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The application of heterobifunctional reactive dyes to nylon 6,6: process modifications to achieve high efficiencies

S.M. Burkinshaw [a,*], Young-A. Son [a], M.J. Bide [b]

[a]*School of Textile Industries and Department of Colour Chemistry, University of Leeds, Leeds LS2 9JT, UK*
[b]*Department of Textiles, University of Rhode Island, Kingston, RI 02881, USA*

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Abstract

A heterobifunctional monochlorotriazine/vinyl sulphone (MCT/VS) reactive dye was applied to nylon 6,6 using various pH and temperature conditions. Optimum dye exhaustion and fixation were achieved at pH 4 and 98°C. The form in which the VS moiety was present during dyeing was examined by capillary electrophoresis. *Preconversion* of the dye to its VS form gave improved fixation and modified dyeing methods in which alkali additions were made at various points during the dyeing were used to achieve high dye fixation. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Of the various types of dye that can be used to dye nylon fibres, acid dyes are the most popular, with 1:2 pre-metallised acid dyes being used when highest wet fastness is required. However, dyeings on nylon of even these dyes suffer colour loss during laundering with the result that the vagrant dye is able to stain adjacent fabrics. While an aftertreatment of the dyed nylon can improve wet fastness deficiencies [1], the wet fastness of dyed nylon, especially to repeated washing, leaves much room for improvement.

Reactive dyes were commercially introduced over 40 years ago for cellulosic fibres and now form one of the most important dye classes for that fibre [2,3]. The mechanism of the interaction/reaction of reactive dyes with cellulosic fibres is well understood [4]. The dye is first absorbed by the fibre and then reacts with it by either a substitution reaction (for dyes containing, for example, a monochlorotriazine (MCT) group) or an addition reaction (for dyes with a vinylsulphone (VS) group). Characteristically high wet fastness is derived from dyes thus covalently bound to the fibre. It is known that the reactive dyes developed for cellulosic fibres or for wool can be applied at the boil to nylon under weakly acidic conditions (pH 4.0–6.0) and that covalent bonds form between the dye and the amino groups of nylon, without an alkaline fixation step [1,5,6]. Since reactive dyes typically do not include heavy metals

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* Corresponding author. Tel. : +44-113-233-3722; fax: +44-113-233-3741.

E-mail address: s.m.burkinshaw@leeds.ac.uk (S.M. Burkinshaw).

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such as chromium, the characteristically high wet fastness of the dyes comes with the concomitant advantages of brightness and low environmental impact. Despite the obvious advantages, the commercialisation of reactive dyes for nylon has not gained widespread success. The rewards for success are likely to be considerable, however, and research on the use of reactive dyes on both conventional and microfibre polyamide has received renewed attention in recent times. A number of studies have been conducted on reactive dyes of all types for nylon, including chlorodifluoropyrimidinyl [7], α-bromoacrylamido [8], chlorotriazine and VS [9], heterobifunctional [10] as well as disperse types [11].

In the context of the use of reactive dyes on cellulosic fibres, high levels of dye fixation have been achieved by the use of dye molecules containing more than one functional group. Dyes in which these groups are dissimilar (heterobifunctional dyes) are particularly flexible in application and have been found to display higher degrees of fixation and bond stabilities on cotton than equivalent dyes furnished with either a MCT or a VS reactive group only [12] and also have achieved wide use on cellulosic fibres.

The VS moiety of reactive dyes, including heterobifunctional types, can exist in two forms. In most instances the unsaturated, reactive (vinyl sulphone) group is not present in the dye as supplied but is formed during dyeing from a precursor in the presence of alkali. The most important precursor for dyes of this type is the sulphuric acid ester of β-hydroxy ethlysulphone, which forms the corresponding reactive, vinylsulphone variant in the dyebath by elimination of sulphuric acid. At lower dyebath pH values, the unreactive sulphatoethylsulphone form continues to predominate and an alkali-moderated, β-elimination step is required to generate the reactive vinylsulphone form [13,14].

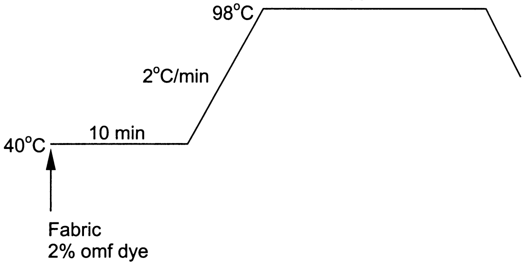

Fig. 1. Dyeing profile for nylon 6.6.

The aim of this work was to examine the use of heterobifunctional reactive dyes on nylon and to explore the effect of factors such as pH, temperature and, in particular, the form of the VS moiety on the level of dye fixation achieved.

2. Experimental

2.1. Materials

Conventional nylon 6,6 knitted fabric (78F68), supplied by DuPont, was used. This was scoured in a solution of 2 g l^{-1} Na_2CO_3 and 5 g l^{-1} nonionic surfactant (*Lanapex R*, Uniqema) for 30 min at 60°C. The fabric was then rinsed thoroughly in tap water and allowed to dry in the open air. *Sumifix Supra Brilliant Red 3BF* (C.I. Reactive Red 195), which was generously supplied by Sumitomo, was used as a typical heterobifunctional (MCT/VS) reactive dye.

2.2. Dyeing

Nylon 6,6 fabric was dyed in sealed, stainless steel dyepots of 200 cm^3 capacity, housed in a Zeltex *Polycolor PC 1000* laboratory-scale dyeing machine using a liquor ratio of 25:1. The dyeing profile is shown in Fig. 1. An initial study was made of the effect of application pH on dyeing; dyeings were conducted:

- *neutral* — with no addition of acid or alkali to the dyebath;
- *acidic* — at pH 3/3.5 provided by the addition of 4 g l^{-1} acetic acid;
- *alkaline* — at pH 10 through the addition of 4 g l^{-1} sodium carbonate.

In a subsequent, detailed study, dyeings over a range of acidic pH values between 2.4 and 6 were carried out with the pH of dyeing being adjusted by McIlvaine buffer (citric acid and sodium hydrogen phosphate). A determination of the effects of dyeing temperature used values other than the 98°C shown in Fig. 1. In latter dyeings, the effect of alkali addition later in the dyeing process was examined, for which details are included in the discussion section.

For all dyeings, at the end of the procedure, the dyed sample was removed, rinsed thoroughly in tap water and allowed to dry in the open air.

2.3. Analysis of dyeings

Absorbance measurements of the original dyebath and the exhausted bath were carried out using a Perkin-Elmer UV/VIS spectrophotometer. Using a previously established absorbance/concentration relationship at the $\lambda_{\max}$ of the dye, the quantity of dye in solution was calculated and the extent of dye exhaustion (*%E*) achieved was determined using Eq. (1), where D_0 and D_t are the quantities of dye initially in the dyebath and of residual dye in the dyebath, respectively.

$$\%E = \left(\frac{D_o - D_t}{D_o}\right) \times 100 \tag{1}$$

Unfixed dye from the samples was extracted using 25% aqueous pyridine solution and then measured spectrophotometically. The extent of dye fixation (*%F*) and dye fixation efficiency (*%FE*) were calculated using Eqs. (2) and (3), respectively, where D_e is the amount of extracted dye.

$$\%F = \left(\frac{D_o - D_t - D_e}{D_o - D_t}\right) \times 100 \tag{2}$$

$$\%FE = \left(\frac{E.F}{100}\right) \tag{3}$$

2.4. Colour measurement

Measurements were carried out using an *X-rite Match-Rite*™ spectrophotometer interfaced to a PC. Measurements were taken with the specular component of the light excluded and the UV component included, using illuminant D_{65} and 10^0 Standard Observer. Samples were folded to ensure opacity and an average of four readings was taken on each; K/S values were derived from the reflectance values and used as a measure of depth of dyeing.

2.5. Capillary electrophoresis (CE) analysis

A *Dionex* capillary electrophoresis instrument was used to analyse the form of the VS reactive group in the dye (sulphatoethylsulphone or VS). A 55 cm coated silica capillary with an internal diameter of 50 mm was employed, using a pH 9 buffer (10 mmol dm^{-3} sodium tetraborate and 10 mmol dm^{-3} sodium phosphate) as eluent. Detection was made by absorbance at 542 nm.

3. Results and discussion

3.1. Effect of pH

This initial study involved dyeings conducted under acidic (4 g dm^{-3} acetic acid), neutral and alkaline (4 g dm^{-3} Na_2CO_3) conditions. It was found that the resulting colour strength (K/S) data were as follows, acidic 22.1; neutral 4.0; alkaline 3.3. As the colour strengths obtained under both neutral and alkaline conditions were very low, it was not considered worthwhile to examine the levels of dye fixation achieved at these two pH values. To examine the effect of application pH further, dyeings were conducted over a range of acidic pH values, from pH 2.4 to pH 6 using McIlvaine buffers, all other application conditions being as outlined in Fig. 1. The data obtained are given in Table 1. Evidently, for this particular dye, highest total fixation efficiency (*%FE*) was achieved at pH 4. Lower pH values led to high

Table 1
Effect of application pH on *%E*, *%F* and *%FE*

pH	*%E*	*%F*	*%FE*
2.4	99.8	54.2	54.1
3	98.8	62.0	61.3
4	96.5	67.4	65.1
5	79.5	80.2	63.8
6	46.4	97.1	45.1

exhaustion as the anionic reactive dye was attracted to the protonated amino groups in the substrate. At the same time, the extent of dye fixation achieved was low, presumably because of a corresponding low amount of neucleophilic amino groups present in the fibre. In addition, under these conditions, it can be assumed that the dye was largely in the sulphatoethlysulphone form and, therefore, few dye molecules were present in the reactive vinyl sulphone form. In contrast, at higher pH values, initial dye exhaustion was low due to the low extent of amino group protonation, while what dye did exhaust underwent a comparatively efficient reaction with the large number of nucleophilic amino groups in the substrate to give the high dye fixation levels observed.

3.2. *Effect of dyeing temperature*

Having ascertained that dyeing was optimally achieved at pH 4, a further set of experiments examined the effect of temperature on dyeability. The results presented in Table 2 show that as maximum colour strength was obtained at a temperature of 98°C, this temperature was used in subsequent experiments.

3.3. *Examination of the form of the VS moiety*

The apparently competing requirements of dye exhaustion and dye fixation under the conditions employed so far, together with the resulting limitations on overall dye fixation efficiency, led to an examination of the form in which the VS moiety was present during a dyeing process. An initial capillary electrophoresis (CE) analysis of the dye was carried out (Fig. 2). Two peaks were present, one around 9 min arising from the VS form and the major one at around 12 min, attributable to the sulphatoethylsulphone dye form. These assignments are made on the basis of previous work conducted in these laboratories [15]. Dyeings were then conducted under "standard" conditions (98°C, pH 4) and samples of the dyebath were removed at various time intervals and subjected to CE analysis to determine the form of the dye present. The results are presented in Fig. 3. The major peak present throughout the dyeing process represents the sulphatoethylsulphone form of the dye from which it can be concluded that under the

Table 2
Effect of dyeing temperature on colour strength

Temperature	*K*/*S*
80°C	19.34
90°C	21.64
98°C	22.48
110°C	20.85

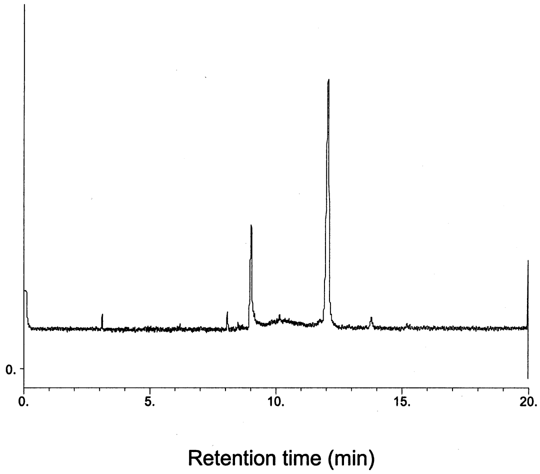

Fig. 2. CE analysis of C.I. Reactive Red 195 as received.

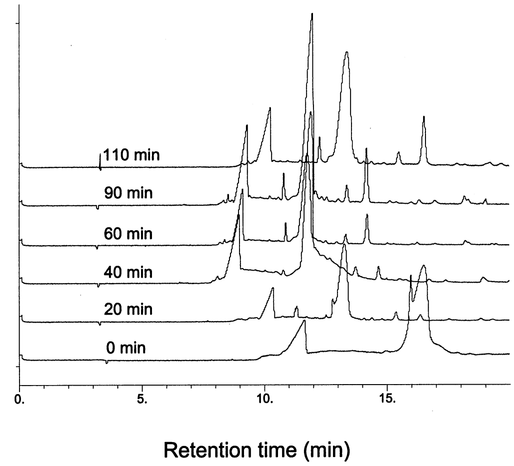

Fig. 3. CE chromatograms of dye solutions at various time intervals.

fixed (buffered) pH conditions that were shown to provide the most efficient use of dye, there is an inherent limitation to the efficiency of the reaction between dye and fibre.

It should be possible to convert the sulphatoethylsulphone moiety of the dye to the reactive VS form in a separate step, before dyeing takes place. The resulting modified dye might then be applied at a pH more appropriate to dye exhaustion but may still undergo an efficient reaction with the fibre. An outline process for converting the dye from sulphatoethylsulphone to the VS form is given in Fig. 4 [1,13,14]. An aqueous solution of the dye was treated in this way, and the solid dye recovered by evaporation. Samples of the dye exposed to this procedure were analysed using CE and the resulting electrophoregram is shown in Fig. 5. While Fig. 2 shows peaks at around 9 min (VS) and 12 min (sulphatoethylsulphone), Fig. 5 shows no remaining sulphatoethylsulphone dye and a clear majority of the dye as the required vinyl sulphone form.

Dyeings were then carried out under "standard" conditions (98°C, pH 4) using both the original dye and the converted dye. The ensuing exhaustion and fixation values for these two forms of the dye are given in Table 3. The pH conditions used here, as expected, furnished good dye exhaustion for both forms of the dye. However, the VS form of the dye reacted more readily under these pH conditions and gave much higher %F than the sulphatoethylsulphone form. This experiment shows that the correct form of the dye is essential for achieving good fixation. However, as such a separate, pre-conversion step is unlikely to be practicable on a routine basis, efforts were thus made to modify the dyeing process to accomplish the conversion as part of the dyeing itself.

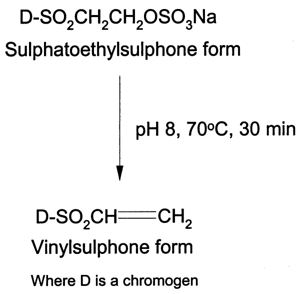

Fig. 4. Conversion of sulphatoethylsulphone form to vinylsulphone form.

3.4. Effect of alkali addition for increasing fixation

The effects of alkali addition to the dyebath at the later stages of dyeing were examined. In this way, it was considered that initial dye exhaustion and subsequent dye-fibre reaction might each be achieved at a suitable pH and result in a greater overall fixation efficiency. Essentially, this approach would parallel the process of cellulosic fibre reactive dyeing in which alkali is added at the later stages of the process. "Standard" dyeings were carried out according to the procedure outlined in Fig. 1, with the modification that 10 g dm^{-3} Na$_2$CO$_3$ was added after 10, 30, or 50 min at 98°C. CE analysis of the dyeing in which the alkali was added after 10 min was conducted on a sample of the bath taken after the alkali addition. The chromatagraph is shown in Fig. 6 and indicates

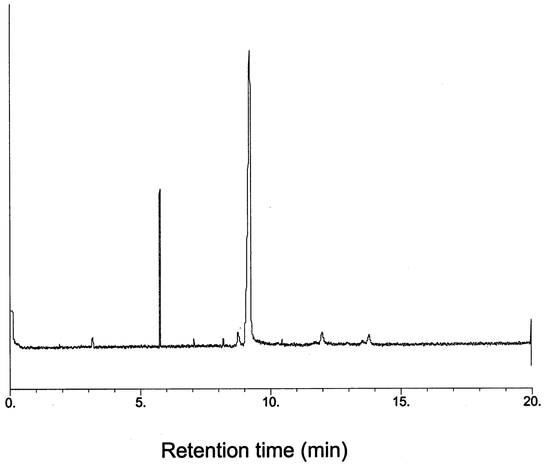

Fig. 5. CE analysis of the vinylsulphone form.

Table 3
%E, %F and %FE achieved for the sulphatoethylsulphone and vinylsulphone forms of C.I. Reactive Red 195

	%E	%F	%FE
Original dye (SES)	96.1	72.0	69.2
Converted dye (VS)	94.5	90.6	85.6

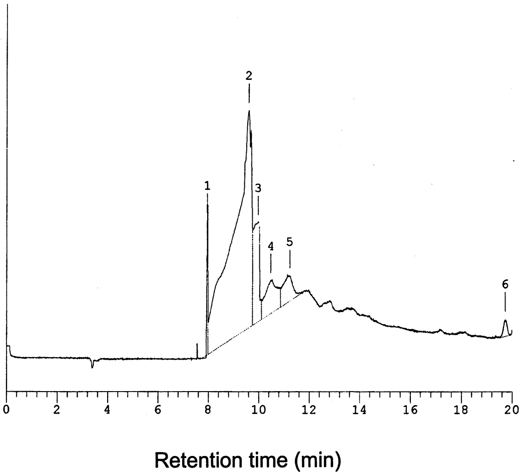

Fig. 6. CE chromatogram of C.I. Reactive Red 195 after alkali addition.

that the conversion to the VS form was virtually complete under these conditions.

The results of dyeings carried out with these alkali additions are given in Table 4. It is clear that dye fixation was increased by this addition: the fixation efficiencies obtained were >10% higher than those found for the "standard" dyeing carried out under fixed (buffered) pH conditions. The efficiency of dye fixation was still below the 85% achieved when the dye had been pre-converted to the VS form and subsequently applied under conditions that favoured dye exhaustion. This inefficiency occurs, presumably, at the expense of dye exhaustion as dye migrated from the fibre under the increased pH conditions that favoured dye-fibre reaction.

Clearly, the VS form of the dye is the preferred one for achieving high fixation. However, the generation of this form of the dye in situ brings with it the reduced dye exhaustion noted here. There is obviously scope for optimising the introduction of alkali during dyeing to achieve maximum fixation efficiency and factors such as the rate of alkali addition, the time of alkali addition, the strength of alkali and the amount of alkali would each, presumably, play a part.

Table 4
%*E*, %*F* and %*FE* as a function of time

	%*E*	%*F*	%*FE*
Nil	95.6	71.5	68.3
10 min	78.8	98.0	77.2
30 min	82.9	96.4	80.0
50 min	86.3	87.6	75.6

4. Conclusions

If fast dyeings are to be achieved on nylon fibres, the use of a reactive dye seems to be the most likely way to achieve them. Heterobifunctional dyes offer the greatest opportunity for efficient dye–fibre reaction, but, when used under fixed (buffered) pH conditions, the conflicting requirements of dye exhaustion and dye–fibre reaction limit the extent of fixation, even when pH and temperature are optimised. This applies particularly to the VS reactive group, which must be generated from the major sulphatoethylsulphone form in which it is present as supplied. When the dye is pre-converted to its VS form, much higher fixation efficiencies are obtained. Modification of the dyeing process to include an alkali addition subsequent to initial dye exhaustion results in successful conversion to the VS form as dyeing proceeds and considerably higher fixation is achieved than is found for dyeing under fixed (buffered) pH conditions. The extent of dye fixation is still lower than that achieved for the two-step (pre-conversion) process and there remains scope for optimising the one-step process to achieve superior dye fixation.

References

[1] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. London: Chapman & Hall, 1995.

[2] Stead CV. In: Shore, J. editor. Colorants and auxiliaries. Bradford: Society of Dyers and Colourists, 1990.

[3] Fox MR, Summer HH. In: Preston C, editor. The dyeing of cellulosic fibres. Bradford: Dyers Company Publication Trust, 1986.

[4] Renfrew AHM. Reactive dyes for textile fibres. Bradford: Society of Dyers and Colourists, 1999.

[5] Ginns P, Silkstone K. In: Nunn DM, editor. The dyeing of synthetic-polymer and acetate fibres. The Dyers Company Publications Trust, 1979.

[6] Lewis DM. In: Lewis DM. editor. Wool dyeing. Society of Dyers and Colourists, 1992.

[7] Burkinshaw SM, Gandhi K. Dyes and Pigments 1996; 32:101.

[8] Burkinshaw SM, Gandhi K. Dyes and Pigments 1997; 33:259.

[9] Burkinshaw SM, Wills AE. Dyes and Pigments 1997; 33:243.

[10] Burkinshaw SM, Wills AE. Book of papers, 1996 AATCC International Conference and Exhibition. p. 520.

[11] Burkinshaw SM, Collins GW. Dyes and Pigments 1994;25:31.

[12] Matusi M, Meyer U, Zollinger H. J Soc Dyers Col 1988; 104:425.

[13] Luttringhaus H. Amer Dyest Rep April 3 (1961), 30.

[14] Lewis DM, Shao JZ. J Soc Dyers Col 1995;111:149.

[15] Tapley KN, Asaf M. Department of Colour Chemistry, Leeds University, Personal communication.