which under mildly acidic conditions should be protonated and thus act as dye sites for sulphonated dyes; clearly the low exhaustion achieved indicates that these modified amino residues are unavailable to the reactive dye due to the bulky residues.

The poor exhaustion of CI Reactive Red 3 on XLC treated nylon fabric is attributable to the blocking of the primary amino groups by bulky residues, whereas in the case of the XLC/NH_3 treated nylon exhaustion is not hindered, since accessible primary or secondary amino groups have

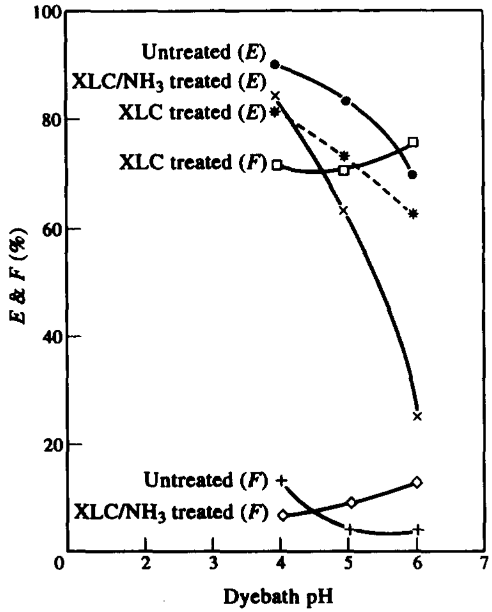


Fig. 17. Exhaustion (E) and fixation (F) of amino-ethyl anionic dye (2% owf) on treated and untreated nylon. All pretreatments of nylon fabric with XLC carried out in a pH 6 bath, the bath being raised to 100°C and treatment continued at 100°C for 1 h.

been re-introduced by the reaction of C=C bonds or C—Cl bonds in XLC treated nylon with ammonia. It is only the amino-ethylsulphonyl groups on this modified nylon fibre which are involved in covalent bonding with reactive dyes, since the amino-triazine residue will have very low nucleophilicity.

3.5 Exhaustion and fixation of an amino-ethyl anionic dye on treated and untreated nylon

The work has been extended to study the dyeing of XLC treated nylon and XLC/NH$_3$ treated nylon with the nucleophilic amino-ethyl anionic dye. From Figs 17, 18 and 19 it can be seen that due to its sulphonate groups this dye shows good substantivity for untreated nylon but, as expected, poor fixation, since there is no possibility for covalent bonding between the amino-ethyl anionic dye and the nylon fibre; the dye molecules were only absorbed as acid dyes and can thus be almost completely extracted in the aqueous pyridine stripping medium. The dyeing behaviour of XLC/NH$_3$ treated nylon with the amino-ethyl anionic dye is almost the same as that of untreated nylon, confirming that most of the potentially reactive sites have been removed by the ammonia treatment.

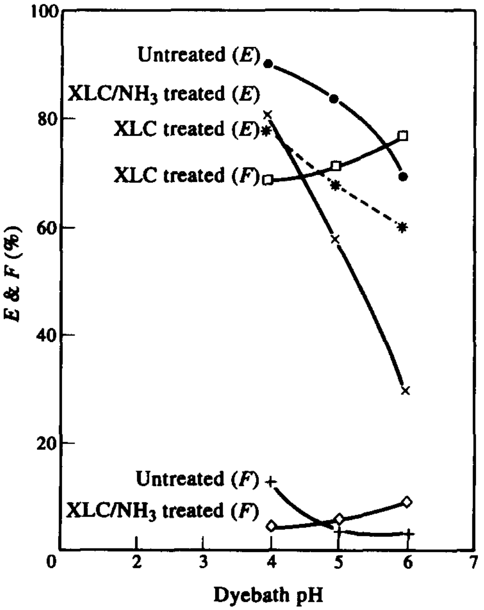


Fig. 18. Exhaustion (*E*) and fixation (*F*) of amino-ethyl anionic dye (2% owf) on treated and untreated nylon. All pretreatments of nylon fabric with XLC carried out in a pH 7 bath, the bath being raised to 100°C and treatment continued at 100°C for 1 h.

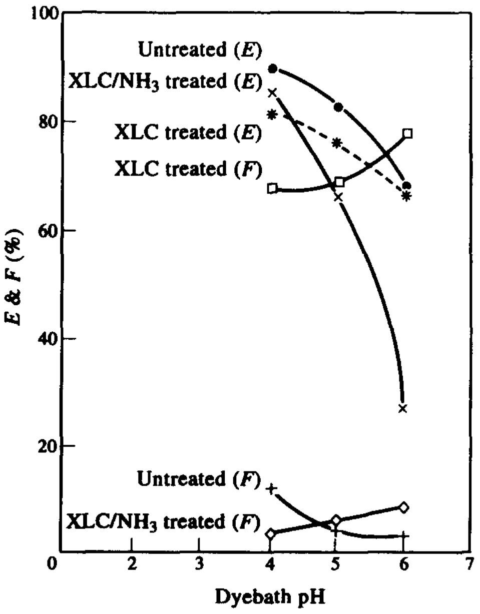


Fig. 19. Exhaustion (*E*) and fixation (*F*) of amino-ethyl anionic dye (2% owf) on treated and untreated nylon. All pretreatments of nylon fabric with XLC carried out in a pH 8 bath, the bath being raised to 100°C and treatment continued at 100°C for 1 h.

However, uptake of the amino-alkyl dye on XLC treated nylon was good and the degree of covalent fixation was also very promising, being of the order of 70–80%.

These results confirm that reactive vinylsulphone or chloro-*s*-triazine residues in the XLC treated nylon fibre are necessary for the covalent fixation of the nucleophilic amino-ethyl anionic dye.

CONCLUSIONS

(i) The water soluble crosslinker, XLC, shows good substantivity for nylon in two distinct pH regions; at pH ≤ 4, where it appears to act as a colourless acid dye, and at pH ≥ 6, where it is clearly activated to the reactive vinylsulphone. In the latter case absorption by nylon appears to be akin to that of a reactive disperse dye.

(ii) XLC treatment of nylon at pH ≥ 6 produces a modified nylon which undergoes fixation with amino-ethyl anionic dyes. These results confirm that residual reactive vinylsulphone bonds or chlorotriazine bonds in XLC treated nylon fibres are necessary for the covalent fixation of the nucleophilic amino-ethyl anionic dye. In contrast, the parent reactive monochlorotriazine dye shows poor uptake on the XLC pretreated nylon, indicating extensive blocking of fibre amino sites.

(iii) XLC/NH_3 treatment gives a nylon which shows good exhaustion and fixation when dyed with monochlorotriazine reactive dyes. The level of fixation achieved is higher than on untreated nylon, which indicates extra amine residues have been introduced. In contrast, the amino-ethyl dye shows poor fixation, indicating that reactive sites have been effectively eliminated in the ammonia treatment stage.

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